Science and Technology of Separation Membranes
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Preface

After reading this book, and having understood its contents, its biggest aim is to be able to contribute to new technical ideas more than existing membrane separation technologies.

At first it is essential to learn the history of the development of the separation membrane; the equilibrium phenomena of the solubility of the material and the electrochemical properties as the basic phenomena of the membrane properties of matter in the field of application, nonequilibrium phenomena such as the mass transfer, the quantitative understanding of various underlying phenomena, the problems of membrane separation technology and the solution methods for existing separation membranes are the same in all fields.

With that in mind, it is strongly wished that each researcher can suggest a new technique beyond the existing membrane separation technology with courage.

There is a membrane at all boundaries. A membrane of the thickness of the order of molecules exists even on a bare surface. Probably the only surface on which there is no membrane at all will be a solid surface newly cut under a high vacuum.

It was known for a long time that the surface of the plant cell had a cell wall. Also there is a membrane called a plasma membrane on the surface of an animal cell, and it came to be known that there is a great variety of filmy structure in the inside of the cell. It came to be recognized widely that it is the most important when the elucidation of the function pursues a life phenomenon.

In particular, from the viewpoint of saving resources, saving energy and environmental conservation, new techniques with membranes have attracted attention. For example, the development of water processing technology using an ion-exchange membrane and the reverse osmotic membrane was propelled by such a strong request. In addition, haemodialysis with a membrane, based on the artificial kidney, is at the forefront of medical technology, and has been used for the treatment of many patients. These technologies are fine examples that indicate the importance of the applied study of artificial membranes.

The principle of reverse osmosis was proposed as a new method for the desalination of seawater by Professor Breton at the University of Florida [1,2]. Today’s prosperity of science and the technique of the polymer membrane are due to Professor Loeb and Sourirajan, who developed excellent semipermeable cellulose acetate membranes using their original membrane preparation method [3], and their membranes went into practical use [4]. And then Dr Kesting evaluated the remarkable developments in his book as being the ‘golden age of membranology’ [5]. Along with such developments has come a large number of books; commentary books have been published about the formation, structure, physical properties, function and application of polymer membranes in many countries from about 1970. Of these, a certain book establishes an important point of fundamental principle, a certain thing is main by the design of the module, and in addition, a certain one puts an important point for the function developed in as a general effect; a characteristic is devised with each book.
I engaged in the fundamentals and development study of polymer membranes and membranes that include polymers and have deepened my understanding about the basic matter that was indispensable in the study of membranes for 40-odd years.

Because the membrane exists as a partition of phases, the barrier characteristics, material permeability or separability, are the most important physical properties. The driving force of the material transportation through such membranes can involve a difference in chemical potential, a difference in electrical potential, a difference in pressure and a difference in temperature; and depending on the particular membrane, the naming of the material transportation is different, too. At first it is an important thing that we unify these and can look. Furthermore, these properties of matter may be modified in response to external stimulation, in this case not only the simple physical properties, but also the function of the membranes.

When a membrane caught some kind of outside stimulation, a fact to produce replies to support is defined as the function of the membrane. The permeability and separability are polymer responses that are brought about by a concentration gradient or a pressure gradient due to an external stimulation, but because they may not bring about a structural change of the polymer itself, a membrane function and way of speaking that it is said are usually done, but are the place where it is difficult whether it may be said that it is a polymer function.

However, in the biomembrane, membrane structure changes, for example, by outbreak of the specific material transmission and electric potential depending on stimulation like excitement phenomena and develops a chemical reaction. It may be said that this is a function enough. There is a thing indicating the behavior very similar to a reaction to participate in the function in the biomembrane with the heterogeneity structure of the artificial membrane as the inanimate object.

These permeability, separability and membrane functions are expressed by an index for the membrane as a whole, but they actually consist of a combination of some basic phenomena. To develop and improve a membrane it is necessary to understand these basic phenomena exactly. Furthermore, for an accurate understanding, quantification of the phenomenon must be accomplished.

In this book, we first describe the history and necessity for membrane science and technology. Thereafter, the structural design of the membrane, the relationship between the membrane formation conditions and the membrane structure are discussed in detail. Furthermore, various membrane preparation methods, shapes of membranes and membrane modules are introduced. And then the analyses of membrane characteristics by various methods are described. The thermodynamic basics of membrane transport phenomena and various transport models are discussed, and then the phenomena during membrane permeation in various kinds of membrane transport method and their solution methods are discussed. After the description of these basic matters, the principles of the various membrane permeation separation methods, fundamental analyses and applied technology are described from different angles. In addition, hybrid systems of membrane separation processes are discussed with interest.

References


Acknowledgements

I studied the kinetics of the formation mechanism of thermosetting resins and the theory of their gelation from 1964 to 1970 and acquired the degree of the doctor of engineering in 1970. I began the study of polymer separation membranes when I became a teacher in Kansai University in 1970. I seemed to engage in the totally different study field at first, but I noticed that it was not so different a field when I looked from the point of view of handling molecules, and so decided that I would make separation membrane study a lifetime friend, and that has been the case for 40-odd years now and has culminated in the opportunity to write this book.

First, I express great gratitude in having got much encouragement and support from many friends during the writing of this book.

In particular, on the occasion of writing this book, I had great aid from Professor Takashi Miyata and Dr Akifumi Kawamura, co-workers in Kansai University. In the true work, the great help from Chisa Norioka (PhD postgraduate) and Kazuki Ueda, Kazuki Matsuo, Masaya Yamada, Yusuke Masuda, Toshiki Shimai, Yuki Tanaka, Saya Yamafuji and Shingo Yamashita (Masters postgraduates) in the preparation of figures, tables, schemes and so on will never be forgotten. Without their help, I think that this book would never have been completed. That is why I want express my great thanks to them. I also appreciate the help given by the associated members of John Wiley & Sons. Finally, I thank my wife, Tamiko Uragami, who always supplies mental support and great encouragement.
Introduction to Membrane Science and Technology

1.1 History of Membrane Science and Technology

The word ‘osmosis’ is used to describe the permeation of water through a diaphragm in contact on one side with a water–ethanol mixture and on the other side with pure water, as shown in Figure 1.1, a process discovered by Nollet in 1748 [1]. Probably, the relation between a semipermeable membrane and the osmotic pressure was recognized first by Nollet.

Graham carried out more systematic studies on mass transport in semipermeable membranes, studied the diffusion of gases through different media and, furthermore, discovered that rubber exhibits different permeabilities to different gases [2]. Membranes in the nineteenth and early twentieth centuries were not applied to industrial or commercial fields, but were used to analyse physical/chemical theories. As a good example, van’t Hoff used the measurements of osmotic pressure of solutions with membranes to develop his limit law, to explain the behaviour of ideal dilute solutions, in 1887; this work led directly to the van’t Hoff equation.

Most of the early studies on membrane permeation were carried out with natural membranes, such as bladders of pig, cattle, fish and sausage casings made of animal gut or gum elastics. Traube was the first to introduce an artificially prepared semipermeable membrane by precipitating cupric ferrocyanide in a thin layer of porous porcelain [3]. This type of membrane was used by Pfeffer in his fundamental studies on osmosis [4]. The theoretical treatment and much of the interpretation of osmotic phenomena and mass transport through membranes is based on the studies of Fick, who interpreted diffusion in liquids as a function of concentration gradients, and van’t Hoff, who gave a thermodynamic explanation for the osmotic pressure of dilute solutions [5,6]. A little later, Nernst and Planck introduced the flux equation for electrolytes under the driving force of a concentration or electrical potential gradient [7,8]. With the classical publications of Donnan describing the theory of membrane equilibria and membrane potentials in the presence of electrolytes, the early history of membrane science ends with most of the basic phenomena satisfactorily described and theoretically interpreted [9].

Until about 1960, interest in membrane technology was mainly in the academic field. Cellulose nitrate, the first synthetic (or semisynthetic) polymer was studied by Schoenbein [10] in 1846. In 1855 Fick [11] used cellulose nitrate membranes in his classic study ‘Über Diffusion’. In the same year, the concept of solution, that is, membrane–permeant interaction, to membrane permeation theory was proposed by L’hermite [12]. Thus, at the very outset, the cast of characters for the ongoing solution–diffusion drama was complete. In 1860, Schumacher dipped test tubes into cellulose nitrate (collodion) solutions and prepared the first tubular membranes [13]. Baranetzky [14] prepared the first
flat membranes in 1872. Bechhold [15] prepared the first series of microfiltration membranes of graded pore size in 1907 and was also the first to define the relationship between bubble point, surface tension and pore radius, and developed a method of making the first synthetic membranes by impregnating a filter paper with a solution of nitrocellulose in glacial acetic acid [16]. These membranes could be prepared and accurately reproduced with different permeabilities by varying the ratio of acetic acid to nitrocellulose. Nitrocellulose membranes were also used in the studies of Zsigmondy and Bachmann as ultrafilters to separate macromolecules and fine particles from an aqueous solution [17]. Based on a patent of Zsigmondy, Sartorius GmbH began in 1927 the production of a series of nitrocellulose membranes with various pore sizes. These membranes were used in microbiological laboratories in analytical applications.

Early attempts to control and vary porosity were largely empirical. Bechhold observed that permeability varied inversely with the concentration of polymer in the sol. Bigelow and Gemberling [18] studied the effects of drying time on the membrane preparation process. Zsigmondy et al. [19] and Elford [20] developed two series of graded pore-size membranes of cellulose nitrate. The former were the basis for the first commercial microfiltration membranes, which appeared in 1927 in Germany.

The concept of pore-size distribution was developed by Karplus, cited by Erbe [21], who combined bubble point and permeability measurements. The development of the first successfully functioning haemodialyser [22] was the key to the large-scale application of membranes in the biomedical area.

Industrial interest of the membrane separation technology suddenly increased from about 1950. On the other hand, with the progress in high polymer chemistry, a large number of synthetic polymers which are excellent for the preparation of new membranes with specific transport properties, excellent mechanical and thermal stability were provided. In addition, a comprehensive theory based on the thermodynamics of irreversible processes for membrane transport properties was proposed by Staverman [23] and Kedem and Katchalsky [24]. Merten described membrane processes based on postulating certain membrane transport models, such as the model of a diffusion–solution membrane [25].

In 1960 the important paper by Maier and Scheuermann [26] provided the basic mechanism which has since been utilized by Kesting to accommodate every (wet, dry and thermal) class of phase inversion membranes within its general framework. The two editions of Synthetic Polymeric Membranes [27,28] provide comprehensive coverage of phase inversion, which is by far the most versatile and important membrane fabrication process.

Figure 1.1 Osmosis across the semi-permeable membrane. $\Delta P$ is the hydrostatic pressure difference.
The beginning of the golden age of membrane science and technology depended significantly upon both the invention of reverse osmosis by Professor Reid [29] and the development of the asymmetric cellulose acetate membrane by Loeb and Sourirajan [30,31]. The development of a reverse osmosis membrane from cellulose acetate which gave high salt rejection and high fluxes at moderate operating pressures by Loeb and Sourirajan was a major advance toward the application of reverse osmosis membranes as an effective technology for the production of potable water from sea water.

The membrane developed by them was an asymmetric structure consisting of a dense skin layer, which determines the selectivity of salt and flux of desalinated water, and a porous layer that holds the mechanical strength of the whole membrane. The preparation of asymmetric cellulose acetate membranes is based on a phase inversion process in which a homogeneous polymer solution is converted into a two-phase system, such as a solid polymer-rich phase forming the solid polymer structure and a polymer lean phase making the liquid-filled membrane pores [27,28,32]. Soon, other synthetic polymers – such as polyamides, polyacrylonitrile, polysulfone and polyethylene – were used as basic material for the preparation of synthetic membranes in reverse osmosis desalination. These polymers often showed better mechanical strength, chemical stability, thermal stability and tolerance for bacteria than the cellulose esters as semi-natural material. However, cellulose acetate remained the dominant material for the preparation of reverse osmosis membranes until the development of the interfacial-polymerized composite membrane [33,34]. These membranes showed significantly higher fluxes, higher rejection, and better chemical stability, mechanical strength, tolerance for bacteria and chlorine sterility than the cellulose acetate membranes.

Microfiltration was developed in 1918 by Richard Zsigmondy, who is a Nobel Prize in Chemistry winner, and then he developed the ultrafiltration membrane in 1922 and established the basics of membrane separation technology as one of founders of Sartorius. In medicine, dialysis (from Greek dialusis, ‘διάλυσις’, meaning dissolution, dia, meaning through, and lysis, meaning loosening or splitting) is a process for removing waste and excess water from the blood and is used primarily as an artificial replacement for lost kidney function in people with kidney failure (https://en.wikipedia.org/wiki/Dialysis). Electrodialysis (ED) is used to transport salt ions from one solution through ion-exchange membranes to another solution under the influence of an applied electric potential difference. This is done in a configuration called an electrodialysis cell. The cell consists of a feed (dilute) compartment and a concentrate (brine) compartment formed by an anion exchange membrane and a cation exchange membrane placed between two electrodes. (https://en.wikipedia.org/wiki/Electrodialysis). This method was proposed for the first time in 1890 by Maigrot and Sabates [35]. Reverse osmosis was proposed by Reid and Breton [29] and developed by Loeb and Sourirajan [30] for the desalination of sea water.

Nanofiltration is a relatively recent membrane filtration process used most often with low total dissolved solids water, such as surface water and fresh groundwater, with the purpose of softening (polyvalent cation removal) and removal of disinfection by-product precursors, such as natural organic matter and synthetic organic matter. Nanofiltration is also becoming more widely used in food processing applications, such as dairy, for simultaneous concentration and partial (monovalent ion) demineralization (https://en.wikipedia.org/wiki/Nanofiltration). Nanofiltration was known as low-pressure reverse osmosis and came to gradually attract attention from the second half of 1980, and the first applications were reported by Eriksson [36], Colonlon and McClellan [37].

Sir Thomas Graham carried out the first membrane gas separation and obtained oxygen-enriched air containing 46.6% oxygen. He proposed that increasing the pressure of a gas mixture to be separated should be beneficial for obtaining higher fluxes. He observed that changes in the thickness of films affect the flux but not the composition of permeated gas. He noted the effect of temperature on permeation rates [38].
Pervaporation is one of the most popular areas of current membrane research, but the concept of pervaporation separation is not new. As early as 1906, Kahlenberg reported a qualitative study on the separation of a mixture of a hydrocarbon and an alcohol through a rubber membrane [39]. As early as 1917, it was recorded that water permeated through collodion films selectively, and the term pervaporation was first introduced by Kober [40]. Schwob [41] demonstrated dehydration of alcohols by using 20 μm thin membranes. However, an analysis of pervaporation literature and patents showed that most of the work in the field was done in more recent times [42]. In 1955, Hagerbaumer conducted the first quantitative investigation with a microporous Vycor glass membrane with a high-pressure drop across it, to allow for the separation of liquid–liquid mixtures [43]. It was the work by Binning and co-workers [44,45] from 1958 to 1961 that established the principles and highlighted the potential of pervaporation separation.

Later, in 1965, Binning and co-workers utilized this operation of separating a liquid–liquid mixture into a vapour mixture using a nonporous polymeric film. This research yielded a high degree of separation along with high permeation rates. The process did not come into commercial use until 1982 when Gesellschaft für Trenntechnik mbH (GFT) of Germany installed a pervaporation plant to separate water from concentrated alcohol solutions. Since then, more than 100 plants have been installed. Recently, Exxon has used pervaporation in its refineries to separate hydrocarbon mixtures containing aromatics and aliphatics. Another commercial use for pervaporation is the removal of methylene chloride from small waste streams [46].

Membrane distillation was developed more than 50 years ago. It is a thermally driven separational programme in which separation is enabled due to phase change. A hydrophobic membrane displays a barrier for the liquid phase, allowing the vapour phase (e.g. water vapour) to pass through the membrane’s pores. The driving force of the process is given by a partial vapour pressure difference commonly triggered by a temperature difference (https://en.wikipedia.org/wiki/Membrane_distillation).

A membrane reactor is a physical device that combines a chemical conversion process with a membrane separation process to add reactants or remove products of the reaction. Chemical reactors making use of membranes are usually referred to as membrane reactors. The membrane can be used for different tasks, such as separation – selective extraction of reactants and retention of the catalyst, distribution/dosing of a reactant and catalyst support (often combined with distribution of reactants). Membrane reactors are an example for the combination of two unit operations in one step; for example, membrane filtration with a chemical reaction.

Uragami et al. [47] proposed ‘evapomeation (EV)’ as a new membrane separation technique method to improve a fault of pervaporation in 1988. This EV has some advantages, such as an improvement of membrane performance with the repression of swelling or shrinking of the membrane due to the feed liquids [48–53] (see detail in Chapter 16) and gives excellent dehydration, organic permselectivity of aqueous organic mixtures and separation of organic–organic liquid mixtures.

Uragami and co-workers also proposed temperature-difference controlled evapomeation (TDEV), further developing the EV method. In this TDEV method, the temperature of membrane surroundings is set less than that of the feed liquid (see detail in Chapter 17) [48–51,54–65].

The first carrier transport experiment was carried out by Osterhout, who investigated the transport of ammonia through algae cell walls [66]. Gliozzi explained biologically the coupled transport mechanism in liquid membranes, as shown in Figure 1.2 [67].

About the middle of 1960s a number of couple transport systems were studied by Shean and Sollner [68]. Bloch et al. published the first paper on coupled transport [69], and the separation of uranium using phosphate ester carriers was later reported [70,71].

Table 1.1 summarizes the history of membrane processes and materials.
**Figure 1.2** Transport model of liquid membrane and fixed carrier membrane.

**Table 1.1** History of membrane processes and materials.

<table>
<thead>
<tr>
<th>Year</th>
<th>Membrane processes</th>
<th>Membrane materials</th>
</tr>
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<tbody>
<tr>
<td>1749</td>
<td>Animal membranes</td>
<td></td>
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<tr>
<td>1750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1829</td>
<td>Rubbery membranes</td>
<td></td>
</tr>
<tr>
<td>1855</td>
<td>Collodion membrane</td>
<td><em>first synthetic membrane</em></td>
</tr>
<tr>
<td>1900</td>
<td>Microfiltration</td>
<td></td>
</tr>
<tr>
<td>1907</td>
<td>Cellulose nitrate membrane</td>
<td>(graded pore size)</td>
</tr>
<tr>
<td>1950</td>
<td>Haemodialysis</td>
<td></td>
</tr>
<tr>
<td>1960</td>
<td>Electrodialysis</td>
<td></td>
</tr>
<tr>
<td>1962</td>
<td>Cellulose acetate membranes</td>
<td>(asymmetric membrane)</td>
</tr>
<tr>
<td>1970s</td>
<td>Composite membranes</td>
<td></td>
</tr>
<tr>
<td>1980</td>
<td>Gas separation</td>
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<td></td>
<td>Fuel cell</td>
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<td>Membrane distillation</td>
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<td></td>
<td>Pervaporation</td>
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<td></td>
<td>EV</td>
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<td></td>
<td>TDEV</td>
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<tr>
<td>1990</td>
<td>Nanofiltration</td>
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<tr>
<td>2000</td>
<td>Membrane reactor</td>
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<td></td>
<td>Membrane contactor</td>
<td></td>
</tr>
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<td></td>
<td>Forward osmosis</td>
<td></td>
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<td></td>
<td>2000 Carbon nanotube membrane</td>
<td></td>
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</tbody>
</table>
1.2 Membrane Module

In industrial membrane plants the membrane area of 100 000 m\(^2\) is required to perform an effective separation. There are several ways to economically and efficiently package membranes to provide a large surface area for effective separation. From an overall cost standpoint, not only is the cost of membranes per unit area important, but also the cost of the containment vessel into which they are mounted. Basically, the problem is how can one pack the most area of membranes into the least volume, to minimize the cost of the containment vessel consistent with providing acceptable flow hydrodynamics in the vessel. These packages are called ‘membrane modules’. Plate-and-frame, tubular, spiral-wound and hollow fibre are the most popular modules.

1.2.1 Plate-and-Frame Modules

The plate-and-frame modules were one of the earliest types of membrane system, but because of their relatively high cost they have been largely replaced in most applications by spiral-wound modules and hollow-fibre modules. Plate-and-frame modules are now used only in electrodialysis and pervaporation systems and in a limited number of reverse osmosis and ultrafiltration applications with highly fouling conditions.

1.2.2 Tubular Modules

These modules are now generally limited to ultrafiltration applications, for which the benefit of resistance to membrane fouling outweighs the high cost. Tubular membranes contain as many as five to seven smaller tubes, each 0.5–1.0 cm in diameter, nested inside a single larger tube. In a typical tubular membrane system, a large number of tubes are manifolded in series. The permeate is removed from each tube and sent to a permeate collection header.

1.2.3 Spiral-Wound Modules

Industrial-scale modules contain several membrane envelopes, each with an area of 1–2 m\(^2\), wrapped around the central collection pipe. Multi-envelope designs minimize the pressure drop encountered by the permeate travelling toward the central pipe. The standard industrial spiral-wound module is 8” (20 cm) in diameter and 40” (~1 m) long. The module is placed inside a tubular pressure vessel. The feed solution passes across the membrane surface and a portion of the feed permeates into the membrane envelope, where it spirals toward the centre and exits through the collection tube. Normally, four to six spiral-wound membrane modules are connected in series inside a single pressure vessel.

1.2.4 Hollow-Fibre Modules

Hollow-fibre modules are characteristically 4–8” (10–20 cm) in diameter and 3–5 ft (1.0–1.6 m) long. Hollow-fibre units are almost always run with the feed stream on the outside of the fibre. Water passes through the membrane into the inside or ‘lumen’ of the fibre. A number of hollow fibres are collected together and ‘potted’ in an epoxy resin at both ends and installed into an outer shell. Hollow-fibre membrane modules are formed in two basic geometries: (a) shell-side feed design and (b) bore-side feed design.
1.3 Necessity of Membrane Science and Technology

Conventional thermal separation processes, such as distillation, sublimation and crystallization, are required a certain high energy for the separation of materials. Therefore, lower energy processes are strongly required. Membrane separation processes operate without heating and consequently use less energy than their processes. Development of more suitable membranes for each membrane separation process is very important. New proposals for membrane separation technologies are constantly required. In other words, the development of membranes for membrane separation processes and new membrane technologies is always required.

The separation process is purely physical, and both fractions (the permeate and retentate) can be used. Cold separation using membrane technology is widely used in the food technology, biotechnology and pharmaceutical industries. Furthermore, using membranes enables separations to take place that would be impossible using thermal separation methods. For example, it is impossible to separate the constituents of azetotropic liquids or solutes, which form isomorphic crystals by distillation or recrystallization, but such separations can be achieved using membrane technology. Depending on the type of membrane, the selective separation of certain individual substances or substance mixtures is possible. Important technical applications include the production of drinking water by reverse osmosis (worldwide approximately $7 \times 10^6$ m$^3$ annually), filtrations in the food industry, the recovery of organic vapours such as petrochemical vapour recovery, and the electrolysis for chlorine production. In wastewater treatment, membrane technology is becoming increasingly important. With the help of ultrafiltration and microfiltration it is possible to remove particles, colloids and macromolecules, so that wastewater can be disinfected in this way. This is needed if wastewater is discharged into sensitive waters, especially those designated for contact water sports and recreation. About half of the market is in medical applications, such as use in artificial kidneys to remove toxic substances by haemodialysis and as artificial lungs for bubble-free supply of oxygen in the blood. The importance of membrane technology is growing in the field of environmental protection. Even in modern energy recovery techniques, membranes are increasingly used; for example, in fuel cells and in osmotic power plants (https://en.wikipedia.org/wiki/Membrane_technology#Applications).

The first ceramic membranes were produced in France in the 1980s for the purpose of uranium enrichment in the nuclear industry. After many of the nuclear plants were set up in France, other industrial application areas for the ceramic membranes were sought out. At the same time, academic research on ceramic membranes was conducted. The leading group was directed by Professor Louis Cot at the National Graduate School of Chemistry in Montpellier. The group growth gave rise to the creation of a laboratory fully dedicated to membrane materials and processes from 1994 and to the European Membrane Institute of Montpellier in 2000. French manufacturers of ceramic membranes include Orelis Environnement, Pall Exekia and Tami Industries. Other companies outside France include Atech, Inopor, Jiangsu Jiuwu, MetaWater, Likuid Nanotek and Liqtech.

While most of the ceramic membrane manufacturers produce the membranes of carriers and membrane layers of alumina oxide, titanium oxide and zirconia oxide, only a few manufacturers work with silicon carbide. Silicon carbide requires higher sintering temperatures (>2000 °C) compared with oxide-based membranes (1200–1600 °C). The pioneers in developing and commercializing silicon carbide membranes are the Danish company Liqtech and the French company Veolia (https://en.wikipedia.org/wiki/Ceramic_membrane).

Ceramic membranes are a type of artificial membrane made from inorganic materials (such as alumina, titania, zirconia oxides, silicon carbide or some glassy materials). They are used in membrane operations for liquid filtration. By contrast with polymeric membranes, they can be used in separations where aggressive media (acids, strong solvents) are present. They also have excellent thermal stability,
which makes them usable in high-temperature membrane operations. Like polymeric membranes, they are either dense or porous (https://en.wikipedia.org/wiki/Ceramic_membrane).

Nanotube membranes are either a single, open-ended nanotube (CNT) or a film composed of an array of nanotubes oriented perpendicular to the surface of an impermeable film matrix like the cells of a honeycomb. ‘Impermeable’ is essential here to distinguish between nanotube membrane and the traditional, well-known porous membranes. Fluids and gas molecules may pass through the membrane en masse, but only through the nanotubes. For instance, water molecules form ordered hydrogen bonds that act like chains as they pass through the CNTs. This results in an almost frictionless or atomically smooth interface between the nanotubes and water which relate to a ‘slip length’ of the hydrophobic interface. Properties like the slip length that describe the non-continuum behaviour of the water within the pore walls are disregarded in simple hydrodynamic systems and absent from the Hagen–Poiseuille equation. Molecular dynamic simulations better characterize the flow of water molecules through the carbon nanotubes with a varied form of the Hagen–Poiseuille equation that takes into account slip length [72,73].

Transport of polystyrene particles (60 and 100 nm diameter) through single-tube membranes (150 nm) was reported in 2000 [74]. Soon after, ensemble membranes consisting of multiwalled and double-walled carbon nanotubes were fabricated and studied [75]. It was shown that water can pass through the graphitic nanotube cores of the membrane at up to five magnitudes greater than classical fluid dynamics would predict, via the Hagen–Poiseuille equation, both for multiwall tubes (inner diameter 7 nm) [76] and double-wall tubes (inner diameter <2 nm) [77]. In experiments by Holt et al. [77], pure water (~1.0020 cP viscosity) was transported through three samples of double-walled carbon nanotubes in a silicon nitride matrix with varying membrane fluxes and thicknesses. These membranes were found to have enhanced flow that was more than three orders of magnitude faster than the expected for no-slip hydrodynamic flow as calculated by the Hagen–Poiseuille equation. These results for nanotubes with the 1–2 nm diameter pores corresponded to about 10–40 water molecules per square nanometre per nanosecond. In a similar experiment by Mainak Majumder et al. [76], nanotubes of about 7 nm in diameter in solid polystyrene were tested for their fluid velocities. These results similarly showed that the nanotubes have long slip planes, and flow rates were found to be four to five orders of magnitude faster than conventional fluid flow predictions.

References


Membrane Structure

2.1 Structural Design of Membranes

The chemical design and physical construction of membranes are very important considerations in balancing the functions of membranes. The structural design of a high-performance membrane depends on the development of advanced membrane materials, membrane surface modification and the membrane preparation method [1].

2.1.1 Chemical Design of Membrane Materials

Novel materials for separation membranes are selected based on: (i) development of systematic structure–property relationships in polymers to provide membranes with enhanced permeability and selectivity, (ii) the ease of membrane preparation and (iii) their stability under permeation conditions, such as pH, temperature and pressure. Furthermore, synthesis of new membrane materials and modification of existing membrane materials are often employed to develop membranes with higher permeability and/or higher selectivity. For polymeric membranes, modification and synthesis of membrane materials are accomplished by polymer blending, cross-linking, formation of internal hydrogen bonding, copolymerization, and graft- and block-copolymerization [1]. In addition, polymer membranes may also be significantly altered by surface modification techniques. There are two general types of polymer membrane surface modifications techniques: chemical or physical modifications. In the case of a chemical treatment, the membrane is contacted with a chemical agent, solvent, coupling agent, vapour, surface-active agent, surface grafting or other additives. Physical membrane treatment techniques include ultraviolet irradiation, plasma irradiation and sputtering.

2.1.2 Physical Construction of Separation Membranes

For the development of high-performance membranes, it is important to construct the membranes by choosing an optimum polymer material based on its physical and chemical properties. This is reflected in improved permeability, selectivity and durability of the resultant membrane. The physical structure of polymer membranes is strongly dependent on the membrane preparation method and the conditions of membrane formation.

In a membrane permeation process, the chemical composition and the physical structure of the membrane can both be important factors. For example, when molecules are permeated and separated...
by a dense, non-porous polymer membrane that has small transient free-volume elements generated by thermal vibrations of the polymer chains, the chemical composition of the polymer governs the solubility of permeants in the membrane. On the other hand, permeant diffusion in the polymer membrane depends largely on the physical structure of a membrane. Such non-porous membranes can be applied to the separation of gases, vapours and liquids. Their selectivity is significantly influenced by both the difference in the solubility of the permeants in the membrane (solution process) and the diffusivity of the permeants in the membrane (diffusion process) [2,3].

2.2 Symmetric Non-porous and Porous Membranes

When we consider the permeation of permeants through a membrane, a relationship between the sizes of ‘pore’ in which the permeants can transfer and of the permeant (physical factor) and an electrochemical interaction between the membrane materials constituting the pore and the permeants (physicochemical factor) are very important [4]; if the pore size of the membrane is extremely large compared with the size of the permeant, the interaction between the membranes and the permeant is negligible. Membranes having such large pores are called ‘porous membranes’, as shown in Figure 2.1b [5]. In such porous membranes, typically used in ultrafiltration (UF) and microfiltration applications, the physical structure mainly governs the permeation and separation characteristics. On the other hand, membranes having extremely small pores, such as molecular gaps between polymer chains based on thermal vibrations of polymer, are called ‘non-porous’ membranes’, as shown in Figure 2.1a [5]. Membranes in which the physical or chemical structure is the same in the whole membrane are termed ‘symmetric membranes’, as shown in Figure 2.2a; and those in which the physical or chemical structure is different in the direction of the membrane thickness are called ‘asymmetric membranes’, as shown in Figure 2.2b. Porous, nonporous, symmetric and asymmetric structures of the membrane are strongly dependent on the preparation method of the membrane; furthermore, fine structures of the membranes can be significantly controlled by the preparation conditions of the membrane, as shown in Table 2.1 [6].

![Figure 2.1](image_url) Structure of (a) nonporous and (b) porous membrane.
2.3 Asymmetric and Composite Membranes

Asymmetric membranes, which can be prepared by the solution wet method, have a dense active layer (thickness <1 μm) and a porous support layer (thickness 100–150 μm) that consist of the same polymer material. On the other hand, membranes in which these layers are made from different polymer materials (Figure 2.2c) are called ‘composite membranes’. The dense skin layer of the asymmetric and composite membrane is the active layer for the separation and the porous sponge layer has the support function for the dense skin layer. In composite membranes, since the dense active layer and the porous support layer consist of different materials, the flexibility in the most suitable design of these layers is significantly high compared with asymmetric membranes. A thin membrane of the dense active layer in composite membranes is prepared by the polymer coating method or monomer polymerization method (in situ) on the porous support film, as listed in Table 2.2. The illustrations of cross-section structure of typical composite membranes are shown in Figure 2.3. In Type I, the ultrathin dense layer is coated or laminated on the porous support layer and the ultrathin layer consists of a linear polymer. Type II is composed of both the ultrathin layer and a gel layer on the porous support layer. The
The thickness of the ultrathin layer is 100–300 μm. Type III consists of the ultrathin layer and a porous support similar to Type I, but the ultrathin layer is a cross-linked polymer penetrating into the support layer; consequently, both layers are in an indivisible state. In Type IV, the surface of the porous support layer is chemically and physically filled and the chemical structure of the ultrathin layer has little change, but the main constituent is based on the chemical structure of the support layer. This point is significantly different from the other composite membranes.

### 2.4 Relation between Structure and Preparation Condition of Membrane

See Table 2.1 for a summary of the preparation conditions on the structure of the polymer membrane [1].

![Illustrations of cross-section of composite membrane.](image-url)
2.4.1 Preparation of Casting Solution

2.4.1.1 Kind of Polymer Material
Many polymers are available for the preparation of membranes and can be selected without any difficulty. In the preparation of the casting solution, the selection of the kind of polymer materials is a very important factor for the subject of separation; membrane materials can be selected from the viewpoints of hydrophilicity, hydrophobicity, and resistance to heat, chemicals and fungus.

2.4.1.2 Polymer Concentration in Casting Solution
The determination of the polymer concentration is significantly related to the density of the resulting membrane and depends on the degree of the entanglement and spread of the polymer chains. The kind of casting solvent is also strongly related to the spread and entanglement of polymer chains in the casting solution, and consequently the density of the resulting membrane.

Poly(vinyl chloride) (PVC) membranes were prepared from different casting solutions. The casting solutions were classified into three types: a casting solution with (i) different solvents, (ii) with different degrees of polymerization of PVC and (iii) with different PVC concentrations. The relationship between the properties of the casting solutions and the morphology of the resulting PVC membranes was investigated. The density and crystallinity of the PVC membrane increased with increasing relative viscosity of the casting solution. It was found that the morphology of the PVC membrane was significantly affected by the character of the casting solution. The permeability, solubility and diffusivity of water vapour through PVC membranes with different physical structures were also investigated. The parameters decreased with an increase in the crystallinity of the PVC membranes. Furthermore, measurements of the pervaporation of the various PVC membranes were conducted with aqueous ethanol solutions. The permeation rate increased and the separation factor decreased with a decrease in the crystallinity of the PVC membrane [7].

Madaeni and Taheri investigated the effects of preparation-influencing parameters, such as polymer concentration, thickness of casting solution and type of solvent, on the morphology and performance of poly(vinylidene difluoride) (PVDF) microfiltration membranes for the treatment of emulsified oily wastewater. Flat-sheet membranes were prepared from a casting solution of polymer and additive in various solvents by immersing the prepared films in nonsolvent-containing mixtures of water and 2-propanol. The membranes were characterized using scanning electron microscopy (SEM). Increasing the polymer concentration and membrane thickness significantly affected the pore size, leading to permeate flux decrease. An attempt was made to correlate the effect of the solvent on membrane morphology and performance employing solubility parameters between solvent and nonsolvent [8].

Ma et al. [9] also studied on the effect of polymer concentration of polyethersulfone (PES) plus sulfonated polysulfone (SPSF) and additives of cast solution on performance of PES–SPSF blend nanofiltration (NF) membranes was investigated. Field emission SEM and X-ray photoelectron spectroscopy were used to analyze characteristic of PES–SPSF blend NF membranes. The water flux of PES–SPSF blend membranes decreased dramatically with an increase in polymer concentration of PES plus SPSF. The rejection of polyethylene glycol (PEG) and salts increased with increasing polymer concentration of PES plus SPSF. When acetone was used as an additive, the water flux declined with increasing mass concentration of acetone, but the rejection of PEGs and salts increased. The PES–SPSF blend NF membranes with minimum rejection of sodium chloride (NaCl) indicated that it could separate monovalent salts from multivalent salts effectively, which would be potential application in softening water for drinking water resource.

Sapkal et al. [10] prepared PES membranes by a phase inversion process. Membrane dope formation consisting of commercial-grade PES resin and N,N'-dimethylformamide and polyethylene glycols...
(PEGs). Tap water was used as the coagulant bath at room temperature. The polymer solution was formulated by varying polymer concentrations, which for PES is in the range 19–23 wt%. PEGs with varying molecular weights were used to characterize the flux and rejection of the membrane. Results showed that the flux of the membrane decreases with increase in polymer concentrations. This means that outer skin layer of the membranes became apparently thicker and denser with increasing polymer concentration. On other hand, a UF membrane from a dilute polymer solution produced a thin and porous skin layer, leading to a high value of flux but a relatively low percentage of rejection for PEG.

A commercial blend of polysulfone (PSF) and acrylonitrile–butadiene–styrene (ABS) resin known as Mindel S-1000 was used to prepare flat-sheet membranes for O₂/N₂ separation [11]. The membranes produced were expected to inherit the excellent gas separation properties of PSF and the strong mechanical properties of ABS. Asymmetric membranes were successfully prepared by a pneumatically controlled casting machine with methanol as the second coagulation medium. Commonly use solvents for pure PSF and ABS – N-methyl-2-pyrrolidone (NMP) and the more volatile tetrahydrofuran (THF) – were chosen in the dope formulation. The polymer concentration was varied between 20 and 23.5% to promote the formation of the desirable membrane morphology that affects the gas separation performance. As the concentration increased, a more oriented membrane with denser skin layer was developed that was responsible for the slight improvement in gas separation factors with slight reduction in gas permeability.

However, as the solution became too viscous due to the high content of polymer, solvent evaporation was hindered during the solvent-exchange process, producing membranes with huge microvoids and thinner skin. To further promote membrane skin formation, the solvent ratio of the dope solution was manipulated. Membrane morphology analysis revealed that the increment of solvent ratio; – reducing the volatile solvent – promoted the membrane porosity while decreasing the skin thickness. Thus, a significant loss of gas pair selectivity was observed as the permeability increased. In order to enhance the membrane performance and plug any possible defects on the skin surface, the membranes produced were silicone coated. This step improved the membrane gas separation performance while retaining the same trend as the uncoated membranes. Owing to the dispersion of rubber particles in ABS that contributed to the toughness of the polymer, the mechanical properties of PSF–ABS membranes were found to be high with comparable elasticity to other common polymeric membranes.

Safiah et al. [12] studied the effects of polymer concentrations on the morphology and performance of ternary mixtures of PES–N-methypyrrolidone–water membrane dope solution. Three dopes with different polymer concentrations (13%: UF13 PES; 15% UF15PES; 17%: UF17 PES) were prepared via a simple dry/wet phase-inversion technique. The membranes were characterized in terms of permeability coefficient, membrane morphology, molecular weight cut-off (MWCO) and membrane surface. Separation performance of lysozyme showed that the optimum transmission at a pressure of 3 bar for UF13, UF15 and UF17 membranes was 95.1%, 97.4% and 46.2% respectively, and the optimum flux was 105 × 10⁻⁶ m³ m⁻² s⁻¹, 10.4 × 10⁻⁶ m³ m⁻² s⁻¹ and 1.6 × 10⁻⁶ m³ m⁻² s⁻¹ respectively. As polymer concentration increased, the morphology of membranes also changed from a large finger-like structure to a thin finger-like structure with the presence of a sponge-type structure and macrovoids. UF15 membrane was selected as the optimum membrane since it was able to promote the highest lysozyme transmission together with an appropriate flux. Its characteristics as a negatively charged membrane, with zeta potential of –62 mV and MWCO around 43 kDa provided good evidence for its suitability in the lysozyme separation process. This study demonstrated that the polymer concentration highly influenced the performance and morphology of UF membranes, which in turn exhibited an improvement in separation ability.

Figure 2.4 shows the effect of PMLG concentration in the casting solution on the permeation and separation characteristics is shown in, where the DCA/FA ratio is kept constant at 90/10 (g/g) and the PMLG concentration is changed. The permeation rates for pure water, aqueous solutions of PEG 20000 and poly(vinyl alcohol) (PVA 205) decrease with increase in PMLG concentration.
Kleman and Friedman [13] and our group [14,15] reported that the magnitude of the average pore radius decreases with an increase in concentration of cellulose acetate (CA) and PMLG. The rejections for PEG 20000 and PVA 205 increase slightly with the PMLG concentration. The results in Figure 2.4 suggest that membranes with a higher PMLG concentration are denser than membranes prepared from lower PMLG concentration. The thickness of membrane swollen with pure water decreases as the PMLG concentration increases. This result is dependent on the formation of a membrane having a very dense structure, because polymer aggregation in the casting solution becomes stronger and swelling of the membrane in the gelation medium becomes smaller with increase in PMLG concentration. The fact that the difference between the membrane thicknesses before and after the pressure treatment decreases with the PMLG concentration suggests that the membrane prepared from higher PMLG concentration is difficult to compact under pressure.

2.4.1.3 Casting Solvent

In the combination of casting solvents, when the mixture of two organic solvents is used as a casting solvent, often one is of low boiling point and the other of high boiling point. An appropriate example in such a combination can be found in the permeability of cellulose nitrate (CN) membranes. The permeability of liquids through polymer membranes is strongly governed by the structure of microporous membranes. It is well known [16–18] that there are many factors determining the structure of microporous membranes: the nature of casting solution (the casting solution composition and the casting solvent, etc.), the evaporation conditions (the evaporation temperature, period and humidity, etc.), the gelation conditions (the gelation medium and temperature, etc.) and the heat treatment conditions (the heat treatment temperature and time, etc.). In the conditions of membrane preparation in Tables 2.3 and 2.4, the conditions of evaporation, gelation and heat treatment processes are kept constant; only the casting solvents are changed. The differences in the structure of membranes by changing solvents depend upon the following factors: (1) the differences of interactions among CN and casting solvent molecules; (2) the differences in formation of an asymmetric double structure by using two organic solvents having different boiling points; (3) the differences of the polymer aggregation [19]...
Table 2.3 Effect of changing the high boiling point (bp) solvent in the casting solution on permeability of pure water.a)

<table>
<thead>
<tr>
<th>High bp solvent</th>
<th>Bp (°C)</th>
<th>Permeability of pure water (mL cm(^{-2}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEG</td>
<td>278</td>
<td>(1.61 \times 10^{-4})</td>
</tr>
<tr>
<td>TEP</td>
<td>215</td>
<td>(7.72 \times 10^{-5})</td>
</tr>
<tr>
<td>FA</td>
<td>210</td>
<td>(4.10 \times 10^{-3})</td>
</tr>
<tr>
<td>NMP</td>
<td>208</td>
<td>(1.16 \times 10^{-3})</td>
</tr>
<tr>
<td>DEGME</td>
<td>202</td>
<td>(1.06 \times 10^{-4})</td>
</tr>
<tr>
<td>DMF</td>
<td>156</td>
<td>(1.05 \times 10^{-4})</td>
</tr>
<tr>
<td>EL</td>
<td>154</td>
<td>(3.15 \times 10^{-6})</td>
</tr>
<tr>
<td>DMSO</td>
<td>149</td>
<td>(8.09 \times 10^{-4})</td>
</tr>
<tr>
<td>AcA</td>
<td>139</td>
<td>(8.43 \times 10^{-6})</td>
</tr>
<tr>
<td>EGME</td>
<td>124</td>
<td>(4.70 \times 10^{-5})</td>
</tr>
<tr>
<td>D</td>
<td>101</td>
<td>(2.32 \times 10^{-4})</td>
</tr>
<tr>
<td>D(^\ast)</td>
<td>101</td>
<td>(3.47 \times 10^{-3})</td>
</tr>
</tbody>
</table>

Source: [16]. Reproduced with permission of Wiley-VCH.
AcA: acetic anhydride; D: 1,4-dioxane; D\(^\ast\): 100 wt% Ba(ClO\(_4\))\(_2\) per CN;
DEGME: diethylene glycol monomethyl ether; DMSO: dimethyl sulfoxide;
EGME: ethylene glycol monoethyl ether; EL: ethyl lactate; TEG: triethylene glycol; TEP: triethyl phosphate.

a) Casting solution composition: CN/MeOH/high boiling point solvent = 13/45/42 (wt%); evaporation period: 30 s; heat treatment: 40 °C, 10 min; operating condition: 40 °C, 2 kg cm\(^{-2}\).

Table 2.4 Effect of changing the low boiling point (bp) solvent in the casting solution on permeability of pure water.a)

<table>
<thead>
<tr>
<th>Low bp solvent</th>
<th>Bp (°C)</th>
<th>Permeability of pure water (mL cm(^{-2}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>56</td>
<td>(3.66 \times 10^{-5})</td>
</tr>
<tr>
<td>MeOH</td>
<td>64</td>
<td>(4.10 \times 10^{-3})</td>
</tr>
<tr>
<td>EtOH</td>
<td>78</td>
<td>(8.75 \times 10^{-4})</td>
</tr>
<tr>
<td>iso-PrOH</td>
<td>82</td>
<td>(1.64 \times 10^{-3})</td>
</tr>
<tr>
<td>n-PrOH</td>
<td>97</td>
<td>(1.95 \times 10^{-4})</td>
</tr>
<tr>
<td>EGME</td>
<td>124</td>
<td>(3.00 \times 10^{-3})</td>
</tr>
</tbody>
</table>

Source: [16]. Reproduced with permission of Wiley-VCH.
A: acetone; MeOH: methanol; EtOH: ethanol; iso-PrOH: isopropyl alcohol; n-PrOH: n-propyl alcohol; EGME: ethylene glycol monoethyl ether.

a) Casting solution composition: CN/low boiling point solvent/FA = 13/45/42 (wt%); evaporation period: 30 s; heat treatment: 40 °C, 10 min; operating condition: 40 °C, 2 kg cm\(^{-2}\).
occurring simultaneously with the evaporation of the casting solvents; (4) the differences of degree of aggregation when casting solvents desolvate (solvent removal) into water during the gelation process, and so on. The differences of water permeabilities in Tables 2.3 and 2.4 are attributed to these factors.

Sulfonated polyethersulfone (SPES) membranes were prepared using dimethylformamide (DMF), dimethylacetamide (DMAc) and NMP as casting solvents, referred to as SPES–DMF, SPES–DMAc and SPES–NMP membranes respectively [20]. Comprehensive and comparative studies have shown that casting solvents have significant effects on the morphology and performance of SPES membranes. The $^1$H nuclear magnetic resonance (NMR) spectra revealed the formation of strong hydrogen bonding between residual DMF and SPES, accompanying the thermal decomposition of DMF during the membrane preparation. The X-ray diffraction indicated a more perturbed randomness of amorphous structure inside the SPES–DMF membranes than other two membranes. Atomic force microscopy demonstrated different surface morphologies of the three solvent-cast SPES membranes, which appeared to be governed by solvent volatility combined with solvent–polymer interactions. A more co-continuous hydrophilic cluster-like structure was observed on the surface of SPES–DMAc membranes. The SPES–DMF membranes exhibited relatively low ionic exchange capacity, low water uptake and large contact angle compared with the SPES–DMAc and SPES–NMP membranes. The SPES–DMAc membranes achieved the highest conductivity values at room temperature among the three membranes. These resulting differences were tentatively correlated with the different degrees of interaction between the SPES and solvents. Moreover, the conductivity differences seemed to correlate with the morphological differences.

The performances of CA membranes prepared with casting solutions, with acetone, DMF, and NMP as solvents, were studied in a series of methanol–methyl tertiary butyl ether separation experiments [21]. The flux and selectivity of the membrane samples were affected by the type of solvent used to prepare the casting solution, as shown in Figures 2.5 and 2.6.

The sample with DMF consistently gave the highest selectivity and lowest flux, followed by the samples with NMP and acetone. The differences in the performances were attributed to the effects of the volatility and evaporation rates of the solvents. Scanning electron microscopy and atomic force microscopy revealed different surface morphologies of the three solvent-cast membranes. The SEM images showed that the SPES–DMAc membranes exhibited a more continuous and uniform structure compared to the SPES–DMF membranes, which had a more porous and layered morphology. The contact angle measurements indicated that the SPES–DMAc membranes had a higher water contact angle, suggesting a more hydrophobic surface compared to the SPES–DMF membranes.

**Figure 2.5** Permeate composition versus feed composition: methanol/methyl tertiary butyl ether separation with CA and Nafion-117 membranes. Source: [21]. Reproduced with permission of John Wiley and Sons.
microscopy (AFM) techniques were used for comparing the morphologies of the membranes. In addition, we used Raman spectroscopy as a novel technique to study the sorption selectivities of the membrane samples prepared with the three different solvents. In a parallel study, the relation between the polymer concentration in the casting solution and the morphology and performance of the membrane samples was studied. Under similar preparation conditions, the morphology of the membrane changed from being porous to being dense when the membrane was prepared with casting solutions with increasing polymer concentration. Also, the selectivity increased and the permeability decreased with increasing polymer concentration in the casting solution.

Tian et al. [22] reported that two different crystalline phase compositions appear in the isothermally dried solvent-cast poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP)) membranes, which was explained based on the different solvent–polymer interactions. The dipolar intermolecular interaction between P(VDF-co-HFP) and DMAc induces a polar $\gamma$ phase with a trans conformation, which is absent in the P(VDF-co-HFP)–acetone system. The different pervaporation behaviour of the two solvent-cast membranes in separating ethyl acetate (EtAc) from water was explained based on the different permeant–polymer interactions which were further deduced from the affinity differences. The difference of polarity between EtAc molecules and the acetone-cast P(VDF-co-HFP) membrane is smaller than that between EtAc molecules and the DMAc-cast P(VDF-co-HFP) membrane, which makes for the different solubilities and diffusivities of EtAc in the two different solvent-cast membranes. And their separation properties in pervaporation of EtAc–water mixture are inevitably varied.

Luu et al. [23] investigated the cast solvent effect on the structure and properties of sulfonated poly(ether ether ketone) (sPEEK) was studied. Poly(ether ether ketone) was sulfonated to have different sulfonation degrees of 65, 70, and 75 %, and its membrane was prepared using the two types of solvents, DMAc and NMP. Ionic cluster size was analysed using small-angle X-ray scattering (SAXS), and it was correlated with a few essential membrane properties such as water uptake, methanol permeability, proton conductivity and cell performance in direct methanol fuel cells (DMFCs). Synchrotron SAXS and solid-state NMR data revealed the structural difference between the sPEEK
membranes prepared using NMP and DMAc, regarding the cluster dimensions of 3.22 nm and 2.70 nm respectively. Although the water uptake, methanol permeability and proton conductivity of the membranes prepared with NMP were higher than those with DMAc, the overall cell performance was the opposite. The dimensional instability associated with high water swelling as well as high methanol permeability were the main causes for this inferior cell efficiency of NMP-cast membranes. This report demonstrates the importance of selection of cast solvent in preparation of sPEEK electrolyte membranes for DMFC application.

2.4.1.4 Combination of Casting Solvent

The composition ratio of two organic solvents in a constant content of polymer significantly influences the membrane structure. Figure 2.7 shows a ternary diagram of the three components (CN, methyl alcohol, 1,4-dioxane) from which successful membranes can be prepared. The effect of the casting solution composition on the pure water permeability (PWP) through the CN membranes is shown in Table 2.4. As can be seen from Table 2.5, the membrane structure is remarkably influenced by the composition of the two casting solvents.

PVDF microporous flat membranes were cast with different kinds of PVDFs and four mixed solvents: trimethyl phosphate (TMP)–DMAc, triethyl phosphate (TEP)–DMAc, tricresyl phosphate (TCP)–DMAc, and tri-n-butyl phosphate (TBP)–DMAc. Li et al. [25] investigated the effects of different commercial PVDFs (Solef® 1015, FR 904, Kynar 761, Kynar 741, Kynar 2801) on membrane morphologies and membrane performances of the PVDF–TEP–DMAc–PEG 200 system. The membrane morphologies were examined by SEM. The membrane performances in terms of pure water flux (PWF), rejection, porosity and mean pore radius were measured. The membrane had a high flux of 143.0 ± 0.9 L m⁻² h⁻¹ when the content of TMP in the TMP–DMAc mixed solvent reached 60 wt%, which was 2.89 times that of the membrane cast with DMAc as single solvent and was 3.36 times that of the membrane cast with TMP as single solvent. Using a mixed solvent with different solvent solubility parameters, different morphologies of PVDF microporous membranes were obtained.
TMP–DMAc mixed solvent and TEP–DMAc mixed solvent showed a stronger solvent power to PVDF due to the lower solubility parameter difference of 1.45 MPa$^{1/2}$ and the membranes prepared showed a faster precipitation rate and higher flux. There were less macrovoids in the membrane prepared with TEP (60 wt%)–DMAc (40 wt%) as mixed solvent contributed to the higher elongation ratio of 96.61 ± 0.41%. Therefore, by using TEP (60 wt%)–DMAc (40 wt%) as mixed solvent, the casting solution had a better solvent power to PVDF, and the membrane possessed excellent mechanical properties. The microporous membranes prepared from casting solutions with different commercial PVDFs exhibited similar morphology, but the water flux increased with the increment of polymer solution viscosity.

Yoo et al. [25] investigated the effect of solvent/cosolvent composition on the morphology and permeance of polyimide membrane. Asymmetric membranes were fabricated through phase inversion using the immersion–precipitation method. A mixture of $\gamma$-butyrolactone and NMP was used as solvent. The membrane morphology changed from finger-like to sponge-like as the proportion of $\gamma$-butyrolactone increased. It was proved that the heat of mixing of solvent and nonsolvent was an important factor in controlling the membrane morphology. Membranes of finger-free morphology and high permeance could be prepared by controlling the solvent/cosolvent ratio.

PVC nanofiltration membrane was prepared using DMAc–THF as solvents via the phase inversion method by Bagheripour et al. [27]. The effect of solvents mixing ratio (DMAc to THF) in the casting solution and also phase separation time in the coagulation bath on membrane flux and selectivity were studied. The membrane tensile strength measurement and SEM analysis were also carried out in membrane characterization. The highest membrane selectivity and flux were found at an 85 : 15 solvents mixing ratio (DMAc to THF).

Table 2.6 shows the effects of the casting solvent on the chemical and physical structure of poly[(1-(trimethylsilyl)-1-propyne)] (PTMSP) membranes. As can be seen from this table, both the

<table>
<thead>
<tr>
<th>Casting solvent</th>
<th>Membrane density (g cm$^{-3}$)</th>
<th>Contact angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.32</td>
<td>98.1</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.41</td>
<td>97.6</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.59</td>
<td>96.8</td>
</tr>
</tbody>
</table>

Source: [24]. Reproduced with permission of Wiley-VCH.

Feed: pure water (40 °C, 2 kg cm$^{-2}$); heat treatment: 40 °C, 10 min.

Table 2.5 Effect of casting solution composition on PWP.

<table>
<thead>
<tr>
<th>Casting solution composition (wt%)</th>
<th>Pure water permeability (mL cm$^{-2}$ s$^{-1} \times 10^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Cellulose nitrate</td>
</tr>
<tr>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
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membrane density and contact angle for water on the membrane surface are significantly different by casting solvents. The differences in the membrane structure remarkably influence the permeation and separation characteristics through their membranes [28].

2.4.1.5 Addition of Additive in Casting Solution

It has been well known [24, 29] that membranes prepared with additives such as magnesium perchlorate and barium perchlorate in the casting solution give a higher permeation rate without lowering rejection for the solute in the feed solution. It is strongly required to control size and number of pores in the membrane in order to make membranes for the separation of polymer solute with higher permeation rate and rejection. From such a viewpoint, polymer additives are added to the casting solution and dissolved out during the gelation process in the coagulation bath or heat treatment in hot water [24].

Figure 2.8 shows the effect of heat treatment time on the permeation characteristics through membranes from PVDF and PEG. The rate of PWP and the permeation rate for aqueous solution of PVA 205 increase remarkably and the rejection for PVA molecules decreases steeply up to 10 min of heat treatment time. In over 10 min the permeation rate decreases and the rejection increases slightly. The former phenomenon is attributed to the fact that PEG molecules in the polymer blend membranes are dissolved out into hot water during heat treatment and consequently membranes having a rough structure are formed. The latter phenomenon is dependent on the shrinkage of the membrane with heat treatment after the dissolution of PEG molecules in the polymer blend membranes.

Figure 2.9 shows scanning electron micrographs of membranes from PVDF and PEG before and after the heat treatment. As can be seen, the membrane after heat treatment has larger pores. This fact suggests the results of permeation characteristics in Figure 2.8. Also, Figure 2.9c shows the cross-section of membrane after heat treatment. The resulting membranes are asymmetric. The pores

Figure 2.8 Effect of heat treatment time on permeation characteristics of polymer blend membranes from PVF₂ and PEG. Casting solution: PVF₂/THF/DMF = 10/40/50 (wt%), PEG 20000/PVF₂ = 25 (wt%); membrane preparation: 25 °C, 2 h; heat treatment temperature: 80 °C; feed: (●) pure water, (○) 1% aqueous solution of PVA 205; operating conditions: 40 °C, 2 kg cm⁻². Source: [30]. Reproduced with permission of Springer-Verlag.
in the skin layer of the membrane are not necessarily penetrated cylindrically and have some complicated network structure. Perhaps the polymer solute, PVA molecules, may be rejected by these polymer network parts in the pores [30].

UF techniques have particular advantages for simultaneous purification, concentration and fractionation of macromolecules. A comparative study was undertaken on novel UF polymeric blend membranes based on CA prepared in the absence and presence of polymeric additives such as PEG 200 and polyvinylpyrrolidone (PVP) by the phase inversion technique using DMF as solvent. Polymer blend composition, additive concentration and casting, and gelation conditions were standardized for the preparation of asymmetric membranes by pore statistics and morphology [31]. These blend membranes were characterized for compaction in UF experiments at 414 kPa pressure in order to attain steady-state flux, which is reached within 4–5 h. The PWF was measured at 345 kPa pressure. Membrane hydraulic resistance derived by measuring water flux at various transmembrane pressures was found to be inversely proportional to PWF. Water content was estimated by simple drying and weighing procedures and found proportional to PWF for all the membranes. The MWCOs of different membranes were determined with proteins of different molecular weights and found to vary from 20 to 69 kDa depending on the PEG 200 and PVP content in the blend in the casting solution. Skin surface porosity of the membranes was analysed by scanning the samples at various magnifications. The characterized CA, CA–PEG 200 and CA–PVP membranes were used for cadmium ion rejection studies at 345 kPa.

Modification of the polymer membrane surface due to the addition of a polymer additive with selective affinity to a specific species in the casting solution can enhance membrane performance [32]. In order to improve surface property of PTMSP membranes, surface-modified PTMSP membranes were prepared by adding a small amount of a polymer additive, which is a graft copolymer PFA-g-PDMS, consisting of poly(fluoroacrylate) (PFA) and poly(dimethylsiloxane) (PDMS) (see Scheme 2.1), in a casting solution of PTMSP. Contact angles for water on air and glass plate sides in the preparation of surface-modified PTMSP membranes were significantly different, with those on the air side being more hydrophobic; and the contact angles for water increased with increasing additional amount of PFA-g-PDMS. High hydrophobicity of the membrane surface on the air side and the increase in

![Figure 2.9](image-url) Scanning electron micrographs of membranes from PVDF and PEG before and after heat treatment: (a) before heat treatment; (b) after heat treatment at 80 °C for 10 min; (c) cross-section of membrane after heat treatment. Source: [30]. Reproduced with permission of Springer-Verlag.
hydrophobicity with an increase of the additional amount of polymer additive were also confirmed by X-ray photoelectron spectroscopy. The permeation rate for an aqueous solution of 10 wt% ethanol in pervaporation of the surface-modified PTMSP membranes decreased slightly, but ethanol permselectivity increased considerably with the increase of the additional amount of PFA-g-PDMS.

2.4.1.6 Temperature of Casting Solution

Figure 2.10 shows the investigation of the effect of the dissolved form of CA molecules in the casting solution on the permeation characteristics. The casting solution composition and the casting solvent were kept constant and the dissolution temperature of the casting solution was changed. The relationship between the rate of PWP, the dissolution temperature and the heat treatment temperature, using membranes with 10 s of solvent evaporation period prepared from the casting solution of the proportion CA : acetone : FA as 15 : 40 : 45 (wt%), is shown [33].

Figure 2.10 Effects of dissolution temperature and heat treatment temperature on PWP. Casting solution: CA/acetone/FA = 15/40/45 (wt%); evaporation period: 10 s; heat treatment: (○) 40 °C, (●) 60 °C, (■) 80 °C, (●) 90 °C; feed: pure water; operating conditions: 40 °C, 2 kg cm⁻². Source: [33]. Reproduced with permission of Wiley-VCH.
At all heat treatment temperatures, the rates of PWPs decrease with an increasing dissolution temperature. If the casting solution is made at higher temperature, CA molecules will entangle densely in a more extended shape and membranes that have apparently higher density are formed; consequently, the rates of PWPs decrease. This consideration is supported by the following fact. When the resulting membranes are treated at a higher temperature, the decrease of PWP grows with an increasing dissolution temperature, because the membranes having apparently higher density are shrunk to a higher extent. It is known [34,35] that the membrane shrinkage increases with the raising of temperature during the heat treatment. The structural changes during the heat treatment of the membrane are due to the fact that almost all oxygen atoms of the carbonyl groups in the side chains of CA molecules are intramolecularly hydrogen bonded in the unheated membrane, and after heat treatment they are converted to intermolecular hydrogen bonds between two neighbouring CA molecules [36]. If the membrane having apparently a higher density exposed to a higher temperature, the intermolecular hydrogen bonds between CA molecules increase naturally, the pore size of the surface layer of membrane decreases, and consequently the rate of PWP diminishes. The relationship between the permeation characteristics, the dissolution temperature and the heat treatment temperature is shown in Figure 2.11, where a 1.0% aqueous solution of PEG 20000 as feed and the membrane with 10 s of solvent evaporation period are used. The relationship between the permeation rate and the dissolution temperature is similar to that of PWP in Figure 2.10. If the membranes are heated at 40 and 60 °C, the rejections are 0%, regardless of the change of dissolution temperature. With membranes heated at 80 and 90 °C, the rejections are higher with an increasing dissolution temperature. From these results, it is seen that the dissolution temperature affects the structure of the resulting membranes, as mentioned earlier.

Several sets of porous CA membranes were made using the same casting solution composition and gelation conditions but varying the casting solution temperature and solvent evaporation conditions [37]. The films were tested in reverse osmosis experiments at 250 psig using aqueous feed solutions containing 3500 ppm NaCl. The results show that the product rate obtained at a given level of solute separation is independent of evaporation time in the range tested and, for a given casting solution

![Figure 2.11 Effects of dissolution temperature and heat treatment temperature on permeation characteristics. Casting solution, evaporation period and operating condition are the same as in Figure 2.10; heat treatment: (○) 40 °C, (●) 60 °C, (□) 80 °C, (●) 90 °C; feed: 1.0% aqueous solution of PEG 20000. Source: [33]. Reproduced with permission of Wiley-VCH.](image-url)
composition, the temperature of the casting solution and conditions of solvent evaporation during film formation together constitute an important interconnected variable governing the porous structure of the resulting membranes. These results offer a new approach to the problem of developing more productive reverse osmosis membranes and have led to a new class of porous CA membranes capable of giving product rates 100% to 150% higher than those of the best membranes reported, at any given level of solute separation under the experimental conditions used. These results are of practical importance in low-pressure reverse osmosis applications.

2.4.2 Casting Condition

2.4.2.1 Temperature and Humidity during Casting

In casting conditions, the ambient conditions such as the casting temperature and humidity in the membrane preparation are delicately related to the fine structure of the resulting membrane. Since the evaporation velocity of the casting solvents is significantly dependent upon the casting temperature, the degree of the entanglement of polymer chains in the casting solution, especially in the surface area of the casting solution is significantly influenced, and the humidity delicately contribute to the formation of the fine structure of the membrane surface with the absorption of water molecules into the casting solution on the interface of the casting solution.

The evaporation period is importantly related to the evaporation amount of the casting solvent and especially to the thickness and density of the active dense layer of asymmetric membranes.

2.4.2.2 Evaporation Period

For the purpose of investigating the effect of low boiling point solvent on the permeation characteristics of CA membranes prepared from ternary systems of CA–low boiling point solvent–high boiling point solvent, FA is selected as high boiling point solvent and acetone, methyl acetate (MAc), THF, EtAc, and 1,4-dioxane are used as low boiling point solvents. The rates of PWPs of CA membranes prepared from casting solutions of the proportion CA : low boiling point solvent : FA as 10 : 45 : 45 (wt%) are shown in Figure 2.12 as a function of the evaporation period.

Figure 2.12 Effects of low boiling point solvents in the casting solutions and solvent evaporation period (EP) on PWP. Casting solutions: CA/low boiling point solvent/FA = 10/45/45 (wt%), (○) acetone, (△) MAc, (●) THF, (▲) EtAc, (●) 1,4-dioxane; heat treatment: 40 °C, 15 min; operating conditions: 40 °C, 2 kg cm⁻². Source: [33]. Reproduced with permission of Wiley-VCH.
As can be seen from Figure 2.12, the rates of PWPs change with the solvent evaporation period and the mode of change differs with the combination of casting solvent. The modes of changing are three types, which have the maximum rate of PWP at a certain solvent evaporation period, and show a decrease or increase of the rate with an increase of evaporation period during membrane formation. All membranes prepared in this work have an asymmetric structure consisting of a microporous thin surface layer and a rough porous back layer. It was reported in earlier papers [15,16,38] that there are many factors determining the structure of microporous membranes. The permeability of liquid through polymer membranes is strongly governed by the structure of microporous membranes. The differences of membrane structures by changing the casting solvent depend upon the following factors: (1) different dissolving forms of CA molecules in the casting solutions; (2) different formations of asymmetric double structures by using two organic solvents having different boiling points; (3) different polymer aggregations [37] occurring simultaneously with the evaporation of casting solvents; (4) different desolvation (solvent removal) velocity of the casting solvents into water during the gelation process, based on interactions between CA molecules and casting solvents and casting solvents with each other. The differences of the rates of PWPs in Figure 2.12 are attributed to these factors.

The same membranes used in the above experiments were tested for separations of aqueous solutions of PEG and PVA. Figure 2.13 shows the relationship between the permeation rate (PR), the rejection (R), the solvent evaporation period and the casting solvent using a 1.0% aqueous solution of PEG 20000 as feed.

The relationship between the permeation rate and the solvent evaporation period is similar to that in Figure 2.12. This fact may imply that the concentration polarization of PEG molecules at the membrane surface is negligibly small. The permeation characteristics of the membranes obtained from the system of EtAc–FA differ remarkably from systems of other combinations of casting solvents. This result suggests that the microporous structure of the membrane is influenced by the casting solvent.

Figure 2.13 Effects of low boiling point solvents in the casting solutions and solvent evaporation period (EP) on permeation characteristics of aqueous solution of PEG 20000. Casting solutions, heat treatment and operating conditions are the same as in Figure 2.12; feed: 1.0% aqueous solution of PEG 20000. Source: [33]. Reproduced with permission of Wiley-VCH.
In the system of EtAc–FA, when the solvent evaporation period is 10 s, a thinner surface layer on the membrane may be formed and larger pore size may be formed by the desolvation of the casting solvent in the gelation process, but not a great number of pores may be formed because EtAc cannot be appreciably dissolved in water. This discussion is understood from the fact that the permeation rate is smaller than that of other systems. Since the thickness of surface layer and the aggregation of CA molecules may act mutually advantageously at 60 s, reasonable pore sizes for the separation of PEG molecules may be formed, and consequently the permeation rate and the rejection are higher than those at 10 s. In the case of 300 s, since the evaporated amount of EtAc is large, the surface layer formed during the evaporation process becomes thicker and much FA, which is a nonsolvent for CA molecules, remains in the casting solution. Therefore, the pore sizes become a little larger because the aggregation of CA molecules is slightly higher than at 60 s. Consequently, the permeation rate increases and the rejection decreases slightly. This result also is supported by the fact that the permeation rate is very high but the rejection is 0% in cases with more than 600 s evaporation period.

The average pore size and pore size distribution of reverse osmosis membranes made of aromatic polyamido hydrazide PPPH 8273 material (abbreviated as PAH membrane) have been determined on the basis of the surface force–pore flow model using separation data for several reference solutes [39]. The results confirm the two-normal distribution of the radius of pores on the membrane surface, and the progressive transition of the pore in the second pore distribution to that in the first pore distribution as the solvent evaporation proceeds. The analysis of the data pore size distribution also reveals the process of formation of asymmetricity on PAH RO/UF membranes.

2.4.3 Gelation Condition

2.4.3.1 Gelation Period and Temperature

In the wet method of membrane preparation a gelation medium is usually employed. Generally, the gelation medium is water. Both the temperature of the gelation medium and the immersion time in the gelation medium are significantly related to the velocity of the solvent exchange between the casting solvents and the gelation medium and, consequently, to the structure of the resulting membrane.

Liu et al. [40] introduced modified reinforced PSF membranes. Their sensitivity to the environmental temperature and humidity in membrane formation can be reduced, and the effect of the gelation medium temperature on membrane pore size can also be improved. They tried to find the membrane’s pore formation rule and overcome the defect of a too thick and easily curled membrane so that they could make the production conditions of the membrane similar to that of CA membranes and suitable to continuous pilot scale-up production. They also briefly illustrated the effect of polymer concentration on machine-case membranes, the effect of operating pressure on PSF UF flux, and trial uses.

Figure 2.14 shows the effect of gelation temperature on the permeation characteristics using pure water and a 1.0% aqueous solution of PEG 20000 as feed and the burst strength of membrane [33]. The rate of PWP and the permeation rate increase with increase of gelation temperature. Since the casting solvents that remain in the casting solution after the evaporation process are removed rapidly into the gelation medium with increased gelation temperature, the aggregation of CA molecules occurs remarkably, and consequently the structure of the resulting membrane becomes rougher. This is understood from the fact that the burst strength of the membrane is decreased with it. This result is similar to that obtained by Kesting et al. [41], who reported that the membrane gel structure which results from immersion of casting solution into water is rapidly converted to a microgel-type structure at higher gelation temperature. The earlier results can be explained by their conclusion.
2.4.3.2 The Kind of Gelation Medium

When casting solvents are hydrophobic, nonsolvents (normally water) for the polymer materials can be employed as gelation media. In these cases, many organic solvents can be applied to gelation media and membranes of different physical structures are able to be prepared.

It was found that the formation of a finger-like cavity is dependent not only on the absorption of water molecules into the casting mixture from the atmosphere during the solvent evaporation process, but also on the exchange velocity of the casting solvent and the gelation medium during the gelation process \[42\]. Then, the formation of a finger-like cavity and the permeation characteristics were investigated by changing the gelation medium. The result obtained is shown in Figure 2.15, where an aqueous solution of NaCl is used as a gelation medium.

In all gelation media, the permeation rates for an aqueous solution of PEG 1000 increase and the rejections for PEG 1000 decrease with an increase in evaporation period. This is attributable to the absorption of water molecules into the casting mixture, which affects the structures of the resulting membranes. In a short evaporation period, the permeation rate is in the following order: pure water > 5% NaCl > 10% NaCl; and the rejection is in the reverse order for these gelation media. In this case, since the absorption of water molecules is small, the membrane structures are governed mainly by the exchange velocity of DMF in the casting mixture and water in the gelation medium. For both the permeation rate and the rejection, the difference caused by the gelation medium becomes smaller with an increase in evaporation period. In a long evaporation period these phenomena are influenced significantly by the absorption of water molecules during the solvent evaporation process, and the effect of the gelation medium on the structure of the resulting membrane is reduced. Therefore, a large difference in both the permeation rate and the rejection is not recognized.

When the concentration of NaCl in the gelation medium increases, the permeation rate decreases and the rejection increases. This is due to a difference in the interaction between the water molecules...
in the gelation medium and DMF molecules. That is, when the solvation between a nonprotonic polar solvent such as DMF and the water molecules is considered, it is expected that the carbonyl groups in DMF molecules react selectively with the water molecules. Here, if the gelation medium contains a strong electrolyte, such as NaCl, the solvation between DMF molecules and water molecules becomes weaker than in the gelation medium consisting only of water because hydration between the electrolyte and the water molecule is strong. Therefore, the migration of DMF molecules into the gelation medium at the moment of gelation is slower than a system using water as a gelation medium, and consequently the degree of heterogeneous aggregation of CN molecules is reduced. The decrease of permeation rate and the increase of rejection with increasing concentration of NaCl in the gelation medium are attributed to these aforementioned factors.

This discussion is suggested by the fact that the evaporation period for the formation of a finger-like cavity becomes longer and the size of the finger-like cavity becomes smaller as the concentration of NaCl in the gelation medium increases, as shown in Figure 2.16.

The scanning electron micrographs of the cross-section of membranes are shown in Figure 2.17, where DMF is employed as a casting solvent, the mixed solvent of DMF and pure water is used as gelation medium and its mixed ratio is changed. The finger-like cavities become smaller with an increase in DMF content in the gelation medium and disappear at an H2O/DMF ratio of 70/30 (wt%). The increase of content in the gelation medium implies that the exchange velocity between the casting solvent and the gelation medium becomes slow and the gelation of CN molecules proceeds gradually. Consequently, the finger-like cavities are not formed in the resulting membranes [42].
Figure 2.16 Effect of gelation medium on cross-section structure of CN membranes. Preparation conditions of membranes same as Figure 2.15. Source: [42]. Reproduce with permission of Elsevier.

Figure 2.17 Effect of mixed ratio of H$_2$O/DMF in gelation medium on formation of finger-like cavities. Casting ambient: same as in Figure 2.15, Casting solvent: DMF, evaporation period: 7 min. Source: [42]. Reproduce with permission of Elsevier.
Yamasaki et al. [43] prepared asymmetric gas separation membranes by the phase inversion technique under different gelation conditions from PSF–DMAc solutions. The dual-bath method was employed to control the skin layer properties: the cast film was immersed in a 2-propanol bath and water bath in sequence. The membranes were characterized by the permeance of oxygen and nitrogen gases and SEM observation. A thin layer of silicone rubber (PDMS) was laminated on the surface of each asymmetric PSF membrane to eliminate the effect of defects in the skin layer. The oxygen permeance was inversely proportional to the square root of immersion time in the first (2-propanol) bath. The skin layer thickness determined by SEM observation increased with an increase in the immersion time in the first bath. For a given immersion time, the oxygen permeance decreased with an increase in the polymer concentration in the casting solution. Selectivity of oxygen over nitrogen also depended both on the immersion time in the first bath and the polymer concentration.

2.4.4 Post-treatment

2.4.4.1 Method of Heat Treatment

There are two types. One is the treatment in a hot water and the other is in a hot air.

2.4.4.2 Temperature and Period of Heat Treatment

The heat treatment of the polymer membrane results in a physicochemically structural change to the intermolecular interaction from the intramolecular interaction between polymer chains in the resulting membranes, and the temperature and period can control the degree of these changes. Consequently, these changes remarkably influence the membrane performance.

With excellent permeability, large specific surface area, high porosity and outstanding internal connectivity, PSF electrospun membrane can be a good filter medium. However, the as-spun PSF electrospun membrane has poor mechanical properties and a bulky structure, and the binding force between fibres is low. Zhang et al. [44] investigated the effects of heating time, temperature and heating method during heat treatment on the morphology, mechanical properties and chemical stability of PSF electrospun membrane. The results show that the PSF membrane achieved its best performance when treated at 190 °C for 3 h with tension heating. After tension heating, dimensional stability, appearance, integrity and mechanical properties improved; chemical stability in alcohol solution increased greatly, but the membrane shrank quickly in acetone solution.

Rahimpour et al. [45] prepared flat-sheet PES and PVDF membranes by the immersion–precipitation technique. The influence of hot air and water treatment on morphology and performance of the membranes was investigated. The membranes were characterized by AFM, SEM, cross-flow filtration of milk and fouling analysis. The PES membrane turns to a denser structure with thick skin layer by air treatment at various temperatures during different times. This diminishes the PWF. However, the milk permeation flux was considerably improved at 100 °C air treatment for 20 min with no change in protein rejection. The smooth surface and slight decrease in surface pore size for air-treated PES membrane at 100 °C compared with untreated membrane may cause this behaviour for the membrane. The water treatment of PES membranes at 55 and 75 °C decreases the PWF and milk permeation flux and increases the protein rejection. This is due to a slight decrease in membrane surface pore size. The treatment of PES membrane with water at higher temperature results in a porous structure with superior performance. The fouling analysis of 20-min-treated membrane indicates that the surface properties of 100 °C air-treated and 95 °C water-treated PES membranes are improved compared with untreated membrane. The SEM observation depicts that the morphology of air- and water-treated PVDF membranes was denser and smoother with increasing heat treatment temperature.
Aggregation in heat-treated Nafion ionomer dispersion and 117 membrane was investigated by $^1$H and $^{19}$F NMR spectra, spin-lattice relaxation time and self-diffusion coefficient measurements [46]. Results demonstrate that heat-treatment affects the average Nafion particle size in aqueous dispersions. Measurements on heat-treated Nafion 117 membrane show changes in the H isotropic chemical shift and no significant changes in ionic conductivity. SEM analysis of the prepared cathode catalyst layer containing the heat-treated dispersions reveals that the surface of the electrode with the catalyst ink that has been pretreated at ~80 °C exhibits a compact and uniform morphology. The decrease of Nafion ionomer’s size results in better contact between catalyst particles and electrolyte, a higher electrochemically active surface area and a significant improvement in the DMFC’s performance, as verified by electrochemical analysis and single-cell evaluation.

Barzin et al. [47] prepared hollow-fibre membranes for haemodialysis from PES and PVP (PES/PVP = 18/3 and 18/6 by weight) solution in DMAc by the dry wet spinning method. Hollow fibres were then heated either in hot water (95 °C for 30 min) or in air (150 °C for 5 min). These membranes were characterized by ultrafiltrating dextrans of different molecular weights (200 ppm in water) at room temperature and an operating pressure of 5 psig. It was observed that the water flux of the hollow fibre increased significantly when heat treated in water, while it decreased when heat treated in air. On the other hand, MWCO of the hollow fibre increased slightly when heat treated in water, while it decreased drastically when heated in air. The morphology of the surfaces of the hollow fibres was studied by AFM in terms of surface roughness. The roughness of both the inner and outer surfaces decreased upon heat treatment, whether heated in water or in air. The membrane heat treated in air exhibited the lowest roughness parameter. SEM images also showed that the surface morphology of membranes was different before and after heat treatment. Discussions are made on the basis of MWCO and AFM results. The performance data of the hollow fibre heated in air at 150 °C was found to be the most appropriate for haemodialysis application. The hollow-fibre membrane prepared from the blend ratio of PES/PVP = 18/3 showed slightly higher flux than the hollow-fibre membrane prepared from a solution with PES/PVP ratio of 18/6.

The effect of heat treatment temperature in hot water on the permeation and separation characteristics through the Nylon 12 membrane is shown in Figure 2.18, where a 1.0% aqueous solution of PEG 20000 was used as feed [48]. The permeation rate decreases and the rejection increases with an increase in heat treatment temperature in hot water. This phenomenon is attributed to the structural changes of the membrane during heat treatment: an intramolecular hydrogen bond is converted into an intermolecular hydrogen bond [49], as revealed in the heat treatment of CA [15,38] and CN membranes.

To control swelling of PVA membranes, mixtures of PVA as an organic component and tetraethoxysilane (TEOS) as an inorganic component were applied to the sol–gel reaction, and PVA–TEOS hybrid membranes were prepared. The relationship between the structure of the PVA–TEOS hybrid membranes and their permeation and separation characteristics for an aqueous ethanol solution during pervaporation are discussed in detail by Uragami et al. [50].

The effects of the annealing temperature on the separation factor of PVA and PVA–TEOS hybrid membranes with a TEOS composition of 5 and 25 wt% are shown in Figure 2.19. In this case, the annealing time of the PVA and PVA–TEOS hybrid membranes was fixed for 8 h and the annealing temperatures were 80, 90, 130 and 160 °C. As can be seen in this figure, the PVA–TEOS hybrid membranes had better separation characteristics than the PVA membranes over the entire range of annealing temperatures. The separation factor for PVA and PVA–TEOS hybrid membranes also increased with increasing annealing temperature, and this tendency increased with an increase in the TEOS content.
Figure 2.18 Effect of the heat treatment temperature in hot water on the permeation and separation characteristics. Exposure period of casting solution: (○) 30 s, (●) 300 s. Feed: 1.0% aqueous solution of PEG 20000. Heat treatment time: 4 h. Operating conditions: 40 °C, 2 kg cm⁻². Source: [48]. Reproduced with permission of Elsevier.

Figure 2.19 Effects of the annealing temperature on the separation factor for water permselectivity of an aqueous solution of 85 wt% ethanol through PVA membranes (○), and PVA/TEOS hybrid membranes with 5 wt% TEOS (■) and 25 wt% TEOS (□). The annealing time was 8 h. Source: [50]. Reproduced with permission of American Chemical Society.

Figure 2.20 shows the permeation rate and membrane density for PVA and PVA–TEOS membranes as a function of the annealing temperature. The permeation rate of every membrane decreased with increasing annealing temperature; however, the decrease for the PVA–TEOS hybrid membrane with higher TEOS contents was smaller. On the other hand, the density of the PVA and PVA–TEOS hybrid membranes increased with increasing annealing temperature. The density of PVA–TEOS hybrid
membranes with higher TEOS content was higher, but the density of the PVA membrane decreased significantly at 130 °C and over. The PVA–TEOS hybrid membrane with a higher TEOS content was also more sensitive to annealing temperature. The increase in PVA membrane density was probably due to the increase in crystallinity of the PVA membrane because of the hydrogen bonds. The increase in the density of the PVA–TEOS hybrid membrane can be attributed to an increase in the hydrogen bonds between the silanol groups in the silane particle, the hydroxyl groups in the PVA and the covalent bonds between them, as shown in Scheme 2.2. The decrease in the density of the PVA membrane annealed at 130 °C affects the decomposition of the PVA molecule. The increase in the separation factor for water permselectivity in Figure 2.19 and the decrease in the permeation rate in Figure 2.20 with increasing annealing temperature and TEOS content significantly influenced the membrane density.

Figure 2.21 shows the effects of the annealing time on the separation factor of annealed PVA and PVA–TEOS hybrid membranes with TEOS contents of 5 and 25 wt% TEOS; the annealing temperature of the PVA and PVA–TEOS hybrid membranes was fixed at 130 °C and the annealing time was changed. As can be seen in Figure 2.21, the separation factor of all membranes increased with increasing annealing time. In particular, the separation factor of the PVA–TEOS hybrid membrane with a TEOS content of 25 wt% increased remarkably with increasing annealing time. This PVA–TEOS hybrid membrane also had a very high separation factor for water permselectivity. This fact suggests that varying the annealing time was more effective for improving separation characteristics of the PVA–TEOS hybrid membrane than varying the annealing temperature.
Figure 2.22 shows the effects of annealing time on the permeation rate of annealed PVA and PVA–TEOS hybrid membranes and on the membrane density. The permeation rate decreased with increasing annealing time, and the PVA–TEOS hybrid membrane density with a higher TEOS content had a lower permeation rate. The density of the PVA and PVA–TEOS hybrid membranes with TEOS content of 5 wt% peaked at an annealing time of 8 h, but the density of the PVA–TEOS hybrid membrane with a TEOS content of 25 wt% increased with increasing annealing time. These results suggest that the partitioning characteristics were improved, but the permeability was slightly decreased, because the structure of the PVA–TEOS hybrid membrane with a higher TEOS content became denser with increasing annealing temperature. These results support that increasing the annealing temperature or time yields PVA–TEOS hybrid membranes with a denser structure.

Figure 2.21 Effects of the annealing time on the separation factor for the water permselectivity of an aqueous solution of 85 wt% ethanol through the PVA membranes (○), and PVA/TEOS hybrid membranes with 5 wt% TEOS (■) and 25 wt% TEOS (□). The annealing temperature was 130 °C. Source: [50]. Reproduced with permission of American Chemical Society.

Figure 2.22 shows the effects of annealing time on the permeation rate of annealed PVA and PVA–TEOS hybrid membranes and on the membrane density. The permeation rate decreased with increasing annealing time, and the PVA–TEOS hybrid membrane density with a higher TEOS content had a lower permeation rate. The density of the PVA and PVA–TEOS hybrid membranes with TEOS content of 5 wt% peaked at an annealing time of 8 h, but the density of the PVA–TEOS hybrid membrane with a TEOS content of 25 wt% increased with increasing annealing time. These results suggest that the partitioning characteristics were improved, but the permeability was slightly decreased, because the structure of the PVA–TEOS hybrid membrane with a higher TEOS content became denser with increasing annealing temperature. These results support that increasing the annealing temperature or time yields PVA–TEOS hybrid membranes with a denser structure.

In general, the permselectivity of polymer membranes is dependent on their chemical and physical structures, which influence the solubility of permeants in the membrane and the diffusivity of permeants through the membrane. Therefore, we investigated the chemical and physical structures of the PVA–TEOS hybrid membranes to elucidate their permeation and separation characteristics.

Figure 2.23 shows the effect of the annealing time on the ethanol concentration in the PVA and PVA–TEOS hybrid membranes for an aqueous solution of 85 wt% ethanol. In this figure, it is clear
that with increasing annealing time the ethanol concentration in these membranes decreased significantly. Furthermore, the ethanol concentration in the PVA–TEOS hybrid membrane was lower than in the PVA membrane. In other words, the increase in annealing time and TEOS content led to the preferential incorporation of water into the PVA–TEOS hybrid membrane from an aqueous ethanol

Figure 2.22 Effects of the annealing time on the permeation rate for an aqueous solution of 85 wt% ethanol through the PVA membranes (○), and PVA/TEOS hybrid membranes with 5 wt% TEOS (■) and 25 wt% TEOS (□) and their density. The annealing temperature was 130 °C. Source: [50]. Reproduced with permission of American Chemical Society.

Figure 2.23 Effects of the annealing time on the ethanol concentration in the PVA membrane (○), and PVA/TEOS hybrid membranes with 5 wt% TEOS (■) and 25 wt% TEOS (□) for an aqueous solution of 85 wt% ethanol. The annealing temperature was 130 °C. Source: [50]. Reproduced with permission of American Chemical Society.
solution. This discussion is supported by the sorption selectivity $\alpha_{\text{sorp}, \text{H}_2\text{O}/\text{EtOH}}$ in Table 2.7, determined from the separation factor $\alpha_{\text{sep}, \text{H}_2\text{O}/\text{EtOH}}$ and Figure 2.23 using

$$\alpha_{\text{sorp}, \text{H}_2\text{O}/\text{EtOH}} = \frac{\alpha_{\text{sorp}, \text{H}_2\text{O}/\text{EtOH}}}{\alpha_{\text{diff}, \text{H}_2\text{O}/\text{EtOH}}}$$

(2.1)

As can be seen in Table 2.7, both separation factor and sorption selectivity of the unannealed PVA and PVA–TEOS hybrid membranes increased with increasing TEOS content. On the other hand, the diffusion selectivity was calculated from these separation factor and sorption selectivity using

$$\alpha_{\text{diff}, \text{H}_2\text{O}/\text{EtOH}} = \frac{\alpha_{\text{sorp}, \text{H}_2\text{O}/\text{EtOH}}}{\alpha_{\text{sep}, \text{H}_2\text{O}/\text{EtOH}}}$$

(2.2)

The diffusion selectivity of unannealed PVA and PVA–TEOS hybrid membranes was very low, regardless of the TEOS content.

Since the selectivity for permeants incorporated in the membranes is significantly influenced by the chemical properties of the membrane surface, the contact angles on the surface of the PVA–TEOS hybrid membrane were measured.

Figure 2.24 shows the contact angles for methylene iodide on the surfaces of PVA and PVA–TEOS hybrid membranes as a function of annealing time. In this figure, since methylene iodide was used for the measurement of the contact angle of the membrane surface, a higher contact angle implies a more

**Figure 2.24** Effects of the annealing time on the contact angles for methylene iodide on the surface of the PVA membranes (○), and PVA/TEOS hybrid membranes with 5 wt% TEOS (■) and 25 wt% TEOS (□). The annealing temperature was 130 °C. Source: [50]. Reproduced with permission of American Chemical Society.

<table>
<thead>
<tr>
<th>TEOS (wt%)</th>
<th>$\alpha_{\text{sep}, \text{H}_2\text{O}/\text{EtOH}}$</th>
<th>$\alpha_{\text{sorp}, \text{H}_2\text{O}/\text{EtOH}}$</th>
<th>$\alpha_{\text{diff}, \text{H}_2\text{O}/\text{EtOH}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>26.3</td>
<td>24.3</td>
<td>1.08</td>
</tr>
<tr>
<td>5</td>
<td>32.8</td>
<td>31.6</td>
<td>1.03</td>
</tr>
<tr>
<td>25</td>
<td>72.3</td>
<td>69.8</td>
<td>1.03</td>
</tr>
</tbody>
</table>

*Source: [50]. Reproduced with permission of American Chemical Society.*
hydrophilic membrane surface. As can be seen in Figure 2.24, the contact angle increased with increasing TEOS content. This result suggests that the surface of the membrane became more hydrophilic and supports the contention that the PVA–TEOS hybrid membranes with a higher TEOS content could preferentially incorporate water from an aqueous ethanol solution, as shown in Figure 2.23. On the other hand, with increasing annealing time, the contact angles for methylene iodide decreased for all membranes, and the membrane surface became more hydrophobic. This result is in contrast with the fact that water could be selectively absorbed into the PVA–TEOS hybrid membrane with an increase in the annealing time, as shown in Figure 2.23.

2.4.4.3 Pressure Treatment
Pressure treatment of the polymer membrane causes a physical structural change. Parameters for the pressure treatment are the temperature, pressure and period. Their control makes it possible to prepare a membrane with the most appropriate structure for a certain aim.

Mänttäri et al. [51] investigated the effect of temperature on the retention in nanofiltration of model substances (glucose) and substances in industrial streams in the temperature interval 2–65 °C. An increase in temperature decreased the retention until a critical temperature of the membrane was exceeded. After that temperature the flux even decreased and the retention increased. The retention of uncharged substances normally decreased due to alkaline cleaning, and the flux of most membranes increased. In the filtration of mechanical pulp mill effluents, an increase of temperature decreased the retention of organic substances but did not affect the retention of conductivity. Only a few nanofiltration membranes withstood a temperature of 65 °C without a significant change in the filtration efficiency. A membrane pretreatment, such as pressurization with pure water, affected dramatically the flux and the flux reduction, and somewhat the retention. Experiments made with incompletely wetted membranes underestimate fouling and the retention of the membrane. Most nanofiltration membranes seemed to be almost completely wetted at a pressure of 25 bar.

Figure 2.25 shows the effect of the press temperature in the pressure treatment of a porous PTMSP membrane on the permeation and separation characteristics for an aqueous solution of 10 wt% ethanol through porous PTMSP membranes during temperature-difference controlled evapomeation in which the temperatures of the feed solution and membrane surroundings are 40 °C and 0 °C respectively. With increasing press temperature in the pressure treatment, although the permeation rate decreases slightly, the ethanol concentration in the permeate increases. This increase in the ethanol
permselectivity is due to the fact that the pore size in the porous PTMSP membrane became smaller and the permeation of the aggregation of water molecule is prevented [28].

2.4.4.4 Elongation Treatment
Monoaxial and biaxial elongation can orient polymer chains constituting the membrane and result in a dense membrane. In general, these elongations are carried out with the heat treatment and the molecular orientation and crystallization can be given.

2.4.4.5 Post-reaction
The effect of heat treatment temperature in formic acid on the permeation characteristics is shown in Figure 2.26 [48].

The permeation rate increases with an increase in heat treatment temperature, and the rejection has a maximum value at a certain temperature. Up to a heat treatment temperature of 45 °C (99% formic acid) or 55 °C (85% formic acid) there is a continuous decrease in the rejection and an increase in the permeation rate. When the heat treatment temperature is raised to more than 45 °C and 55 °C, the rejection and the permeation rates increase. This increase may be attributed to a decrease of pore size and an increase of pore number, which causes the formation of intermolecular hydrogen bonds of polymer chains, together with the effects of swelling ability of formic acid for Nylon 12 and thermal movement of Nylon 12 molecules as the heat treatment temperature increases (see Figure 2.27). The membranes treated with heat in 99% and 85% formic acid are dissolved at 55 °C and 75 °C respectively.

**Figure 2.26** Effect of the heat treatment temperature in the system of formic acid/water on permeation and separation characteristics. Exposure period of casting solution: ○ 30 s, ● 300 s. Feed: 1.0% aqueous solution of PEG 20000. Heat treatment time: 4 h. Treatment solution: (○) 85% HCOOH, (●) 99% HCOOH. Operating condition: 40 °C, 2 kg cm⁻². Source: [48]. Reproduced with permission of Elsevier.
The permeation characteristics and the properties of membranes are shown in Figure 2.28, where the concentration of formalin in the treatment solution is kept constant and the concentration of formic acid is changed. The rate of PWP and the permeation rate increase as the concentration of formic acid increases. The rejection decreases with an increase in formic acid concentration and shows a constant value over a certain concentration. The degree of substitution (total combined formaldehyde) is more or less constant. The burst strength of the membranes containing water increases in proportion to the concentration of formic acid. When Nylon 12 reacts with formaldehyde in the presence of an acidic catalyst, the addition in the first step is hydroxymethylation, and condensation in the second step is mainly a methylene cross-link between the hydroxymethyl group and the amido group. These reactions change the polymer molecular structure forming the membranes and consequently result in fine structural changes of the membranes. It is well known [52–59] that these reactions are influenced by the reaction temperature, time and the concentration of the catalyst (pH). In Figure 2.28 the reaction temperature and time are kept constant at 80 °C for 4 h; only the concentration of formic acid is changed. Therefore, the extents of these reactions may be varied. The degree of substitution is approximately equal, but the burst strength of the membranes is influenced significantly by the variation of the concentration of formic acid. These results may be based on the following two factors. The first of these factors relates to the fraction of hydroxymethyl groups and methylene bonds. When the concentration of formic acid is lower, predominantly hydroxymethyl groups are formed but the formation of methylene bonds is relatively small. When it is higher, hydroxymethyl groups react with amido groups and consequently many methylene cross-links are formed. The second of these factors depends upon the fractions of intramolecular and intermolecular cross-links of methylene bonds. In the case of a lower concentration of formic acid in the treatment solution, the intramolecular cross-links appear because Nylon 12 molecules turn out in the state of a rolled form, as shown in Figure 2.29b. When the concentration is higher, since polymer chains of Nylon 12 molecules exist in the state of a more lengthened form, the formation of the intermolecular cross-links predominates, as shown in Figure 2.29c.

As mentioned earlier, the rate of PWP and the permeation rate increase and the rejection decreases based on the extension and an increase in pore sizes with formic acid. The methylene linkages may not affect the permeation characteristics as they are formed intermolecularly or intramolecularly in a space that is very narrow and does not participate in the permeation; and even if the hydroxymethyl groups are formed in a wall of relatively large pores that governs mainly the permeation characteristics, the methylene linkages do not prevent the permeabilities of the permeating species increasing markedly.

Figure 2.27 Scheme of hydrogen bonds: ○ intramolecular; ● intermolecular. Source: [48]. Reproduced with permission of Elsevier.
Figure 2.28 Effect of formic acid in the system of formic acid/formalin on the membrane characteristics. Exposure period of casting solution: 300 s. Feed: ○ pure water, ● 1.0% aqueous solution of PEG 20000. Heat treatment: 80 °C, 4 h. Operating conditions: 40 °C, 2 kg cm⁻². Source: [48]. Reproduced with permission of Elsevier.

Figure 2.29 Scheme of cross-link: – intramolecular; = intermolecular. Source: [48]. Reproduced with permission of Elsevier.
Figure 2.30 shows the effect of heat treatment temperature in the system of formic acid/formalin on the membrane characteristics. As can be seen from Figure 2.30, the permeation rate has a maximum value at 80 °C. The rejection, the degree of substitution and the burst strength of the membranes increase as the heat treatment temperature increases. It was described that the permeation characteristics were influenced by the shrinkage of membranes with heat treatment temperature in hot water. The membrane performance in this system is governed by the shrinkage of membranes and the formation of hydroxymethyl groups and methylene linkages. When the permeation characteristics at 80 °C are compared with those at a heat treatment temperature below 70 °C, the shrinkage of membrane at 80 °C is more or less higher than the shrinkage below 70 °C, but polymer chains are more lengthened as soon as formic acid appears in the treatment solution. Therefore, below 70 °C the membranes may be in a state that is intramolecularly cross-linked (see Figure 2.31b), and at 80 °C the membranes may be forced to form intermolecular cross-links (see Figure 2.31c). However, if other hydroxymethyl groups or amido groups in the neighbourhood of the hydroxymethyl groups are absent, the cross-link does not appear, and consequently the unreacted hydroxymethyl groups remain. The increase of the permeation rate at 80 °C is attributed to these factors. The decrease of the rate of PWP and the permeation rate and the increase of rejection at 90 °C are dependent on the fact that the membrane which is remarkably shrunk with heat is significantly cross-linked (see Figure 2.31d).
2.4.4.6 Post-solvent Treatment

In pressure-driven membrane permeation, the permeation rate often decreases with the permeation time due to the compaction of the membrane under the pressurization. The treatment of the membrane by an organic solvent is effective in giving permeation stability [60].

The permeation rates for aqueous solutions of alcohols and amine compounds through cellulose membranes were greater than for pure water as the solutes in aqueous solutions were not rejected [61]. These phenomena were related to the behaviour of water molecules and solute molecules in aqueous solution, and of these molecules on the membrane surface and in the membrane. Revealing these behaviours is very important in order to elucidate the permeation mechanism through the polymer membrane. For the purpose of investigating whether the permeation phenomena through cellulose membranes are normal or abnormal, PVA, which is a hydrophilic polymer as well as cellulose, was selected as membrane material. Untreated PVA membrane is dissolved in aqueous solution. Therefore, it is required to make a water-insoluble membrane in some way. It was reported that water-insoluble membranes can be prepared from mixtures of PVA aqueous solution and various

Figure 2.31 Structural change with heat treatment temperature in formic acid/formalin system. – intramolecular cross-link; = intermolecular cross-link. Source: [48]. Reproduced with permission of Elsevier.
monovalent alkali metal hydroxide solutions, but the rate of PWP of alkali-bridged PVA membranes decreased considerably with an increase in permeation period; that is, this decrease of rate was dependent on the membrane compaction under pressure [62]. Then, the preparation of alkali-bridged PVA membranes with the permeation stability was investigated [59]. Attempts to improve the permeability were made by treating the membranes with various organic solvents. Of the alkali-bridged PVA membranes treated with the organic solvents n-pentane, benzene, toluene, xylene, methyl alcohol, ethyl alcohol, DMF and m-cresol, those membranes treated with m-cresol have excellent permeation stability, but the permeabilities of the untreated membranes and the other treated membranes decrease with an increase in permeation period. Figure 2.32 shows the relationship between the rates of PWP of an untreated membrane and the membrane treated with m-cresol and the permeation period. The permeability of the former membrane diminishes with an increased permeation period, but that of the latter membrane is very stable. The reasonable decrease of rate with the permeation period depends on the compaction of alkali-bridged PVA membrane plasticizing with water under pressure. When the alkali-bridged PVA membranes are treated with m-cresol, which is a nonsolvent for PVA molecules, at relatively high temperature, the number of hydrogen bonds between the hydroxyl groups of PVA molecules increases. An aggregation of PVA molecules occurs during treatment in m-cresol; consequently, a denser membrane is formed. Therefore, the rate of PWP becomes significantly small compared with that of an untreated membrane. The permeation stability is attributable to the aforementioned factors. This discussion is supported by the facts that the area, thickness and water content of the latter membrane are smaller than those of the former membrane.

The scanning electron micrographs of the surfaces of untreated alkali-bridged PVA membrane and membrane treated with m-cresol are shown in Figure 2.33. It is found that the latter membrane is denser than the former membrane. In spite of the fact that the pore sizes of these membranes are very large, the rate of PWP is not so large. Since these membranes are hydrophilic, bound water exists in the membranes. Therefore, apparent effective pore size is very small. Consequently, the rate of PWP is governed by the apparent effective pore size. The effect of feed solute on the permeation rate is
summarized in Table 2.8, where the rejections for all solutes are 0%. The permeation rates for aqueous solutions of hydrophilic solutes such as methyl alcohol, ethyl alcohol, PEG 200, LiCl, NaCl and KCl are greater than the rate for pure water. It has been well known that hydrophilic groups such as hydroxyl, amino, carboxyl and aldehyde break ‘clusters’ of water molecules \([63,64]\) connected with hydrogen bonds. When the hydrophilic solutes exist in the feed, water clusters in aqueous solution become smaller than those in pure water. Furthermore, the hydrophilic solute brings about an activation of the movement of water molecules that attach very weakly to the bound water layers on the membrane surface and in the membrane, promotes the permeation of these water molecules and consequently extends apparent effective pore sizes in the membranes. The greater permeabilities for aqueous solutions containing the hydrophilic solutes are caused by these two factors.

On the other hand, the permeation rates for aqueous solutions of \(n\)-amyl alcohol and phenol are smaller than for pure water. These solutes tend to increase the size of water clusters, because the
hydrophobicity of these solutes is higher. These molecular sizes are large. Consequently, the permeability of water molecules in aqueous solution decreases and the permeation resistance of feed solute increases. When benzene is used as feed solute, it is expected that the permeation rate becomes very small compared with the rate of PWP, because benzene is significantly hydrophobic. As can be seen from Table 2.8, however, its permeation rate is not very small. This result is due to the fact that it is difficult to prepare a comparable concentration with other solutes because the solubility of benzene for water is very low.

Liu et al. [65] studied the effect of different kinds of organic-solvent-treated PSF tubular UF membrane on performances and structure. The results show that the surface of membranes treated with n-hexane are smoother and less hydrophilic; the content of carbon element increased at the same time. On the other hand, the water flux of membranes treated with alkane decreases, but the rejections to MgSO₄ and egg protein increase. While the surfaces of membrane treated with ethanol are rougher and more hydrophilic, the contents of carbon and oxygen increase too. The water flux of membranes treated with alcohols increase obviously, but the rejection to egg protein decreases slightly.

### 2.5 Structure of Liquid Membranes

The structures of the liquid membrane are classified into three categories: bulk, emulsion and supported types.

#### 2.5.1 Bulk Liquid Membrane

This type is useful for laboratory experiments. As shown in Figure 2.34, the feed water phase (F phase), the liquid membrane phase (M phase) – consisting of some type of carrier dissolved in a hydrophobic organic solvent placed in the bottom of the U-tube cell – and the permeation water phase (P phase) are formed. A magnetic stirrer is set in the M phase and rotated at a fairly slow speed. The amount of permeated material in the P phase is determined by an instrument such as a gas chromatograph.
2.5.2 Emulsion Liquid Membrane

The structure of the emulsion liquid membrane is shown in Figure 2.35. In this type the P phase aqueous solution (inside water phase) and the M phase organic solution with carrier, emulsion and solvent are emulsified and a water-in-oil (W/O) emulsion is prepared. This W/O emulsion is dispersed as a W/O emulsion droplet in the F phase aqueous solution (outside water phase) and a (W/O)/W multiphase emulsion is formed. In this case metal ions in the F phase can permeate to the P phase and concentrate. In this emulsion liquid membrane, the (O/W)/O type can also be prepared for the removal of aromatic compounds.

The thickness and surface area of the membrane in this type are very thin and large. Therefore, the permeation rate of the material from the F phase to the P phase is enhanced. When the emulsion in the M phase is added to an even larger quantity of the F phase, a factor based on the ratio of the F phase volume to the P phase volume becomes larger, and consequently the concentration of the permeated material in the P phase is increased.
2.5.3 Supported Liquid Membrane

2.5.3.1 Thin-Porous-Film-Supported Liquid Membrane
In this type membrane, the mixture of hydrophobic organic solvent and carrier is filled into pores of hydrophobic porous polymer membranes, such as polyethylene, polypropylene and poly(tetrafluoroethylene), as shown in Figure 2.36.

This supported liquid membrane is very simple, but the formation of a thin membrane is very difficult because the membrane function is lowered because the liquid membrane phase is gradually replaced by the water phase. Developments of measures against the rupture of the membrane and methods of regeneration of the membrane are urgently required.

2.5.3.2 Hollow-Fibre-Supported Liquid Membrane
Figure 2.37 shows the structure of an HFSLM. The immobilization of the liquid membrane into pores in a microporous hollow fibre is similar to TPFSLM, but the surface area and thickness of

Figure 2.36 Thin-porous-film-supported liquid membrane (TPFSLM).

Figure 2.37 Hollow-fibre-supported liquid membrane (HFSLM).
the membrane in an HFSLM are larger and thinner compared with those in a TPFSLM. Consequently, the membrane performance is much higher.

### 2.6 Structure of Inorganic Membranes

The heat-, chemical- and organic-solvent-resistant membranes are prepared from inorganic materials such as ceramics, metal, glass, carbon and zeolite. In organic membranes the preparation of nonporous membranes is difficult, but the porous, asymmetric and hybrid membranes can be easily prepared similarly to polymer membranes.

Bicole glasses produced by Corning Incorporated are very famous as porous glass membranes and have smaller pores than those in a UF membrane. Subsequently, asymmetric porous glass membranes with pore sizes between the UF and microfiltration were developed. Although the pore distribution of these membranes is very sharp, the permeation rate is low because the membrane thickness is greater. Since ceramic membranes are prepared by sintering fine ceramics particles, asymmetric membranes with high permeation rate can be formed. The composite membranes are fabricated by topping the thin zeolite membrane on porous supports such as sintered α-alumina and stainless steel. Figure 2.38 shows a composite membrane consisting of a silica-selective dense layer, mesoporous interlayer and α-Al₂O₃ porous support layer developed by a group at the University of Twente (http://www.utwente.nl/tnw/im/introduction/).

In carbon membranes there are asymmetric and symmetric types. Their structures depend upon the membrane preparation technique. The former type are due to the carbonization of the polymer precursor on a porous support and the latter are formed by carbonizing the independent polymer precursor membrane [66].

### References


Preparation Methods of Membranes

Membranes are the heart in every membrane process. Therefore, appropriate selection of the membrane preparation method for each membrane process is the most important factor in achieving a higher membrane performance to meet our purpose, because the membrane preparation methods significantly give different membrane structures, functions and transport properties, in addition to different transport mechanisms.

3.1 Polymer Membranes

Polymer membranes can be easily made in various types, such as plate, tube and hollow fibre from a large number of different polymer materials. The membrane structures, such as nonporous, porous, symmetric, asymmetric, non-charge, charge and composite form, can be technically controlled. Modules with polymer membranes also can be easily fabricated, and their membrane processes are very competitive in terms of economics [1].

Table 3.1 summarizes the preparation methods of various polymer membranes [2].

3.1.1 Solution-Casting Method

For solution casting (method 1), there are two types of methods: wet [3–13] and dry [14]. In the former method, polymer membranes at the laboratory level are made by pouring casting solutions onto an applicator for a thin-layer chromatograph (1), drawing a blade across a glass plate (2), allowing the solvent to evaporate at a certain temperature for a prescribed period (3), and immersing the glass plate together with the membrane into a gelation medium (usually water (H₂O)) (4). After resting in the gelation medium for a desired period, the membranes are removed from the glass plate (5) and heat or pressure treatment applied as required (6) (see Figure 3.1). The resulting membranes from this wet method are asymmetric structures consisting of dense, thin skin layers and rough, porous support layers.

On the other hand, since a gelation medium is not used and the casting solvent is completely evaporated in the dry method, the resulting membranes have a dense symmetric structure and are reversible in the wet–dry membrane cycle. Polymer membranes prepared by the wet and dry method have been applied to a variety of industrial applications, such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis, gas separation and pervaporation fields. In those applications, specific requirements for the material and structure of the membrane are imposed. In microfiltration, ultrafiltration...
and nanofiltration membranes, the pore size and porosity of the membrane play an important role in the filtration performance. In gas separation and pervaporation membranes, the selectivity of the membrane material and the density of the resulting membrane significantly influence the efficiency of the gas and pervaporation separation. It is well known that sintering, elongation and phase separation processes are the techniques used to prepare porous polymer membranes. The sintering and elongation are physical techniques, but the phase separation is a physicochemical technique.

A number of porous polymer membranes are prepared by controlling the phase separation state of polymer solutions into two phases, one with a low concentration. The concentrated phase is solidified shortly after phase separation and the membrane is formed. The performance of this membrane is strongly dependent upon the morphology formed during the phase separation, and subsequent (or almost simultaneous) solidification [15–20].

There are four processes for membrane formation through phase separations induced from polymer solutions [21], discussed in Sections 3.1.1.1–3.1.1.4.

Phase inversion is a process in which an initially homogeneous polymer solution thermodynamically becomes unstable due to external effects and separates into a continuous polymer-rich phase that surrounds dispersed polymer-lean droplets. This process is widely used in the fabrication of polymeric membranes for a variety of applications. Phase inversion of polymer solutions can be induced by any one or a combination of the following driving forces: temperature (thermally induced phase separation (TIPS)) [22–24], nonsolvent (diffusionally induced phase separation (DIPS)) [25], evaporation (drying-induced phase separation (DrIPS)) [26–30], nonsolvent vapour (vapour-induced phase separation (VIPS)) [31–35].

3.1.1.1 Thermally Induced Phase Separation

This method is based on the phenomenon that the solvent quality usually decreases when the temperature is decreased. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying. In this process the most important process is liquid–liquid demixing. Liquid–liquid demixing processes play an important role in most of the TIPS processes. In addition, crystallization of the polymer from solution, gelation of the polymer solution and associations between the components in solution can occur. Some of these processes can also induce the formation of structures in solution. The combinations of liquid–liquid demixing with crystallization of the polymer, gelation association are of special importance for the generation of porous structures.

When a solution of a certain polymer dissolved in a solvent with lower molecular weight exhibits liquid–liquid demixing, a strongly asymmetric liquid–liquid demixing gap is observed. Figure 3.2 shows a schematic phase diagram for a binary polymer–solvent system [20,36]. In this

<table>
<thead>
<tr>
<th>Membrane preparation methods.</th>
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</thead>
<tbody>
<tr>
<td>1. Solution-casting method (dry and wet)</td>
</tr>
<tr>
<td>2. Composite method (polymer cast)</td>
</tr>
<tr>
<td>3. Casting-reaction method (cross-link, chemical modification)</td>
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<tr>
<td>4. Polymer ion complex method</td>
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<tr>
<td>5. Freeze-dry method</td>
</tr>
<tr>
<td>6. Surface treatment method (surface modification)</td>
</tr>
<tr>
<td>7. Filling polymerization method</td>
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<td>8. Expansion method</td>
</tr>
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</table>
figure the temperature is plotted as a function of the polymer concentration in the casting solution. At high temperatures the solution is still homogeneous. At lower temperatures liquid–liquid phase separation into a polymer-poor and a polymer-rich phase can take place. These systems are characterized by an upper critical solution temperature and are characterized by a lower critical solution temperature. Liquid–liquid phase separation induced by heating the polymer solution almost does not lead to a porous structure.

The boundary of the liquid–liquid demixing gap is usually called the binodal, but for polydisperse polymers the term ‘cloud-point curve’ is more appropriate. Usually, the liquid–liquid demixing gap is subdivided into a region of spinodal demixing and two regions of nucleation and growth between the binodal and the spinodal. Compositions that are in equilibrium are located on the binodal, and are connected by horizontal tie lines. It is important to note that the transition between binodal decomposition and spinodal decomposition should not be regarded as a sudden change in decomposition mechanism, but as a gradual change [37].

A mathematical model that describes the solid–liquid (S–L) TIPS membrane-formation process and captures the fundamental features of the evolving structure was developed by Krantz et al. [38]. This is the first mathematical model to describe the S–L TIPS process from the initiation of casting to the development of the final membrane structure. The model predictions were validated with experimental measurements for the isotactic polypropylene (iPP)–dotriacontane system using both scanning electron microscopy (SEM) and optical microscopy to determine the final spherulitic size. These experiments encompassed two different process (boundary) conditions: controlled cooling rate and constant cooling-block temperature. The final spherulite diameter was in statistical agreement with the model predictions for the controlled cooling rate condition and the constant cooling-block temperature condition when the latter was equal to or higher than 25 °C. The predicted spherulite diameter was larger than observed for lower block temperatures most likely due to diluent solidification, which was not accounted for in the model. This model can be used to determine the operating conditions required to produce desired membrane morphologies in the S–L TIPS process. Moreover, the formalism used to incorporate nucleation and growth of the dispersed phase in this model can be extended to other phase-inversion processes utilized for membrane manufacture.

![Diagram of TIPS process](image-url)
Kim et al. [39] investigated the TIPS mechanism for the iPP and diphenyl ether (DPE) system. Drop-let growth was monitored by using a thermo-optical microscope. The degree of supercooling for liquid–liquid phase separation affected the size and growth rate of the droplets. Increasing the polymer content affected the solution viscosity and interaction parameter, which resulted in a decrease of the size and growth rate of the droplets. Crystallization interfered with the droplet growth at lower quench temperatures from the onset of crystallization. The droplet growth rate followed the equation proposed by Furukawa, and the droplet growth was well described by the theories for coarsening and coalescence. Equilibrium droplet size was estimated by the Laplace equation and was in good agreement with the experimental data. The cell size of the membrane was about half of the droplet size of the melt sample due to shrinkage of the sample during extraction of the diluent and the drying process.

The effect of diluents on iPP membrane formation via thermally induced phase separation was investigated. The diluents were methyl salicylate (MS), DPE and diphenylmethane (DPM). The cloud-point curve was shifted to a lower temperature in the order iPP–MS, iPP–DPE and iPP–DPM, whereas the crystallization temperature was not influenced so much by diluent type. Droplet growth processes were investigated under two conditions: quenching the polymer solution at the desired temperature and cooling at a constant rate. Although droplet sizes were in the order iPP–MS, iPP–DPE and iPP–DPM in both cases, the difference was more pronounced with the constant cooling rate condition. SEM indicated that interconnected structures were obtained when the polymer solution was quenched in iced H₂O. The effect of the diluents on these structures was observed [40].

Porous poly(vinylidene fluoride) (PVDF) microporous membranes were successfully prepared from a ternary system including PVDF, solvent and nonsolvent via the TIPS process. Tributyl citrate (TBC)
as solvent and di-(2-ethylhexyl) phthalate (DEHP) as nonsolvent were used in this study. The effect of mixed diluent composition on the PVDF–TBC–DEHP system phase diagram was studied. The phase separation mechanism changed from S–L phase separation to L–L phase separation with increased content of nonsolvent DEHP. The effects of mixed diluent composition, polymer concentration, cooling condition on morphology, H₂O permeability, porosity and pore size were studied. The membranes whose formation is controlled by an L–L phase separation mechanism have a narrow pore size. For the 30 wt%–70 wt% TBC–DEHP system with L–L phase separation, bicontinuous morphology was observed. For the 90 wt%–10 wt% TBC–DEHP system with S–L phase separation, a spherulitic structure was obtained. With the polymer concentration increased, the values of porosity, pure H₂O permeability flux and mean pore radius all decreased. For the same polymer content, the membranes prepared from the 30 wt%–70 wt% TBC–DEHP system performed better. Those membranes prepared in the 20 °C water bath performed nicely [41].

Porous PVDF hollow-fibre membranes were fabricated via the TIPS method for application in a gas–liquid membrane contactor. For this purpose, a long air gap distance was used (90 mm). SEM was used for membrane characterization. A gas permeation test was performed using carbon dioxide (CO₂) as test gas. It was observed that the effective surface porosity and membrane pore size increased with increased glycerol concentration. CO₂ absorption using the fabricated hollow-fibre membranes were measured in a gas–liquid hollow-fibre membrane contactor. The results of the CO₂ absorption rate of the tested fibres revealed that complete removal of CO₂ was achieved using 7% glycerol added to the cast solution at normal operating conditions for equal gas-to-liquid volumetric flow rates using sodium hydroxide as absorbent liquid [42].

Poly(ethylene chlorotrifluoroethylene) (ECTFE) is a 1:1 alternating copolymer of ethylene and chlorotrifluoroethylene that offers excellent resistance in chemically and thermally challenging environments. ECTFE membranes with a variety of microstructures have been fabricated via TIPS with dibutyl phthalate (DBP) as the diluent. A continuous flat-sheet extrusion apparatus with a double rotating drum was used that permitted controlling both the casting solution thickness and axial tension on the nascent membrane. Initial compositions of ECTFE–DBP solutions in the L–L region of the binary phase diagram were chosen, resulting in membranes with an interconnected pore structure. The effects of several important process parameters were studied to determine their effect on the structure and properties of the membrane. The parameters evaluated included the initial ECTFE concentration, cooling rate, membrane thickness, co-extrusion of diluent and stretching of the nascent membrane. The resulting membranes were characterized using SEM, porometry and permeation measurements. For the range of process parameters studied, ECTFE membranes exhibited a decrease in surface porosity with increasing initial polymer concentration and cooling rate. The effect of membrane thickness on the permeation flux was not significant. Co-extrusion of diluent increased the surface porosity and eliminated the dense skin that was otherwise present under rapid cooling conditions. Subsequent stretching of the nascent membrane resulted in a more open structure and a significant increase in the permeation flux [43].

Wu et al. [44] investigated the effects of polyethylene glycol (PEG) as a polymeric additive on the phase behaviour of polyacrylonitrile (PAN)–dimethyl sulfone (DMSO2) mixtures and the structure formation of PAN membranes via TIPS. DMSO2 was chosen as a crystallizable diluent, while PEG was considered in terms of molecular weight (Mw) and dosage. Their effects on the phase behaviour and the droplet growth kinetics of the PAN–DMSO2–PEG ternary system were systematically derived from optical microscopy and differential scanning calorimetry, as well as solubility parameter theory. We found that the addition of PEG brings about a thermodynamically less stable ternary system, facilitates L–L phase separation and suppresses the crystallization of DMSO2. The L–L phase separation can be promoted by raising the Mw or the dosage of PEG, and is accompanied by an increase in the
growth rate of droplets. These results match with the pore size of the PAN membranes obtained. SEM images indicate that needle-like pores are obvious in the membrane when 10 wt% PEG 200 is added, whereas lacy pores gradually appear as the Mw of PEG increases from 200 to 1000. In addition, cellular pores can be created by raising the dosage of PEG 200 or reducing the cooling rate. Correspondingly, the membrane presents a relatively high H2O flux (1528 L m\(^{-2}\) h\(^{-1}\)) and porosity (83.6%) when the ternary system contains 10 wt% PEG 1000 and cools in an air bath at 30 °C. In addition, the presence of PEG in the membrane matrix was examined by Fourier transform infrared (FTIR) spectroscopy. PEG with different Mw almost completely leaches out, and the pore structure is retained well after immersing the membrane in H2O for 144 h.

Porous PVDF hollow-fibre membranes were successfully prepared from a ternary system including PVDF, solvent and non solvent via the TIPS process. Glycerol triacetate (triacetin) as solvent and glycerol as non solvent were used in this study [45]. The effect of non solvent concentration on the polymer–solvent–non solvent phase diagram was studied. The addition of glycerol brought about a change of phase separation mechanism from S–L phase separation (polymer crystallization) to L–L phase separation. Based on these results, hollow-fibre membranes were fabricated. The effects of non solvent concentration, air gap distance and water bath temperature on morphology, H2O permeability, solute rejection and strength of fabricated membranes were studied. Using a shorter air gap distance, a higher bath temperature and a higher glycerol concentration were effective in obtaining higher H2O permeability. In another set of experiments, the effect of polymer extrusion temperature on morphology and permeability of the hollow-fibre membrane was studied. It was observed that changing the polymer extrusion temperature had different effects on membrane permeabilities for both membranes with crystalline and interconnected structures. In addition, the performance of membranes prepared from the PVDF–triacetin–glycerol system was compared with that prepared from the PVDF–triacetin system.

### 3.1.1.2 Diffusively Induced Phase Separation

In this membrane formation process a polymer solution is cast as a thin film on a support or extruded through a die, and is subsequently immersed in a non solvent bath. Precipitation is formed by occurrence of the phase separation with diffusional exchange of the good solvent in the polymer solution and the non solvent in the coagulation bath, as shown in Figure 3.3. In this case there are two phase separation processes: one is L–L demixing, which forms porous structure with pores, which are the voids between the crystalline units; the other is S–L demixing, resulting in the crystalline parts of the membrane.

To accurately understand the formation of phase inversion membranes, thermodynamic analysis of the membrane formation process is very important. It has been shown, however, that kinetic conditions may result in another phase separation process not predicted by the thermodynamic equilibrium properties of the system [46, 47]. In order to understand the mass transfer of the components during the diffusion processes, a model on the basis of earlier work of Cohen et al. [44] was developed [49]. After that, a number of papers on the mass transfer in the diffusion-induced phase separation were published [50–52]. Two different kinds of circumstances leading to different types of morphology in the final membranes, in both cases determined by L–L demixing [53], were found. The first is that demixing results in membranes with a dense skin layer and a porous support layer with isolated pores. The second is instantaneous demixing, being visualized by the occurrence of immediate turbidity in the membrane after the immersion, resulting in membranes with a porous skin. The model developed by Reuvers et al. [53] allows predictions concerning the type of membrane morphology that can be expected.
In order to gain further insight into the morphology of a membrane that is formed by S–L demixing, it was required to study the mass transfer in ternary systems. On the other hand, since many polymers, such as aliphatic nylons, cellulose acetate, cellulose nitrate, chitosan, poly(phenylene oxide) and so on, as membrane materials can be crystallized and the crystallization of the resulting membranes significantly influences the membrane properties, the crystallization process during the membrane formation could not be neglected. Then Koenhen and Smolders [54] studied the thermodynamics of crystallization in binary and ternary systems for poly(phenylene oxide) and cellulose acetate respectively.

Better understandings of the initial concentration profiles of the different components during the phase inversion in which crystallization is involved and of the relationship between the permeation and separation characteristics and of the final morphology of membranes are very important for the preparation and application of membranes.

DIPS is more complicated than TIPS, because at least three components are involved in the casting solution. As can be seen from Figure 3.3, complex diffusion and convection of the good solvent and nonsolvent play an important role. From the discussion on binary systems in TIPS, it is clear that a large number of phase transitions and combinations of phase transitions can play a role. Introduction of a third component in DIPS has to make more complex phase diagrams. Most of the transitions that occur in TIPS can also occur in DIPS.

All of the possible combinations of a ternary composition can be plotted in a triangle, as shown in Figure 3.4 [20]. The phase diagram is divided into a homogeneous region and an area representing an L–L demixing gap. The L–L demixing gap is entered when a sufficient amount of nonsolvent is present in the solution. In principle, the same three parts of the demixing gap are present as in the binary diagram. A metastable area exists between the spinodal and the binodal at low polymer concentrations, an unstable area is enclosed by the spinodal, and there is a second metastable area at higher polymer concentrations. The phase separation proceeds analogously with binary solutions [21].
Tompa has clarified from the Flory–Huggins description of polymer solutions that the size and location of the demixing gap depends on the molar volumes of the components, the polymer–solvent interaction parameter, the polymer–nonsolvent interaction parameter, and the solvent–nonsolvent interaction parameter [55]. Tompa [55], Altena and Smolders [56] and Yilmaz and McHugh [57] discussed in detail the influence of these variables on the resulting phase diagrams. The effect of polydispersity of the polymer on these phase diagrams has been discussed by Koningsveld [58] and Kamide and Matsuda [59].

Zhang et al. [60] fabricated PVDF membranes by the nonsolvent-induced phase separation (NIPS) process using Tween 80 and H2O as a mixture additive from both 60 °C and room-temperature casting solution. Resultant PVDF membranes revealed improved pure H2O flux, improved mechanical properties and good bovine serum albumin and dextran rejection as a result of addition of H2O into the PVDF–DMAc–Tween 80 system. The improved performance was attributed to the existence of nonsolvent, which was solubilized by polar head groups of Tween 80 reverse micelle to form the H2O pool. Further, the interaction between the polar head of the surfactant and H2O provided a balance resistance to the interconnection between PVDF and hydrophobic chains of surfactant, which enhanced the thermodynamic stability of the casting solution. During the demixing process, H2O diffusion from the interior of the casting solution increased the precipitation rate and led to an insufficient crystallization process of the polymer. Finally, the Tween 80 reverse micelle confined the movement of H2O in solution, making the finger-like structure slim and confined, with a wall structure between macrovoids.

Guillen et al. [61] reviewed NIPS membrane preparation and characterization for many commonly used membrane polymers. The key factors in membrane preparation discussed include the solvent type, polymer type and concentration, nonsolvent system type and composition, additives to the polymer solution, and film casting conditions. A brief introduction to membrane characterization is also given, which includes membrane porosity and pore size distribution characterization, membrane physical and chemical properties characterization, and thermodynamic and kinetic evaluation of the phase inversion process. One aim of this review is to lay out the basics for selecting polymer–solvent–nonsolvent systems with appropriate film casting conditions to produce membranes with the desired performance, morphology and stability, and to choose the proper way to characterize these properties of nonsolvent-induced phase inversion membranes.

Membrane formation by NIPS was directly observed using light microscopy. Polysulfone (PSF) was used as a model polymer, while 1-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), H2O and glycerol were used as model solvents and nonsolvents. Direct observation and kinetic analyses suggest finger-like macrovoids formed by convective flow of nonsolvent into the polymer–solvent solution; convective flow arose from interfacial energy gradients at the polymer solution–nonsolvent interface. Convective nonsolvent flow into the polymer solution was hindered by the formation of surface skin layers or viscous gel layers within the polymer solution film. Viscous gel layers were often formed when using a poor nonsolvent, poor solvent or an insufficient supply of a good nonsolvent. Greater viscous hindrance resulted in membranes with shorter or no finger-like macrovoids. Large finger-like macrovoids propagated only when nonsolvent convective flows into the polymer solution film exceeded viscous hindrance forces; that is, when a good solvent, ample supply of good nonsolvent, and polymer solution of relatively lower viscosity were used [62].

The thermal–nonsolvent-induced phase separation method was used for the fabrication of porous membranes from polyamide 12 (PA12), an attractive engineering polymer; the H2O–formic acid (FA)–PA12 ternary system was explored in detail [63]. SEM, differential scanning calorimetry, X-ray diffractometry, tensile strength analysis and H2O flux were used to characterize the structure and properties of the fabricated membranes. The morphology of the membranes was found to depend
on the FA content in the bath. The top surface of the membrane becomes less dense with increasing FA content in the bath. The cross-section and bottom surface of all membranes exhibited a cellular morphology, except for the case of the novel procedure of dope precipitation in a cold neat solvent (FA) bath. In all cases membranes exhibited a crystallinity of ~38% with a melting point of ~179 °C; tensile strengths in excess of 10 MPa were found possible in some cases.

Asymmetric membranes (see Figure 3.5) are prepared via the NIPS process from a polystyrene-block-poly(N,N-dimethylaminoethyl methacrylate) (PS-b-PDMAEMA) block copolymer. The polymer is prepared via sequential living anionic polymerization. Membrane surface and volume structures are characterized by SEM. Owing to their asymmetric character, resulting in a thin separation layer with pores below 100 nm on top and a macroporous volume structure, the membranes are self-supporting. Furthermore, they exhibit a defect-free surface over several 100 μm². PS serves as the membrane matrix, whereas the pH- and temperature-sensitive minority block, PDMAEMA, renders the material double-stimuli responsive. Therefore, in terms of H₂O flux, the membranes are able to react on two independently applicable stimuli: pH and temperature. Compared with the conditions where the lowest H₂O flux is obtained, low temperature and pH, activation of both triggers results in a sevenfold permeability increase. The pore size distribution and the separation properties of the membranes obtained were tested through the pH-dependent filtration of silica particles with sizes of 12–100 nm [64].

Schacher et al. [65] reported on the formation of self-supporting, double-stimuli-responsive ultrafiltration membranes via the NIPS process. The polymers, PS-b-PDMAEMA, were synthesized via living anionic polymerization in THF using sec-butyllithium as initiator. Two amphiphilic diblock copolymers were used, S(81)D(19)(75) and S(68)D(32)(100). The membranes were cast from mixtures of tetrahydrofuran (THF) and DMF. The influence of the solvent composition, the ‘open-time’ before immersion into the coagulation bath and the casting film thickness onto the membrane morphology were thoroughly investigated, and flux values obtained for the different membrane systems were compared. The higher hydrophilic polymer content in S(68)D(32)(100) resulted in a better compatibility with the nonsolvent bath consisting of H₂O, leading to a slower precipitation and thus an improved control of the phase separation occurring. Under certain conditions, ordered microphase-separated porous morphologies were observed in parts of the membrane cross-section. Further, the ‘smart’ properties of those novel materials are shown for two representative systems. It could be demonstrated that both stimuli for PDMAEMA (i.e. pH and temperature) can be reversibly and independently applied in order to significantly change the transmembrane H₂O flux.

3.1.1.3 Drying-Induced Phase Separation

In this process, the polymer is dissolved in a mixture of a volatile solvent and a less volatile nonsolvent. During the evaporation of the solvent, the solubility of the polymer decreases, and then the phase separation occurs.
The DrIPS process is based on a change of thermodynamic state of the polymer solution to achieve the phase inversion. It is characterized by the evaporation of good solvent and nonsolvent from initially homogeneous single-phase solution [66,67]. Under the external environmental change, in the initial stage a homogeneous polymer solution becomes thermodynamically unstable and a two-phase solution is formed due to the evaporation of solvent [68]. These phases separate into the polymer-lean and polymer-rich phases. On solidification the polymer-rich phase precipitates to form the solid matrix that envelops the polymer-lean phase that is rich in good solvent, and nonsolvent fills the pores. This process avoids the complication associated with the use of coagulation baths, as in the wet-cast process. The polymer concentration increases to reduce the solvation character of the casting solvent as the good solvent evaporates from the solution. The evaporation step significantly influences the final membrane morphology in the dry- and wet-cast phase inversion process. When the drying rate is high and the coating thickness is thin, the top surface layer becomes dense in the resulting membrane due to a high evaporation of the good solvent and nonsolvent. When skin formation occurs, the nonsolvent penetrates at the weak spots in the skin and it initiates the macrovoids. L–L phase separation occurs when a homogeneous solution becomes thermodynamically unstable due to introduction of a nonsolvent and takes place below the skin layer [69]. L–L demixing is caused either by nucleation growth or spinodal decomposition. Nucleation growth occurs in the metastable region between spinodal and bimodal regions; however, spinodal decomposition occurs in the unstable region inside the spinodal curve [28]. The membrane structure evolves according to the spinodal decomposition mechanism if the composition passes through the critical point and the phase separation occurs in the unstable region. If the composition changes slowly in the metastable region, the phase separation occurs in the nucleation growth region. This is followed by the growth of macrovoids because of the diffusion of good solvent from the surrounding polymer solution and nonsolvent from the precipitation bath. The formation of macrovoids takes place during the dry-casting process and precipitation in the wet-casting process.

A phase-separation simulation study related to cellulose acetate–H₂O–acetone has been done. The results show that porous asymmetric and symmetric membranes can be produced by changing the nonsolvent concentration or by the drying conditions without altering the polymer content using the dry-casting process. The dry-casting process is the process in which complete evaporation of solvent and nonsolvent takes place. Phase separation may not take place at low initial nonsolvent concentration, and dense polymer film may be obtained rather than a porous membrane. At high air velocity the phase separation is completely suppressed, and a uniformly dense coating devoid of substantial microstructure will result [70].

Fu et al. [71] studied the development of the morphology and microstructure in dry-cast membranes from polycarbonate (PC)–dichloromethane (DCM) and PC–THF solutions. It was shown that changing the relative humidity (RH) of the air altered the transparency and the surface morphology of the membranes. Positron lifetime spectra for membranes with different surface morphologies gave similar free-volume parameters, which are believed to be mainly responsible for the constant selectivity of the membranes. In this study, the permeation and adsorption properties of the PC membranes cast from PC–DCM and PC–THF solutions were characterized as a function of the RH. The results demonstrated that the permeability of membranes increased with increasing RH of the air. The change in the permeability is presumably related to the forming of pores on the membrane surface due to the vapour-induced phase separation during casting.

Hopkinson and Myatt [72] studied the phase-separation behaviour in ternary polymer solutions consisting of dextran, PEG and H₂O induced by solvent loss using laser scanning confocal microscopy.
and image analysis. Figure 3.6 shows the phase diagram for their system, obtained using ultraviolet–visible spectrometry.

These results for fluorescently labelled polymers are consistent with phase diagrams for dextran–PEG–H₂O solutions [73]. The morphology development is strongly affected by the inhomogeneous nature of the solvent quench and by gravitational sedimentation. A range of transient structures is seen in which the morphology varies with depth into the sample. The origin and development of these structures are explained using simple models. For mixtures where the overall volume fraction of the dextran-rich phase \( \phi_s \) is 0.1 or 0.34, a droplet morphology is observed whose development is analysed in detail. The mean radius of the largest droplets is found to increase linearly with time. For mixtures with \( \phi_s = 0.5 \) a bicontinuous morphology is seen in which the characteristic length scale decreases with depth into the sample as a result of the inhomogeneous distribution of H₂O in the drying film.

3.1.1.4 Vapour-Induced Phase Separation
In polymeric membranes there are two types of asymmetric and symmetric membranes. They each have advantages in the membrane separation technology. These membranes are fabricated by phase separation processes of homogeneous polymer solutions. The phase inversion can be achieved by TIPS, DIPS, DrIPS and VIPS [28,74]. In the TIPS process, with the dissolution of the polymer into the diluent at elevated temperature, after casting of the polymer solution this casting solution is subjected to cooling to induce phase separation. The diluent is extracted by a solvent exchange process and the evaporation of extractant results in a microporous structure [75]. In the DIPS process, the immersion of the polymer casting solution in the nonsolvent bath results in porous membranes with the good solvent loss from the casting solution and the counter diffusion of nonsolvent into the casting solution [76]. The DrIPS process is based on a change of thermodynamic state of the polymer solution to achieve the phase inversion.

During the VIPS process, the phase separation of the polymer solution is induced by penetration of nonsolvent vapour in the casting polymer solution. VIPS involves a dry–wet casting process in which the casting polymer solution is exposed to a nonsolvent vapour (almost humid air) for a desired time prior to immersion in a coagulation bath. In this VIPS process a slow transfer of H₂O from the vapour phase into the casting solution occurs, and membranes with unique morphologies, such as an ‘hourglass’ structure, can be prepared by controlling the exposure time of humid air, RH, air temperature and moving velocity of the gas phase [77].

The formation of PVDF membranes by VIPS is depicted schematically in Figure 3.7. The casting solvent is DMF, a high boiling solvent that evaporates slowly. Figure 3.7a shows a PVDF–DMF solution being cast on a support and H₂O vapour from humid air is fully miscible with DMF and penetrates the casting solution by diffusion. DMF in the casting solution is evaporated more slowly than the intake of H₂O. Since H₂O is a nonsolvent for PVDF, a phase separation occurs. The phase separation
itself is a complex interplay between the equilibrium thermodynamics and mass transfer kinetics, which is, nonetheless, well understood [31,32]. The isothermal ternary phase diagram of PVDF–DMF–H₂O in VIPS is shown schematically in Figure 3.7b [31,32], where the black and white circles are the critical point and starting composition respectively. Three compositional trajectories of the PVDF membranes upon drying are represented by the dotted, broken and thick line curves. In this study the binodal and spinodal lines were calculated from the Flory–Huggins parameters and the isothermal crystallization line was obtained from the melting point depression. The mass transfer was calculated by solving the one-dimensional diffusion equations.

Matsuyama et al. compared the membrane morphology characterized experimentally by SEM and the calculated composition path in the phase diagram [32]. The morphology of the membranes could be explained from the compositional trajectories through the phase diagram of Figure 3.7b. The thick line curve shows a case for a low RH where the compositions do not cross the binodal. The wet film then is stable, L–L phase separation cannot occur and a dense microstructure is obtained. The broken line curve shows the hypothetical case at a higher RH where the composition of the membrane crosses the binodal upon drying but does not cross the spinodal. Because the composition is above the critical point, in the metastable region between the binodal and spinodal, L–L demixing occurs; the microstructure evolves through nucleation and growth and eventually coarsens. A membrane will be obtained with isolated cellular pores. At very high humidity, represented by the dotted line curve, the composition crosses the spinodal and enters the unstable region. The spinodal decomposition then leads to a lace-like structure of loosely connected globular spherulites. In short, the compositional trajectories explain the formation of the microstructure of the membrane [78].

VIPS involves a dry–wet casting process in which the dope solution is exposed to a nonsolvent vapour (often humid air) for a fixed time interval prior to immersion in a coagulation bath.
Humid air exposure leads to a slow transfer of $\text{H}_2\text{O}$ from the vapour phase into the dope solution. By controlling the humid air exposure time, RH, air temperature and gas phase velocity, the VIPS process can be used to obtain membranes with unique morphologies, including an hourglass structure. This hourglass morphology refers to the situation in which the porosity is a minimum at some location (plane) within the membrane cross-section, and systematically increases from this plane in a perpendicular direction toward each surface. In this paper a fully predictive first-principles model is developed for the humid air exposure step for the quaternary $\text{H}_2\text{O}–\text{NMP}–\text{polyethersulfone (PES)}–\text{polyvinyl pyrrolidone (PVP)}$ system. Model predictions indicate that $\text{H}_2\text{O}$ transfer leads to an increase in the cast film thickness as well as a dilution of the polymer at the vapour–casting solution interface (top surface). This polymer concentration decrease can explain the evolution of the characteristic hourglass morphology. Model simulations indicate that the degree of asymmetry in the region from the minimum porosity to the top surface of the membrane can be increased by increasing the mass-transfer coefficient or decreasing the PES : PVP mass ratio in the dope solution [77].

Park et al. [79] systematically studied the effect of the $\text{H}_2\text{O}$ vapour absorption into the cast polymer solution before immersing into the water coagulation bath in the preparation of asymmetric membranes by the phase inversion process. It was observed that both the RH of the contacting air and the contact time had a pronounced effect on the membrane morphology. The pore size in the top skin layer and the skin layer thickness of membranes increased with increase in the RH of the contacting air as well as the contact time. When a membrane was prepared by coagulating a poly(ether imide) (PEI)–NMP solution in a water bath, the longer contact time with $\text{H}_2\text{O}$ vapour resulted in the larger pores in the top skin layer and also a thicker skin layer. But the membrane morphology was slightly affected by the variance in the RH. When PVP was added in the membrane casting solution, both the contact time and RH had significant effects on the membrane morphology. The morphological change was confirmed by measuring the pure $\text{H}_2\text{O}$ transport characteristics through the membranes.

A novel positively charged asymmetrical membrane was manufactured from brominated polyphenylene oxide–NMP–$\text{H}_2\text{O}$ via in-situ amination with triethanolamine and a dry–wet phase inversion. The casting solution was exposed to the humid surroundings before immersing into the coagulation bath. The positive charge character of the membrane surface was examined by streaming potential, and the effect of the evaporation time and the RH on the membrane properties and microstructure respectively was investigated. Interestingly, it was found that the role of evaporation time and the RH on the membrane performance and morphologies for a positively charged casting system was different from the conventional rule. This was mainly due to the competition of two influence factors: evaporation of solvent and $\text{H}_2\text{O}$ absorption of the casting solution. The results were confirmed by SEM observation and pore size distribution. Furthermore, the process of $\text{H}_2\text{O}$ absorption of the casting solution was monitored using attenuated total reflectance infrared spectroscopy. Additionally, in order to compare with the dry–wet phase inversion method, the membranes were obtained by prolonging the exposure time to more than 12 h (which was similar to vapour-induced phase inversion) at different RHs. Polymer nodules on the membrane surface and a symmetrical morphology were observed by SEM [80].

The interplay between membrane morphology and elaboration parameters during NIPS processes was studied by Annamalai et al. [81]. This investigation correlated the solvent–nonsolvent mass transfer kinetics with the structural morphology and properties of polymeric membranes obtained via the $\text{H}_2\text{O}$ VIPS process. For the first time, the mass transfer kinetics were monitored and quantified during the VIPS process on a homogeneous solution of PVDF dissolved at two different temperatures in NMP, using near-infrared spectroscopy with a chemometric model. A significant change in mass transfer rate (i.e. $\text{H}_2\text{O}$ penetration) was observed much earlier than the liquid demixing of the polymer solution occurs for two dissolution temperatures studied. Consecutively to the $\text{H}_2\text{O}$ penetration, modifications in the physical state (gelation) of the polymer started to occur prior to reaching the demixing
process. This phenomenon was discussed in terms of macromolecular organization of PVDF caused by the decrease of the solvency power. It is assumed that this physical evolution of the polymer solution influences the phase separation mechanisms, and thus the surface obtained and the structural morphology of the PVDF membranes.

The formation of a surface liquid layer on the top of membrane-forming systems made of PEI and NMP was clearly demonstrated during H$_2$O VIPS through several in-situ investigation methods, including optical microscopy and dynamic H$_2$O contact-angle measurements for a qualitative approach, and Raman confocal and FTIR microscopy for a quantitative one. A mechanism involving the shrinkage from the polymer-rich phase consecutively to the surface phase separation is proposed to account for the significantly high concentration of PEI in the surface liquid layer. The emergence of a surface liquid layer during the phase separation process is discussed in terms of implications on the morphology of membranes fabricated using VIPS and how it contrasts with liquid-induced phase separation [82].

The formation of low-biofouling PSF membranes by VIPS was investigated by Venault and Chang [83]. Membranes were prepared by blending an amphiphilic additive, Pluronic® F108, Pluronic F127 or 3-(N,N-dimethylmyristylammonio)propane-sulfonate (DMMSAPS) with PSF, before inducing phase separation of the solution. The additive affected both membrane morphology and surface chemical composition. F127 and DMMSAPS tended to increase the porosity of membranes, while the final structure of membranes prepared with F108 was close to that of virgin PSF membrane. The additive molecular weight as well as micelle formation are believed to be responsible for these different porous structures. Whatever the additive, the hydrophilicity of membranes was enhanced. Protein adsorption tests performed with polyethylene glycolated PSF membranes revealed that both F108 and F127 led to a decreasing of biofouling, but better performances were obtained using F127, for which stronger interactions with membrane matrices were achieved.

Using a dope comprised of 17 : 43 : 40 (wt%) PES : N,N-dimethylacetamide : diethylene glycol, microporous PES hollow-fibre membranes were prepared by nonsolvent VIPS. The effects of bore fluid solution composition, coagulation bath temperature, air gap distance and humidity on the morphologies of microporous PES hollow-fibre membranes were investigated. Light transmission microscopy was used to determine the precipitation rate during the VIPS stage as well as during the NIPS stage. The mean pore radius of PES hollow-fibre ultrafiltration membranes with sponge-like structures could be calculated by image software from the SEM images. The mean pore radius of the outer surface was about 0.1 μm (0.092–0.131 μm, PES3–PES14), while the mean pore radius of the inner surface of PES hollow-fibre membranes was 0.051–0.064 μm (PES12 and PES14). Pure H$_2$O permeation rates and rejections were closely related to both the inner and outer skin layers. When inner and outer surfaces possessed open structure, the pure H$_2$O permeation rates increased, whereas rejections decreased accordingly. PES hollow-fibre membranes with pure H$_2$O permeation flux from 387 to 1210 L m$^{-2}$ h$^{-1}$ as well as rejection of 10.1–98.1% could be achieved by adjusting air humidity, air gap distance and composition of bore fluid solution. Pure H$_2$O permeation rates of PES12, PES13 and PES14 with sponge-like structures were higher than 1000 L m$^{-2}$ h$^{-1}$, and their bovine serum albumin rejections were only about 10% [84].

The differences between the four techniques for phase separation processes correspond to differences in desolvation mechanisms.

### 3.1.2 Composite Method

In the composite method (method 2), thin active layers consisting of a hydrophilic or hydrophobic polymer are coated onto a porous support for separation [85]. Asymmetric membranes prepared by solution casting have physical asymmetric structures in which the dense, thin skin layer and the porous support layer consist of the same material. In the composite method, membranes with physical
and chemical asymmetric structures that consist of different materials can be prepared, and their membranes are prepared by two preparation methods: the monomer polymerization method and the polymer coating method, as shown in Table 3.2 [86].

### 3.1.3 Casting–Reaction Method

In the casting–reaction method (method 3), some polymers are cross-linked and chemically modified. Modified materials cannot be dissolved in feed mixtures, and membranes can be formed simultaneously. Namely, some polymer membranes are modified by reaction reagents added to the casting solution during membrane formation.

### 3.1.4 Polyion Complex Method

In the polyion complex method (method 4), membranes are prepared by the formation of polyion complexes with mixing between aqueous solutions of cationic polyelectrolytes and anionic polyelectrolytes [87,88]. An example of a polyion complex membranes from quarternized chitosan (q-Chito) and sodium carboxymethyl cellulose (Na-CMC) is shown in Figure 3.8. The resulting polyion complex membranes are not dissolved in H₂O and organic solvents.

### 3.1.5 Freeze-Dry Method

In the freeze-dry method (method 5), membrane materials are dissolved in a solvent with a relatively high freezing point; this casting solution is then cast onto a Teflon dish and frozen, and then the membranes are prepared by drying under reduced pressure [89].

### 3.1.6 Chemical Modification

In the surface treatment method (method 6), the property of the membrane surface prepared by methods 1–5 is improved by surface modifiers and surface cross-linkers.

### 3.1.7 Filling Polymerization Method

In the filling polymerization method (method 7), the membrane surface is modified by modifiers on a porous support membrane, as shown in Figure 3.9 [90].
3.1.8 Expansion Method

When porous membranes are fabricated from crystalline polymers such as polypropylene, the expansion method (method 8) is applied. In this case, expanded film membranes, shown in Figure 3.10, are formed in an orientation and annealing process.

3.2 Inorganic Membranes

Inorganic membranes are made from ceramic, carbon, silica, zeolite, various oxides (such as alumina, titania, zirconia) and metals (such as palladium, silver and their alloys). The advantages of inorganic membranes are their long stability at high temperature and under high pressure, microbiological inertness, resistance to harsh environments, ease of cleaning for fouling and catalytic activity. However, inorganic membranes have disadvantages, such as being brittle, having low permeability due to low membrane surface area per module volume and in dense membranes with a high selectivity, difficulty of sealing of a membrane in the module and their membrane processes are high cost.
3.2.1 Process for Preparation

In general, the preparation of inorganic membranes is accomplished by the following five-step processes: (1) powder preparation (milling, chemical powder preparation); (2) shaping (pressing, slip casting, extrusion, tape casting, suspension spinning, foam techniques, leaching techniques, techniques for straight pores); (3) temperature treatment (drying, calcination, sintering); (4) layer deposition (powder suspension layers, sol–gel layers, chemical vapour deposition, carbon layers, zeolite layers, metal layers); (5) functionalization (hydrophobization, catalytically active coating) [91].

3.3 Organic–Inorganic Hybrid Membranes

Composite materials consisting of organic and inorganic materials have been recognized in various fields [92,93] as functional materials that have the merits of the lightness, pliability and moulding of organic materials coupled with the heat resistance and strength of inorganic materials. As represented by fibre-reinforced plastics, however, these composite materials consist of a dispersed phase from the organic and inorganic compounds on the order of a micrometre in size. Consequently, physical properties of these composite materials are due to the additivity rule of each component. Therefore, special or specific physical properties cannot be expected. Recently, the size of the dispersed phase at a nanometre or molecular size order has been controlled, and hybrid materials in
which the organic and inorganic components are ideally homogeneous are being studied in a variety of fields. This organic—inorganic hybridization is dependent on the sol–gel method, in which the starting materials are in solution and syntheses at a low temperature are possible. Nano-ordered hybrid membranes consisting of organic polymers and inorganic materials are noteworthy for the purpose of the creation of high-functional or high-performance polymeric membranes [94–106].

### 3.4 Liquid Membranes

The liquid membrane system consists of a feed phase (F phase, H$_2$O solution), liquid membrane (M phase, organic solution) and permeation phase (P phase, H$_2$O solution), and a desired material in the F phase can be permeated and concentrated to the P phase. Combinations of F–M–P are H$_2$O phase–organic phase–H$_2$O phase, gas phase–H$_2$O or organic phase–gas phase, organic phase–H$_2$O phase–organic phase. The liquid membrane process can take the place of solvent extraction, ion exchange and gas absorption processes. The liquid membrane is composed of the carrier (1), solvent (2), emulsion (3) and porous support (4).

#### 3.4.1 Carrier

Reagents that are employed in solvent extraction and gas absorption can be applied as the carrier in the liquid membrane. For example, in gases and aromatic hydrocarbon, Ag$^+$ ion for ethylene, propylene, benzene (liquid); Cu(I) for CO, olefin, benzene (vapour); HCO$_3^-$/CO$_3^{2-}$ for CO$_2$, H$_2$S; monoethanol amine for CO$_2$; metal complex for O$_2$; Fe(II) for NO.

Table 3.3 lists carriers for the transport of metal ions.

#### 3.4.2 Solvent

Aliphatic solvents such as Schellsol T®, n-decane and kerosene, which have low H$_2$O solubility, can be used as the solvent for the liquid membrane. Although aromatic solvents are often employed to increase the solubility of the carrier and complex, the stability of the liquid membrane is not so good compared with that of aliphatic solvents.
Table 3.3 Typical carriers and transported metal ions.

<table>
<thead>
<tr>
<th>Acid extraction reagent</th>
<th>Chelate</th>
<th>Nonchelate</th>
<th>Alkaline extraction reagent</th>
<th>Neutral extraction reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Hydroxyoxime (e.g. Cu(^{2+}), Ni(^{2+}), Pd(^{2+}))</td>
<td>[Diagram]</td>
<td>[Diagram]</td>
<td>(a) Primary amine (e.g. Th(^{4+}), Fe(^{3+}), Zn(^{2+}), U(^{6+}), Mo(^{6+}), acid such as nitric acid)</td>
<td>(a) Neutral phosphoric ester (e.g. U(^{6+}), Pu(^{3+}), Fe(^{3+}), Zn(^{2+}), Mo(^{6+}), V(^{3+}), acids such as nitric acid)</td>
</tr>
<tr>
<td>(b) 8-Hydroxyquinoline (e.g. Cu(^{2+}), Fe(^{3+}), Co(^{2+}), Ni(^{2+}), Al(^{3+}), Br(^{3+}), Ga(^{3+}))</td>
<td>[Diagram]</td>
<td>[Diagram]</td>
<td>(b) Secondary amine (e.g. U(^{6+}), Mo(^{6+}), acids such as hydrochloric acid)</td>
<td>(b) Phosphine oxide (e.g. U(^{6+}), V(^{3+}), Fe(^{3+}))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D(_2)ERPA (2-diethylphosphoric acid)</td>
<td>TOPO (oxidized trioctylphosphine acid)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(b) Phosphoric acid (e.g. Cu(^{2+}), Co(^{2+}), Zn(^{2+}), In(^{3+}))</td>
<td>(c) Phosphine sulfides (e.g. Ag(^{+}), Pd(^{2+}), Pt(^{2+}), Hg(^{+}))</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>(c) Acidic phosphoric ester (e.g. Co(^{2+}), In(^{3+}))</td>
<td></td>
<td></td>
<td>(c) Tertiary amine (e.g. Fe(^{3+}), Zn(^{2+}), Co(^{2+}), Cd(^{2+}), U(^{6+}), Zr(^{4+}), Mo(^{6+}), Hg(^{+}), acids such as sulfonic acid)</td>
<td>(c) Organic phosphoric extraction reagent with bifunctional group (actinide)</td>
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<tr>
<td>(d) Acidic dithiophosphoric acid (e.g. Zn(^{2+}), Pb(^{2+}), Co(^{2+}), Cd(^{2+}))</td>
<td></td>
<td></td>
<td>(d) Quaternary ammonium salt (e.g. W(^{5+}), Re(^{5+}), Cr(^{3+}), anions such as halogen ion)</td>
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</table>

(Continued)
Table 3.3 (Continued)

<table>
<thead>
<tr>
<th>Acid extraction reagent</th>
<th>Nonchelate</th>
<th>Alkaline extraction reagent</th>
<th>Neutral extraction reagent</th>
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<tbody>
<tr>
<td><strong>Chelate</strong></td>
<td></td>
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<td></td>
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<tr>
<td>(c) β-Diketone</td>
<td></td>
<td></td>
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<tr>
<td>(e.g. Cu(^{2+}), Co(^{2+}))</td>
<td></td>
<td></td>
<td>Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide</td>
</tr>
</tbody>
</table>
| \[
\begin{array}{c}
R_1 \\
\text{C}=\text{O} \\
\text{H}_2 \text{C}=\text{O} \\
\text{H}_2 \text{C} \text{C}=\text{O} \\
\text{H}_2 \text{C} \text{C}=\text{O} \\
\end{array}
\] |
| (d) Sulfoamidoquinoline  |            |                            |                           |
| (e.g. Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\)) |            |                            |                           |
| \[
\begin{array}{c}
\text{N} \\
\text{OH} \\
\text{SO}_2\text{R} \\
\end{array}
\] |
| 2-Bromodecanoic acid     |            |                            |                           |
| (f) Sulfonic acid        |            |                            |                           |
| (metal ions, cation of amino acid) |            |                            |                           |
| \[
\begin{array}{c}
\text{C}_9\text{H}_{19} \\
\text{R} \\
\end{array}
\] |
| DNNSA (diononylnaphthalene sulfonic acid) |            |                            |                           |
| (g) Proton dissociation-type crown ether |            |                            |                           |
| (e.g. alkali metal ion)  |            |                            |                           |
| \[
\begin{array}{c}
\text{C}_9\text{H}_{17} \\
\text{H} \\
\text{OCHCO}_2\text{H} \\
\end{array}
\] |

(a) Henkel, (b) Acorga, (c) Shell, (d) Sherex, (e) Daihachi Chemistry, (f) American Cyamamide, (g) Rohm and Haas.
3.4.3 Emulsion

In a water-in-oil/water ((W/O)/W) system a hydrophobic emulsion whose hydrophilic–lipophilic balance is about 4 can be used. The important matters of the emulsion are as follows: (i) the liquid membrane is well stable; (ii) the de-emulsification is easy; (iii) the H₂O permeation due to a difference of the osmotic pressure between the both H₂O phases is low (i.e. the swelling of the droplet of W/O emulsion is low); (iv) the emulsion does not interfere with complex formation at the oil–water interface. Typical emulsions for the liquid membrane are listed in Table 3.4. Span 80 has a high H₂O permeability. ECA4360 has a low H₂O permeability and is stable, but the rate of de-emulsification is slow. 2R–GE in the carrier from an extraction reagent of the hydroxyoxime type and has both excellent stability and de-emulsification characteristics, but the H₂O permeability is a little high.

3.4.4 Support

Hydrophobic microfiltration membranes such as polypropylene (Celgard, Celanese Plastic) and Teflon (Furoropore®, Sumitomo Denko), Teflon (Gore-Tex®, Gore-Tex) plate membranes, and Teflon (Gore-Tex), polypropylene (Accurel®, Enka) and polyethylene (EHF®, Mitsubishi Rayon) hollow-fibre membranes can be employed as the support for the impregnated liquid membrane. Their thickness, pore size and porosity are about 20–400 μm, 0.02–1 μm and 35–85% respectively. The membrane with a small pore can tightly hold the organic liquid membrane phase but when the pore size is too small, the flux is low. Consequently, an average pore size of about 0.1 μm is better.
References

3 Loeb, S., Sourirajan, S. (1960) UCLA, Department of Chemical Engineering Report, No. 60-60.


Membrane Shapes and Modules

There are several types of membranes available for use in material separation: flat sheet, tubular, capillary and hollow fibre. Their modules are applied in a variety of fields – industrial, petrochemical, pharmaceutical, medical, food, water treatment. They contribute to our life science and demonstrate high membrane performances and with the operating costs reduced in each field.

4.1 Membrane Shapes

4.1.1 Flat-Sheet Membranes

Flat membranes have been used from the time of the first membrane study and are the most popular. There are two types of flat membrane: without and with a support sheet. They are constructed of a sheet-like backing material with a membrane cast on the surface of the sheet to increase the strength of membranes. They are termed asymmetric and composite membranes. The former consists of a surface thin layer and a support sheet layer with the same materials, and the latter is composed of different materials.

A membrane module name is determined by how flat membranes are inserted into the membrane filtration apparatus: flat sheet and spiral module. The flat membranes are applied to dialysis, electrodialysis, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), forward osmosis, gas separation, pervaporation (PV), evapomeation, temperature-difference controlled evapomeation, membrane distillation, carrier transportation, membrane reactor, membrane contactor, fuel cell, and so on.

Flat-sheet membranes made from poly(vinylidene fluoride) (PVDF) were prepared by the phase inversion process [1]. The effects of the casting solution composition, exposure time prior to coagulation and temperature of the coagulation bath on properties of prepared membranes were investigated. LiCl was used as a modifying agent. The membrane structure was studied by scanning electron microscopy (SEM). An asymmetric structure, sometimes without a dense skin layer, was observed for all membranes prepared. The porosity of the prepared membranes before the drying process varied from 72 to 88%. After drying, the membranes become hydrophobic. The contact angle of a water droplet on the membrane surface was 107°. The nitrogen permeability varied from 12 to 2205 m^3 m^{-2} day^{-1}, depending on the preparation conditions. The maximum pore size, liquid entry pressure of water and the mechanical properties were also determined. The membrane
distillation process of 1–2% aqueous NaCl solution was applied as a final test of membrane performance. A permeate flux up to 233 dm$^3$ m$^{-2}$ day$^{-1}$ was achieved at feed and permeate temperatures of 333 K and 293 K respectively. A chloride elimination in the permeate higher than 99% was reached.

Ma et al. [2] prepared high-performance PVDF flat-sheet UF membranes by an immersion precipitation phase inversion method using perfluorosulfonic acid (PFSA) as a pore former and as a hydrophilic component of the membranes and polyethylene glycol (PEG) 400 ($M_w = 400$) as a pore-forming agent. The effects of the presence of PEG and the concentration of the PFSA on the phase separation of the casting solutions and on the morphologies and performance of UF membranes, including their porosity, water flux, rejection of bovine serum albumin (BSA) protein and antifouling property, were investigated. Phase diagrams, viscosities and the phase separations upon exposure to water vapour showed that both PEG 400 and PFSA promoted demixing of the casting solution. SEM measurements showed that the PVDF–PFSA blend membranes had more macropores and finger-like structures than the native PVDF membranes. The PVDF–PFSA membrane (5 wt% PEG 400 + 5 wt% PFSA) had a pure water flux of 141.7 L m$^{-2}$ h$^{-1}$, a BSA rejection of 90.1% and a relative pure water flux reduction (RFR) of 15.28%. These properties were greatly superior to those of the native PVDF membrane (pure water flux of 5.6 L m$^{-2}$ h$^{-1}$, BSA rejection of 96.3% and RFR of 42.86%).

Membranes with controlled morphology were prepared by wet phase inversion from polyether ether ketone (PEEKWC), a modified polyether ether ketone [3]. Different membrane structures were obtained by using different nonsolvent–solvent pairs. The influence of several parameters, such as the composition of the polymer solution (concentration, type of solvent), the composition of the coagulation bath and the exposure time before immersion in the coagulation bath, on the membrane morphology was studied. The PEEKWC–solvent–nonsolvent phase diagrams, with various solvent–nonsolvent combinations, were determined and correlated to the process of phase separation during membrane formation. Using solvent–nonsolvent pairs with a high mutual affinity (dimethylformamide–water, dimethylacetamide–water), porous membranes for possible application in MF were obtained. The tetrahydrofuran–water combination allowed the formation of asymmetric membranes with a dense skin layer, suitable for gas separation applications. Nitrogen permeance of all porous membranes was measured as a function of pressure. Application of the dusty gas model permitted a qualitative description of the pore size and membrane morphology in relation to the membrane preparation conditions.

Han et al. [4] prepared PVDF membranes and investigated using a scanning electron microscope, a universal testing machine and an apillary porometer for its potential use as a separator in lithium-ion batteries. The membranes were prepared by phase inversion with different polymer types, concentrations of solution, amounts of additive and nonsolvent ratios of water/ethanol. The morphology of membranes is affected by the ratio of both the coagulation bath (water–ethanol) and a low molecular weight additive (polymer–solvent–additive). The results showed that significant variations in the membrane were detected when adding an additive to the casting solution or ethanol to the coagulation bath. With an increased concentration of ethanol, the upper structure was found to be transformed into a sponge-like arrangement. In the case of Solef®1015 of the same polymer concentration, despite the higher molecular weight of 1015, a relatively small-sized nucleus was formed, resulting in a denser network and relatively uniform membrane structure being formed. Mechanical testing showed that the tensile strength of the PVDF membranes increased when added to a 25 wt% ethanol coagulation bath, whereas it is decreased when added to higher concentrations of ethanol in the bath or additives in the casting solution. In a bath condition of 75/25 (wt%) water/ethanol (bath no. 2), the values of tensile strength were 7.11 MPa and 7.52 MPa for 20 wt% Solef6010 and 17 wt% Solef1015 respectively. The
thickness of the prepared membrane was 21–34 μm and the porosity was up to 50%. The electrolyte absorption changes of the fabricated membranes at different conditions were measured as being from 151 to 223 ± 15%.

Dense flat-sheet membranes were prepared from poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) using the casting solvents chloroform and 1,1,2-trichloroethylene [5]. X-ray diffraction, tapping-mode atomic force microscopy and contact-angle studies were used to characterize the membranes. The surface energy and the solubility parameters of the PPO membranes were determined from the measured contact angles and compared with the predicted ones from the group contribution method. Swelling experiments and PV separation of methanol from its mixture with ethylene glycol over the entire range of concentration, 0–100%, were conducted using these membranes. Flory–Huggins theory was used to predict the sorption selectivity. The results were discussed in terms of the solubility parameter approach and as a function of the morphological characteristics of the membranes. It was found that PPO membranes prepared with chloroform exhibited better PV performance than PPO membranes prepared with 1,1,2-trichloroethylene.

4.1.2 Spiral Membranes

The spiral-wound membrane has been recognized as an economical form of packaging RO and NF membranes. This is due to the following reasons. (1) A large variety of RO and NF flat-sheet membranes have been invented by polymer chemists that can be cast with a significant range of flow and feed pressure requirements along with a significant range of inorganic salt and organic rejection capabilities. (2) This configuration offers the highest membrane packing area capability, which results in the smallest water plant footprint size while maintaining reasonable antifouling characteristics, when compared with other membrane configurations like hollow fibre, tubular or plate-and-frame. (3) A wide range of materials offer an optimal blend of low material cost, high quality, chemical stability and physical ruggedness. (4) Offers the highest degree of automatic manufacturing capability, reasonable labour cost, high quality and high yields. (5) The modular nature of stacking RO/NF elements into pressure vessels and arrays allows for a wide range of system design features, including hybrid RO designs [6].

4.1.3 Tubular Membranes

Tubular membranes are not self-supporting membranes. They are located on the inside or outside of a tube, made of a special kind of material. Organic and inorganic membranes are used as materials of tubular elements. Organic tubular membranes are used as a single tube immobilized onto a porous support. Sintered resins and porous fibre-reinforced plastics are also used as the support. Ceramics are usually employed in inorganic membrane elements, and sometimes the monolith type with a number of pores in a single element. In the monolith type the feed solution flows through the inside of the tube and the filtrate flows out from the outside surface of the monolith element. Tubular membranes have a diameter of about 5–15 mm.

Stable mesoporous membranes with a cubic structure, based on the MCM-48 material, were successfully prepared on alumina (Al₂O₃) supports by hydrothermal synthesis, starting from sols having both cetyltrimethylammonium bromide and tetrapropylammonium hydroxide structure-directing agents. The inclusion of a zeolite (MFI-type) precursor during membrane synthesis led to partial zeolite incorporation into the porous structure, giving rise to a hydrothermally stable membrane. The mean pore diameter of the membrane was 2.5 nm, and permeation experiments confirmed that transport across the membrane was governed by Knudsen diffusion and that there were no pinholes. The hydrothermal stability of conventionally prepared (MCM-48) and partly zeolitized (MCMZ) powders
was studied. Unlike MCM-48 samples (whose surface area sharply decreased after the hydrothermal treatment), the MCMZ surface area remained constant (1031 m$^2$ g$^{-1}$ before and 1009 m$^2$ g$^{-1}$ after the hydrothermal treatment), indicating a high hydrothermal stability. MCMZ membranes were tested in the gas-phase separation of binary organic (cyclohexane, benzene and $n$-hexane)–O$_2$ mixtures. A maximum selectivity of 124 was obtained for the separation of cyclohexane–O$_2$ mixtures. The selective permeation of the organic compound was made possible by specific interactions between the organic molecules and the mesoporous host materials, and/or by capillary condensation within the membrane pores [7].

Liu et al. [8] reviewed the preparation and application of macroporous ceramic-supported polymer composite PV membranes. The separation materials of polymer–ceramic composite membranes presented include hydrophobic polydimethylsiloxane and hydrophilic poly(vinyl alcohol) (PVA), chitosan and polyelectrolytes. The effects of ceramic support treatment, polymer solution properties, interfacial adhesion and incorporating or blending modification on the membrane structure and PV performance were discussed. Two in-situ characterization methods developed for polymer–ceramic composite membranes are also covered in the discussion. The applications of these composite membranes in the PV process are summarized as well; these include biofuels recovery, gasoline desulfuration and a PV-coupled process using polydimethylsiloxane–ceramic composite membrane, and dehydration of alcohols and esters using ceramic-supported PVA or PVA–chitosan composite membrane. Finally, a brief conclusion remarking on polymer–ceramic composite membranes is given and possible future research is outlined.

The performance of a hydrophilic polyester tubular pervaporative membrane in treating high-salinity water for irrigation was investigated [9]. The membrane was filled with contaminated water and placed in air, soil or sand media. When this occurs, water diffuses through the tube, trapping salts within the tube. Sorption and permeation tests and SEM were used to assess salt rejection and permeate flux through the tubular membrane when surrounded by deionized water, air, topsoil or silver sand. Mean water uptake by the membrane was 0.5 L m$^{-2}$ at room temperature, and the water diffusion coefficient was $3.8 \times 10^{-4}$ cm$^2$ s$^{-1}$. The permeate flux across the membrane was $7.9 \times 10^{-3}$ L m$^{-2}$ h$^{-1}$ in sand and $5.6 \times 10^{-2}$ L m$^{-2}$ h$^{-1}$ in air. The rejection of sodium chloride by the tubular membrane in sand was 99.8% or above under all test conditions. However, when the tube was filled with sodium chloride solution and placed in deionized water, salt was observed to permeate the membrane. SEM images confirmed that variable amounts of sodium chloride crystals were retained inside the membrane walls. These results support the potential application of such a tubular pervaporative membrane for irrigation applications using saline waters; however, there may be reduced salt rejection under waterlogged soil conditions.

Zeolite NaA membranes were prepared on the surfaces of porous tubular supports composed of mullite, $\alpha$-Al$_2$O$_3$ and/or cristobalite using hydrothermal synthesis. The zeolite NaA crystals and the surface morphologies of the membranes were characterized by X-ray diffraction and SEM. Electron probe microanalysis revealed that the zeolite composite membranes consisted of three layers: the zeolite layer, the intermediate layer and the multisupport. According to PV measurements using an H$_2$O–EtOH mixture, the permselectivity increased in the Al$_2$O$_3$ content of the substrate and reached a constant at $>70$ wt% Al$_2$O$_3$. Zeolite NaA membrane showed very high water-selective permeation through all the ethanol concentrations. The tubular-type module with $\sim$0.5 m$^2$ membrane area was composed of 17 pieces of zeolite membrane using 65 wt% Al$_2$O$_3$ content substrate, which has high PV performance and can be purchased at a low price. The efficiency of the module on permeation rate increased in proportion to the feed flow rate and exhibited 100% at Reynolds number $>$80. PV flux and separation factor of the module for 5 wt% water–95 wt% ethanol mixture at 95 °C was $\sim$2.35 kg m$^{-2}$ h$^{-1}$ and was greater than 5000 respectively [10].
Lin et al. [11] studied silicalite membrane preparation conditions related to membrane separation properties, focusing on in-situ crystallization to prepare highly selective silicalite membranes on porous tubular supports by a single hydrothermal treatment. The membrane morphologies prepared under typical synthesis conditions were characterized by SEM. The silicalite membrane, well-oriented with c-axis normal to the support surface, could be prepared by in-situ crystallization and a seeding method. The membrane separation properties were controlled by synthesis conditions such as seeding, temperatures, supports and silica sources. Under certain conditions, such factors as tube pore size played an important role. Silicalite membranes would be prepared better by in-situ crystallization than by a seeding method under the same conditions. For example, the highest ethanol–water separation factor of 106 with a flux of 0.9 kg m$^{-2}$ h$^{-1}$ for a feed concentration of 5 wt% ethanol at 60°C was obtained for the silicalite membrane prepared on an unseeded mullite tube at 175°C for 16 h with colloidal silica, whereas the membranes prepared on the silicalite-seeded tubes had separation factors up to 70. The higher separation selectivity for ethanol over water would be attributed to reduction in nonzeolitic pores, supported by gas permeations of n-butane and isobutane.

Zeolite NaA membranes were prepared reproducibly by a one-time-only hydrothermal synthesis with a short reaction time of 3 h at 373 K using a gel with the composition Al$_2$O$_3$ : SiO$_2$ : Na$_2$O : H$_2$O = 1 : 2 : 2 : 120 (in moles) and porous $\alpha$-Al$_2$O$_3$ support tubes seeded with zeolite NaA crystals [12]. A dense intergrown zeolite crystal layer of about 30 μm in thickness was formed on the outer surface. The zeolite NaA membranes were highly permeable to water vapour but impermeable to every gas unless dried completely. The completely dried membranes displayed gas permeation behaviour attributed to Knudsen diffusion, indicating the presence of interstitial spaces between the zeolite crystal particles, or nonzeolitic pores. The membranes displayed excellent water-permselective performance in PV and vapour permeation (VP) toward water–organic liquid mixtures. With an increase in temperature, both the permeation flux Q and the separation factor $\alpha$ increased, and the membrane performance was much better for VP than for PV. For VP at 378 K and 10 wt% of feedwater, Q values were 4.5 kg m$^{-2}$ h$^{-1}$, 3.5 kg m$^{-2}$ h$^{-1}$ and 7.8 kg m$^{-2}$ h$^{-1}$ and $\alpha$ values were >30 000, 5700 and >9000 for the water–ethanol, water–methanol and water–dioxane systems respectively. A mechanism of PV and VP based on the capillary condensation of water in the zeolitic and nonzeolitic pores and the blocking of other molecules from entering the pores was proposed.

4.1.4 Capillary Membrane

With capillary membranes the membrane serves as a selective barrier, which is sufficiently strong to resist filtration pressures. Because of this, the flow through capillary membranes can be both inside out and outside in.

The diameter of capillary membranes is much smaller than that of tubular membranes, namely 0.5 to 5 mm. Because of the smaller diameter the chances of plugging are much higher with a capillary membrane. A benefit is that the packing density is much greater.

Majewska-Nowak et al. [13] investigated the suitability of capillary modules to the decolorization of both synthetic and actual dye solutions by UF. The process involved capillary membranes made of polysulfone and modified polysulfone. Membrane modules (UFTA PS10; UFTA PS30 and UFTA PSA50) of various molecular cut-off were applied. Comparable studies including the effect of hydraulic conditions existing in the system on membrane performance were reported. Transport and separation properties of the membranes in the presence of model dye solutions were investigated at three pressure values (0.05, 0.1 and 0.15 MPa), the linear velocity in the modules being varied for each of them (0.5, 1.0 and 1.5 m s$^{-1}$). Three organic dyes (Direct black meta, Helion grey and methyl orange) were used in the experiments. The study on actual textile effluents (exhausted dye and rinsing baths)
were carried out for 50 h at a pressure of 0.1 MPa and a linear velocity of 1.0 m s\(^{-1}\). The results showed that increasing the linear velocity generally improves the permeability and selectivity of the membranes. This relationship becomes particularly pronounced at increasing molecular weight and for the UFTA PS10 module. It has been found that at an optimum velocity of feed flow (1.0 m s\(^{-1}\)) the retention coefficient for organic dyes of molecular weight higher than 780 exceeds 92–99% for all modules tested. In the presence of actual textile effluents the removal efficiency of total organic compounds and colour amounted to 42–65% and 70–98% respectively, and the permeability remained at a constant level (0.5–0.65 m\(^3\) m\(^{-2}\) day\(^{-1}\) for the UFTA PS10 module).

The gas separation characteristics of ultramicroporous glass capillary membranes were investigated by Kuraoka et al. [14]. Glass capillary membranes which had ultramicropores (pore diameter less than 1 nm) were prepared by elution of alkali metal ions from glass capillaries. It was found from elution treatment that alkali metal ions of three Na (composition: 77 mol% SiO\(_2\), 22 mol% Na\(_2\)O) and three K (composition: 77 mol% SiO\(_2\), 22 mol% K\(_2\)O) glass capillaries were completely eluted after 90 min and 10 min with 3 mol L\(^{-1}\) HNO\(_3\), 240 min and 10 min with 3 mol L\(^{-1}\) CM\(_3\)COOH and 24 min and 10 min with 3 mol L\(^{-1}\) H\(_3\)PO\(_4\) respectively. Permeations of N\(_2\), He and CO\(_2\) were measured at 298, 373 and 473 K. Permeation rates of the three Na and three K glass capillary membranes were 11 cm\(^3\) (STP) cm\(^{-2}\) s\(^{-1}\) cmHg\(^{-1}\). The ratios of permeation rates, CO\(_2\)/N\(_2\) and He/N\(_2\), were similar to the theoretical Knudsen values.

Bonyadi et al. [15] reported the experimental results for the processing of microcapillary film (MCF) membranes. MCFs are films with embedded multiple hollow capillaries and can be considered as a hybrid geometry between flat sheet and hollow fibres. Compared with the conventional membrane geometries, MCFs potentially provide a higher surface area per unit volume, better mechanical strength, ease of handling and more efficient module fabrication. MCF membranes were fabricated out of ethylene vinyl alcohol (EVOH) copolymer through a solution extrusion followed by a nonsolvent-induced phase separation process. Single capillary EVOH membranes were also fabricated prior to the fabrication of MCFs to establish a base process. Fluid flow observations were carried out at different regions in the process in order to better understand the dynamics of extrusion and phase inversion. It was observed that polymer solution and bore fluid rheology as well as processing conditions, including air gap distance and take-up rate, have significant effects on the flow dynamics and consequently the macrostructure of the membranes. Furthermore, the flow observations led to the identification of an extrude expansion phenomenon in the external coagulation bath which strongly influenced the membrane formation process. The microstructure characterization of the fabricated membranes showed the formation of a highly porous, interconnected and macrovoid-free microstructure in the membranes. MCF membranes can be applied with a potentially promising performance in a variety of membrane applications, such as MF and UF, membrane bioreactors and porous microfluidic devices, as well as membrane contactors for process intensifications.

Capillary NF membrane modules can combine favourable properties such as high packing densities, low costs and beneficial fouling behaviour of tubular and spiral-wound modules. To achieve further improvement of mechanical strength and specific membrane surface per volume, multichannel capillary membranes (MCMs) with several feed channels within one fibre have been developed. In a study by Spruck et al. the salt rejection and pure water flux performance data of novel composite MCMs was discussed [16]. The new composite capillary membranes were fabricated by a dry-jet wet spinning process and subsequent interfacial polymerization. The influence of the dope composition on the membrane structure and the separation performance of composite MCMs was studied. When tested at an operation pressure of 0.5 MPa and 20 °C, the MCMs had a rejection of MgSO\(_4\) and CaCl\(_2\) of 57% and 21% respectively and a pure water flux of about 47 L m\(^{-2}\) h\(^{-1}\) [16].
4.1.5 Hollow-Fibre Membrane

Membrane materials for hollow fibre are almost all organic polymers, such as cellulose acetate, polyethylene, polyacrylonitrile, polysulfone, polyethersulfone (PES), sulfonated-imidazole polymer, sulfonated polyphenylenesulfone, PVDF, polyurethane and some block copolymers [17]. On the other hand, inorganic hollow-fibre membranes were recently prepared as follows. Cellulosic precursors were regenerated from cellulose acetate hollow fibres using an optimized deacetylation process, which were further used for preparation of hollow-fibre carbon membranes using a specific carbonization procedure for the separation of a real flue gas containing water vapour and acid gases of SO$_2$ and NO$_x$ [18].

Brittleness is the main obstacle for commercial implementation of ceramic hollow-fibre membranes. The reinforcement of porous Al$_2$O$_3$ hollow-fibre membranes using commercial SiC nanofibers was investigated by Xu et al. [19]. The SiC-reinforced Al$_2$O$_3$ hollow-fibre membranes were produced by the polymer-assisted phase inversion method and subsequent removal of the polymer and sintering at high temperatures. The effects of the amounts of SiC nanofibers (2.5–10.0 wt%) on the mechanical strength and microstructure and water flux of the hollow-fibre membranes were investigated. The results showed that without addition of SiC nanofibers the maximum bending strength was about 154 MPa for the porous Al$_2$O$_3$ hollow fibre sintered at 1510 °C. However, the maximum bending strength of the reinforced membrane reached 218 MPa, in which 5 wt% SiC was incorporated and sintered at 1450 °C; in other words, a 40% improvement in bending strength was achieved. After being sintered at 1450 °C, the 5% SiC-reinforced membrane exhibited a porosity of 41.7% and a peak pore size of 1.35 μm, whereas the pure Al$_2$O$_3$ membrane had a porosity of 37.5% and a peak pore size of 1.25 μm; the former showed a water permeability of 7.99 L m$^{-2}$ h$^{-1}$ kPa$^{-1}$, which is 3.3 times higher than that of the latter. Therefore, ceramic nanofibre reinforcement is promising for the development of high-performance ceramic hollow-fibre membranes for practical applications.

PVDF hollow-fibre membranes were prepared via a phase inversion/chemical treatment method, using N,N-dimethylacetamide as solvent, calcium carbonate as inorganic additive, and water and HCl as coagulation media. Effects of external coagulation bath and bore fluid composition on membrane performance were investigated by using SEM, mechanical properties, porosity, average bubble point pressure and permeation performance. The results were as follows. (1) The cross-section morphology of membranes showed no significant change, exhibiting a two-layer finger-like structure extending to the middle of the cross-section. (2) The roughness of the external surface increased considerably, and the number of the surface pores increased as well when HCl was introduced as the second coagulation. The permeation experiments revealed that acid treatment had no impact on fibres that had precipitated completely. (3) The number and pore size underlying the inner skin layer increased when bore fluid changed from deionized water to 10% acetic acid, leading to a decrease of porosity and tensile strength. Moreover, the pure water flux increased from 360 to 580 L m$^{-2}$ h$^{-1}$) without a significant change of BSA rejection. The PVDF–CaCO$_3$ membranes prepared from the dope with 10% acetic acid as the bore fluid and 1 mol L$^{-1}$ HCl as second coagulation bath had the best UF performance [20].

Ma et al. [21] synthesized 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and used it as a solvent to dissolve bamboo pulp. Dimethyl sulfoxide (DMSO) was selected as co-solvent to adjust the solution viscosity. Compared with the bamboo pulp/[Bmim]Cl system, the addition of DMSO decreased the solution viscosity dramatically. Afterward, cellulose hollow-fibre membranes were prepared by dry–wet spinning process using 75 wt% [Bmim]Cl + 25 wt% DMSO as solvent. SEM, mechanical testing, pure water permeability and retention rate were used to characterize its properties. SEM showed that
the prepared cellulose hollow-fibre membrane presents a dense surface structure, which leads to a relative high tensile strength and retention rate to BSA (28 MPa and 98% respectively), but a relatively low pure water permeability (83 L m\(^{-2}\) h\(^{-1}\)). In the end, the [Bmim]Cl was recovered by azeotropy, and the recycling yield reached 99 wt%.

Wang et al. [22] prepared Al\(_2\)O\(_3\) hollow-fibre membranes by a combined phase inversion and sintering method. The organic binder solution (dope) containing suspended Al\(_2\)O\(_3\) powders was spun to a hollow-fibre precursor, which was then sintered at elevated temperatures in order to obtain the Al\(_2\)O\(_3\) hollow-fibre membrane. The dope solution consisted of PES, N-methyl-2-pyrrolidone and polyvinylpyrrolidone, which were used as polymer binder, solvent and additive respectively. The prepared Al\(_2\)O\(_3\) hollow-fibre membranes were characterized by SEM and thermogravimetric analysis. The effects of the sintering temperature and Al\(_2\)O\(_3\)/PES ratios on the morphological structure, pure water flux, pore size and porosity of the membranes were also investigated extensively. The results showed that the pure water flux, maximum pore size and porosity of the prepared membranes decreased with an increase in Al\(_2\)O\(_3\)/PES ratios and sintering temperature. When the Al\(_2\)O\(_3\)/PES ratio reached 9, the pure water flux and maximum pore size were at 2547 L m\(^{-2}\) h\(^{-1}\) and 1.4 \(\mu\)m respectively. Under 1600 °C sintering temperature, the pure water flux and maximum pore size reached 2398 L m\(^{-2}\) h\(^{-1}\) and 2.3 \(\mu\)m respectively. The results showed that the Al\(_2\)O\(_3\) hollow-fibre membranes prepared were suitable for the MF process. The morphology investigation also revealed that the prepared Al\(_2\)O\(_3\) hollow-fibre membrane retained its asymmetric structure even after the sintering process.

Niwa et al. [23] developed a membrane oxygenator using a novel asymmetric polyimide hollow fibre. The hollow fibres were prepared using a dry/wet phase-inversion process. The gas transfer rates of O\(_2\) and CO\(_2\) through the hollow fibres were investigated in gas–gas and gas–liquid systems. The polyimide hollow fibre has an asymmetric structure characterized by the presence of macrovoids, and the outer diameter of the hollow fibre is 330 \(\mu\)m. It was found that the polyimide hollow-fibre oxygenator enhanced the gas transfer rates of O\(_2\) and CO\(_2\), and that the hollow fibre provided excellent blood compatibility in vitro and in vivo.

PTFE hollow-fibre membranes, because of their excellent physical and chemical properties, can be used in the harsh environment of water treatment [24]. But the membranes cannot be prepared by conventional methods, such as the melting processing methods and the dry–wet spinning processing methods and because of a high melting point of 327°C and chemical stability. This paper explored using a method of extrusion–stretching–sintering, obtaining membranes with high fracture strength (10 MPa) and high pure water flux (1500 L m\(^{-2}\) h\(^{-1}\)); the retention rate of BSA also reached 50%, which meets the laboratory MF membrane requirements.

4.2 Membrane Module

Flat-sheet, tubular, capillary, and hollow-fibre membranes are set up in several membrane modules. Flat-sheet membranes are fabricated with plate-and-frame, rotating disk, and spiral-wound configurations, annular-gap dynamic membrane modules and pleated membrane cartridges. Tubular, capillary and hollow-fibre membranes are set up in tubular membrane modules. Hence, membrane modules are chosen based on various treated targets. Computational fluid dynamics (CFD) has been widely used to understand the hydrodynamic behaviour of membrane processes, including membrane modules [25,26]. Therefore, CFD technology is very important for the optimum design of membrane modules. The main modules used for membrane separation technology are discussed in the following subsections.
4.2.1 Plate–Frame Module

In the sheet type the space between the flat membrane plates is the flow channel, and the permeate can be obtained from the inside of the flat membrane plate. There are two types in flat membrane modules: plate–frame and stack type. The former type has multicompartments constituted of the pressurized feed and permeate chambers, as shown in Figure 4.1. This module does not have a high membrane layer density but can be favourably applied for a feed with high concentration of suspended material by controlling spaces between spacers. The latter type can have high membrane layer density by horizontally piling up membranes, as shown in Figure 4.2, and is generally operated by the cross-flow filtration technique.

Figure 4.3 shows the pleats-type module in which membrane pleated flat sheets are set in a housing. The character of this module can maintain a high membrane area in the same space.

The optimization of the flat-sheet module design and operating conditions, which depends on the geometry (membrane plate spacing) and aeration intensity (bubble size), was done from the experimental and CFD investigations results [27]. The most effective flow profiles for fouling mitigation by using a gas–liquid two-phase CFD model are optimized by using the two-phase flow in a submerged flat sheet membrane module system [28].
4.2.2 Spiral Module

Spiral-wound membranes are tightly packed filter media where a flat-sheet permeable membrane is wrapped around a centre core in a spiral fashion similar to a roll of fabric, as shown in Figure 4.4. The permeable membrane is sealed at the edges and is gapped with a spacer material that allows flow of the liquid that is to be filtered. Water to be filtered enters the membrane module from one end. Filtration occurs inside the module when backpressure is applied to drive the clean water through the membrane surface. Clean water (permeate) can be collected on way out of the module at the other end.

These modules can be used in parallel and in series as the need arises. The modules are placed inside housings. There are plumbing connections at the entrance and exit of the vessel. Pumps are used ahead of the system to generate the flow into the filter module. A backpressure valve is used on the concentrate outlet to set the flow rate out and provide resistance for pressure to develop in the module. The speed of the pump on the inlet is controlled to develop the desired pressure level. These modules can be applied to MF, UF, NF and RO, and they have also been tested in PV for separation of organic liquids [29].

Substantial literature describes the complex structure of the spiral-wound membrane module [25,30], pointing out that the appropriate cell types and periodic boundary conditions have been...
suggested based on the three-dimensional CFD analysis of spacer-filled membrane module designs with various spacer arrangements. Li and Tung [31] noted that the flow field in spiral-wound membrane modules was affected by the curvature of a spacer-filled channel and also found that the shear stress at the inner wall was greater than that at the outer wall in a curved, spacer-filled channel by using a two-dimensional numerical scheme. Furthermore, Li et al. investigated the particulate deposition on the membrane surface in a spacer-filled channel by a CFD technique [32]. In addition, they [33] declared that a three-dimensional CFD technique and an experimental set-up with a curved channel filled with a two-layer-filament spacer were used to understand the fluid flow in the channel. A spacer with unequal filament diameters between the inner layer and outer layers was adopted owing to mitigating the curvature effect of the spacer-filled channel in a spiral-wound membrane module. This type of spacer could be considered to reduce the imbalance in shear stress between the inner and outer walls so as to extend the life of a membrane module [34].

4.2.3 Tubular Module

Tubular modules are usually made with ceramic or stainless steel porous tubular membranes. The inside diameters of the tube are more than 3–5 mm. Elements less than these diameters are called capillary or hollow-fibre membranes. The skin layer is cast on ceramic or a stainless steel supporter. The tubular-type module is fabricated as in Figure 4.5.

In addition there is the monolith type, which has a number of small pores in one membrane element, as shown in Figure 4.6. CFD analysis to efficiently increase the area of the membrane unit containing

![Figure 4.5 Tubular-type module (tubular membrane).](image1)

![Figure 4.6 Monolith-type module (tubular membrane).](image2)
the ceramic membranes gave several configurations by changing parameters such as the diameter, membrane geometry and the form of the channels (cylindrical, square section, triangular, hexagonal, etc.) [35].

4.2.4 Hollow-Fibre Module

The hollow-fibre module has been widely used in separation processes. This module is fabricated in a tubular housing, with the membrane element potted one side or both sides of a bundle with a number of hollow fibres of inside diameter less than 1 mm. Since the hollow fibre has functions for both separation and support, a material for the flow is not required. Consequently, the density and volume efficiency of the membrane can be improved. Operation techniques in hollow-fibre modules are divided into two types: pressurized and immersion. The former type, furthermore, is divided into internal and external pressurized types, as shown in Figure 4.7. In the internal type (Figure 4.7a), the feed solution is supplied in the inside of hollow fibres and filtrated from the inside of the membrane to the outside of the membrane. In this type the concentration polarization can be controlled in a low state because a high flux on the membrane surface in a small flow can be maintained. But proper

![Figure 4.7](image_url)

Figure 4.7 A schematic illustration of a hollow-fibre module: (a) internal pressurized module; (b) external pressurized module.
operations are required because a high pressure loss and close of the flow by suspended particles are a danger. In the external type (Figure 4.7b) the feed is supplied in the outside of hollow fibres and filtrated from the outside of membrane to the inside of the membrane. With the external pressurized type it is difficult to keep a high flow on the membrane surface compared with the internal pressurized type. However, in MF and UF, since air scrubbing and backwashing can be done, this type is advantageous for a feed with a lot of suspended particles. In general, this external pressurized module is used in a vertical configuration because this module needs air scrubbing.

Figure 4.8 shows the whole illustration of a hollow-fibre module.

Mitigating fouling, clogging phenomena and controlling production quantities depends on selecting a suitable operating pressure and fibre locations within the module. The hydraulic-path variation within the connection box for the hollow-fibre module depends upon the geometry of the permeate outlet [36]. The CFD results found vortex zones at the side which is opposite to the feed inlet. The increasing recirculation velocity in these vortex zones reduces the risk of clogging. The degree of clogged hollow fibres was determined and the modular energy consumption by using a CFD technique to calculate the pressure drop with adjustments to the inlet velocities, inlet pressures, internal diameters and permeabilities of the hollow fibres being estimated [37]. Li and Tung [34] reported that a spacer-filled disk-type membrane module was optimized by considering the collection-tube size, spacer thickness and membrane module sizes. Fluid flow in the membrane module and permeate flux, permeate volumetric flow rate and the distribution of permeation rates on the membrane surfaces were analysed by a three-dimensional CFD technique. This analysis gave the optimum conditions and configurations to yield a module design with maximum performance.

Mat et al. [38] described that module design in hollow-fibre membrane modules, which are used in a wide range of separation applications, is critical to optimizing process performance, and they reviewed the state of the art in fibre bundle and module manufacture by emphasizing industrial practice as reflected by the patent literature. The review details typical hollow-fibre membrane modules, as shown in Figures 4.9 (hollow-fibre module) and 4.10 (hollow-fibre module).

4.2.5 Types of Membrane Filtration Modules

Membrane modules come in two basic configurations: self-contained and open immersion type. The most common module type for MF, UF, NF and RO membranes is the self-contained (or housed) membrane module where feed water is pumped through the housing. In those membrane separation
techniques, tubular, capillary and hollow-fibre membranes are set in a housing, as shown in Figures 4.3, 4.4, 4.5, 4.6 and 4.8. All feed, concentrate and filtrate piping connections are integral to the module. The open immersion-type modules are placed into the feed-water tank with the membrane exposed [39].

4.2.6 Durability of Membrane Modules

Presently there are no clear-cut criteria on how to rate the durability or the useful service life of membrane modules, nor what properties or metrics to stipulate or measure. Deterioration in filter performance is classified in two broad categories. One is membrane degradation from mechanical, chemical or biological causes. These may be membrane compaction, decomposition or degradation of the membrane material, or actual membrane rupture. The second is degradation in performance due to membrane fouling or blocking/occlusion of the module’s flow channels.

4.2.7 Degradation of Membrane Module Materials

Degradation of membrane module materials depends on use and exposure. Factors such as temperature, water quality and physical loading, as well as cleaning frequency and the membrane’s resistance to the cleaning chemicals employed. Offline module storage conditions also impact service life. As a general rule, a 3-year service life is a reasonable benchmark for modules with organic membranes. For membrane modules with inorganic membrane, a 7-year service life can be expected.
4.2.8 Decline of Membrane Performance

With extended processing the membrane filter capacity tends to decline with an attendant increase in trans-membrane pressure. There is added resistance to permeation due to formation of a fouling layer at the membrane surface consisting of suspended solids, dissolved high molecular weight polymers and compounds having low solubility. There may also be clogging of the porous support structure of the membrane and/or blockage of the module flow channels. Filter performance may often be recovered with hydromechanical techniques, such as backwashing and air scrubbing. Modifying operating conditions may also help prevent membrane fouling. Chemical cleaning is used to restore filter performance when the physical techniques prove inadequate. Eventually, the membrane modules are replaced when chemical cleaning becomes too frequent or is no longer adequate.

Figure 4.10 Sources of nonideal flow distribution within hollow-fibre modules: (a) flow distribution from the lumen manifold into the fibre lumens; (b) flow distribution from the shell manifold into the shell; (c) fibre inner-diameter-induced lumen flow variation; and (d) inter-fibre-spacing-induced shell flow variation. The length of the arrows indicates the relative magnitude of the flow rate variation anticipated for each source. (a) and (b) contain the module elements indicated in Figure 4.9, while (c) and (d) are abstracted pictorial illustrations of a bundle axial cross-section.
References

Characterization of Membrane

Membrane processes can cover a wide range of separation problems, with a specific membrane being required for every problem. Membranes may differ significantly in their structure, and consequently in their functionality. To know what membrane to use in a particular separation process, different membranes must be characterized in terms of structure and mass transport properties. Because very different membranes are used for each object in membrane separation processes, a lot of different techniques are required to clearly characterize a membrane. To characterize the membrane is very important both for fundamental membrane research and for development of practical membrane processes, because the design of membrane processes and systems depends on reliable data relating to membrane properties.

5.1 Methods and Subjects of Evaluation

Table 5.1 summarizes the methods and subjects of evaluation in characterization of membrane.

5.1.1 Bubble-Point Method

The bubble-point method is the most widely used for pore size determination. It is based on the fact that, for a given fluid and pore size with a constant wetting, the pressure required to force an air bubble through a pore is inversely proportion to the size of the hole.

The theory of capillarity states that the height of a water column in a capillary is indirectly proportional to the capillary diameter. Surface tension forces hold up the water in the capillary, and as its diameter gets smaller the weight in the water column gets higher. Water can be pushed back down by a pressure that has the same equivalent height as that of the water column. Thus, by determining the pressure necessary to force water out of the capillary, the diameter of the capillary can be calculated.

In practice, the pore size of the membrane element can be established by wetting the element with the fluid and measuring the pressure at which the first stream of bubbles is emitted from the upper surface of the element.² The procedure for the bubble-point test is described in the American Society

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for Testing and Materials (ASTM) Standard Method F316. The top of the membrane is placed in contact with the liquid, the bottom with air, and the membrane holder is connected to a source of a regulated pressure, as shown in Figure 5.1.

The air pressure is gradually increased and the formation of bubbles on the liquid side is noted. At pressures below the bubble point, gas passes across the membrane only by diffusion, but when the pressure is high enough to dislodge liquid from the pores, bulk flow begins and bubbles will be seen. The initial bubble test pressure determines the size (and location) of the largest hole; the open bubble point pressure determines the mean pore size of the element. The latter can be affected by flow velocity as well as pressure.

The theoretical relation between this transition pressure and the bubble-point pressure is

\[
D = \frac{4\gamma \cos \theta}{P}
\]  

(5.1)
where $P$ (Pa) the is bubble-point pressure, $\gamma$ (N m$^{-1}$) is the surface tension of the liquid (0.72 N m$^{-1}$ for water), $\theta$ (rad) is liquid–solid contact angle (which for water is generally assumed to be zero), $D$ (mm) is diameter of the pore.

Since no pores in a practical filter element are likely to be shaped like capillary tubes it is necessary to introduce a shape correction factor $K$ into the formula.

Since $\gamma$ and $\theta$ are constant, the formula can be simplified by introducing an empirical factor $K_1$ dependent on the filter material and form of the units employed:

$$D = \frac{K_1}{P}$$

(5.2)

$D$ (mm) is again the maximum average diameter of the pores.

Figure 5.2 shows the effects of the maximum pore size on the EtOH in the permeate and permeation rate for an aqueous solution of 10 wt% EtOH through porous PTMSP membranes during temperature-difference-controlled evaporation. As can be seen from this result, the permeation and separation characteristics of porous PTMSP membranes are significantly influenced by the maximum pore size of those membranes [1].

### 5.1.2 Mercury Intrusion Porosimetry

Mercury intrusion porosimetry is an extremely useful characterization technique for porous materials. This method is effective for porous materials with pores size between about 500 $\mu$m and 3.5 nm, as shown in Figure 5.3.

A complete analysis may take as little as half an hour of analysis time. Mercury intrusion porosimetry provides a wide range of information; for example, the pore size distribution, the total pore volume
or porosity, the skeletal and apparent density, and the specific surface area of a sample. No other porosity characterization technique can achieve this. However, one should realize that mercury intrusion porosimetry also has limitations. One of the most important limitations is the fact that it measures the largest entrance toward a pore (see Figure 5.4), but not the actual inner size of a pore. For obvious reasons it also cannot be used to analyse closed pores, since the mercury has no way of entering that pore. Through various software techniques, an interpretation of the pore network (cross-linking structure between pores) can be achieved. However, one should realize that numerous assumptions are made in that process and the final results are somewhat arbitrary. A key assumption in mercury porosimetry is the pore shape. Essentially, all instruments assume a cylindrical pore geometry using a modified Young–Laplace equation, which is most of the time referred to as the Washburn equation:

$$\Delta P = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) = \frac{2\gamma \cos \theta}{r_{\text{pore}}}$$

(5.3)
This relates the pressure difference across the curved mercury interface \( r_1 \) and \( r_2 \) describe the curvature of that interface) to the corresponding pore size \( r_{pore} \) using the surface tension of mercury \( \gamma \) and the contact angle \( \theta \) between the solid and mercury. The real pore shape, however, is quite different, and the cylinder pore assumption can lead to major differences between the analysis and reality.

As indicated in Equation 5.3, we need to know surface tension and contact angle for the given sample and then measure pressure and the intruded volume in order to obtain the pore size–pore volume relation. Key measurement variables are the pressure and pore volume. Accurate measurement of those parameters is strongly required [2].

Figure 5.5 shows the pore distribution and pore size of a porous chitosan membrane determined by mercury intrusion porosimetry. As can be seen from Figure 5.5, this porous chitosan membrane has a pore distribution and average pore size estimated about 10 \( \mu \)m [3].
5.1.3 Adsorption–Desorption Method (BET Method)

BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. In 1938, Stephen Brunauer, Paul Hugh Emmett and Edward Teller published the first article about the BET theory in the Journal of the American Chemical Society [4].

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is

\[
\frac{1}{v[(p_0/p) - 1]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0}\right) + \frac{1}{v_m c}
\]

where \(P\) and \(P_0\) are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, \(v\) is the adsorbed gas quantity (e.g. in volume units), and \(v_m\) is the monolayer adsorbed gas quantity. \(c\) is the BET constant:

\[
c = \exp \left(\frac{E_1 - E_L}{RT}\right)
\]

where \(E_1\) is the heat of adsorption for the first layer and \(E_L\) is that for the second and higher layers and is equal to the heat of liquefaction.

Equation 5.4 is an adsorption isotherm and can be plotted as a straight line with \(1/v[(p_0/p) - 1]\) on the \(y\)-axis and \(\phi = p/p_0\) on the \(x\)-axis according to experimental results. This plot is called a BET plot (Figure 5.6). The linear relationship of this equation is maintained only in the range of \(0.05 < p/p_0 < 0.34\). The value of the slope \(A\) and the \(y\)-intercept \(I\) of the line are used to calculate the monolayer adsorbed gas quantity \(v_m\) and the BET constant \(c\). The following equations can be used:

\[
v_m = \frac{1}{A + I}
\]

\[
c = 1 + \frac{A}{I}
\]

The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. The total surface area \(S_{\text{total}}\) and the specific surface area \(S_{\text{BET}}\) are given by

\[
S_{\text{total}} = \frac{v_m N_s}{V}
\]

\[
S_{\text{BET}} = \frac{S_{\text{total}}}{a}
\]
where $v_m$ is in units of volume, which are also the units of the molar volume of the adsorbate gas, $N$ is Avogadro's number, $S$ is the adsorption cross-section of the adsorbing species, $V$ the molar volume of the adsorbate gas and $a$ is the mass of the adsorbent.

### 5.1.4 Scanning Electron Microscope


#### 5.1.4.1 Sample Preparation

All samples must also be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Several models of scanning electron microscope can examine any part of a 6" (15 cm) semiconductor wafer, and some can tilt an object of that size to $45^\circ$.

For conventional imaging in SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Nonconductive specimens tend to charge when scanned by the electron beam, especially in secondary electron imaging mode, and this causes scanning faults and other image artefacts. They are therefore usually coated with an ultrathin coating of electrically conducting material, deposited on the sample either by low-vacuum sputter coating or by high-vacuum evaporation. Conductive materials in current use for specimen coating include gold, gold–palladium alloy, platinum, osmium [5], iridium, tungsten, chromium and graphite. Additionally, coating may increase signal/noise ratio for samples of low atomic number $Z$. The improvement arises because secondary electron emission for high-$Z$ materials is enhanced.

An alternative to coating for some biological samples is to increase the bulk conductivity of the material by impregnation with osmium using variants of the OTO (osmium–thiocarbohydrazide–osmium) staining method [6,7]. Nonconducting specimens may be imaged uncoated using an environmental scanning electron microscope (ESEM) or the low-voltage mode of scanning electron microscope operation [8]. ESEM instruments place the specimen in a relatively high-pressure chamber where the working distance is short and the electron optical column is differentially pumped to keep vacuum adequately low at the electron gun. The high-pressure region around the sample in the ESEM neutralizes charge and provides an amplification of the secondary electron signal. Low-voltage SEM is typically conducted in a field emission gun scanning electron microscope because the field emission gun is capable of producing high primary electron brightness and small spot size even at low accelerating potentials. Operating conditions to prevent charging of nonconductive specimens must be adjusted such that the incoming beam current is equal to the sum of outcoming secondary and backscattered electrons currents. It usually occurs at accelerating voltages of 0.3–4 kV. Embedding in a resin with further polishing to a mirror-like finish can be used for both biological and materials specimens when imaging in backscattered electron mode or when doing quantitative X-ray microanalysis. The main preparation techniques are not required in the ESEM outlined in Section 5.1.6, but some biological specimens can benefit from fixation.

Figure 5.7 shows SEM micrographs of the surface and cross-section of a porous chitosan membrane [3]. As can be seen from these micrographs that the chitosan membrane has a fine porous structure.

### 5.1.5 Transmission Electron Microscopy

5.1.5.1 Sample Preparation

Sample preparation in TEM can be a complex procedure [9]. TEM specimens are required to be at most hundreds of nanometres thick as, unlike neutron or X-ray radiation, the electron beam interacts readily with the sample, an effect that increases roughly with atomic number squared [10]. High-quality samples will have a thickness that is comparable to the mean free path of the electrons that travel through the samples, which may be only a few tens of nanometres. Preparation of TEM specimens is specific to the material under analysis and the desired information to obtain from the specimen. As such, many generic techniques have been used for the preparation of the required thin sections.

Materials that have dimensions small enough to be electron transparent, such as powders or nanotubes, can be quickly prepared by the deposition of a dilute sample containing the specimen onto support grids or films. In the biological sciences, in order to withstand the instrument vacuum and facilitate handling, biological specimens can be fixed using either a negative staining material such as uranyl acetate or by plastic embedding. Alternately, samples may be held at liquid-nitrogen temperatures after embedding in vitreous ice [11]. In material science and metallurgy the specimens tend to be naturally resistant to vacuum, but still must be prepared as a thin foil, or etched so that some portion of the specimen is thin enough for the beam to penetrate. Constraints on the thickness of the material may be limited by the scattering cross-section of the atoms from which the material is comprised.

5.1.5.2 Tissue Sectioning

By passing samples over a glass or diamond edge, small, thin sections can be readily obtained using a semi-automated method (microtome: a diamond knife blade used for cutting ultrathin sections, typically 70–350 nm for TEM) [12]. This method is used to obtain thin, minimally deformed samples that allow for the observation of tissue samples. Additionally, inorganic samples have been studied, such as aluminium, although this usage is limited owing to the heavy damage induced in the less soft samples [13]. To prevent charge build-up at the sample surface, tissue samples need to be coated with a thin layer of conducting material, such as carbon, where the coating thickness is several nanometres. This may be achieved via an electric arc deposition process using a sputter coating device.

5.1.5.3 Sample Staining

Details in light microscope samples can be enhanced by stains that absorb light; similarly, TEM samples of biological tissues can utilize high atomic number stains to enhance contrast. The stain absorbs electrons or scatters part of the electron beam that otherwise is projected onto the imaging system. Compounds of heavy metals, such as osmium, lead, uranium or gold (in immunogold labelling), may be used prior to TEM observation to selectively deposit electron-dense atoms in or on the sample in desired cellular or protein regions, requiring an understanding of how heavy metals bind to biological tissues [14].
Figure 5.8 shows TEM images at a magnification of 100,000× for cross-sections of the P(BMA-co-VTES) (I)/TEOS (II) hybrid membranes with TEOS contents of 25 mol% and 150 mol% respectively. The dark region represents the TEOS or VTES component containing Si atoms. A distinct microphase-separated structure was observed in the hybrid membranes with a TEOS content of 25 mol%. It can be presumed that this microphase-separated structure in the P(BMA-co-VTES)/TEOS hybrid membrane with low TEOS content was due to differences in the reactivity of BMA and VTES monomers. On the other hand, in the P(BMA-co-VTES)/TEOS hybrid membranes with excess TEOS (150 mol%), the dark region was dispersed in the hybrid membranes and an aggregated structure of TEOS was observed. As a result, the P(BMA-co-VTES)/TEOS hybrid membranes with appropriate TEOS content were transparent and homogeneous, and TEM observation demonstrated that organic and inorganic domains were dispersed on a scale of less than a micrometre. However, at the molecular level, silica network structures are typically heterogeneous [15].

\[
\begin{align*}
&\text{(I)} \\
&\text{(II)}
\end{align*}
\]

5.1.6 Environmental Scanning Electron Microscope


The ESEM is a scanning electron microscope that allows for the option of collecting electron micrographs of specimens that are ‘wet’, uncoated, or both by allowing for a gaseous environment in the specimen chamber. Although there were earlier successes at viewing wet specimens in internal
chambers in modified scanning electron microscopes, the ESEM with its specialized electron detectors (rather than the standard Everhart–Thornley detector) and its differential pumping systems to allow for the transfer of the electron beam from the high vacuums in the gun area to the high pressures attainable in its specimen chamber, make it a complete and unique instrument designed for the purpose of imaging specimens in their natural state. The instrument was designed originally by Gerasimos Danilatos while working at the University of New South Wales.

Patterson et al. [16] observed the ESEM image (see Figure 5.9) of integrally skinned polyimide membranes that have been used to achieve selective separations in a range of solvent-based industrial and laboratory-scale chemical operations.

Figure 5.9 demonstrates that the ‘wispy’ and ‘fluffy’ microstructure is present in the EtOH-wetted membrane in the ESEM and not in the ‘dry’ membrane, despite the 1 h pre-saturation of both membrane samples, indicating that the difference in microstructure seen in the ESEM images may be attributed to the EtOH wetting. These results therefore demonstrate that the microstructures observed in dry membranes may change significantly when in solvent. Consequently, any transport and separation mechanisms in the literature based on the microstructures of dry membranes may not accurately reflect the microstructure of wetted membranes and therefore most likely need to be rethought.

### 5.1.7 Atomic Force Microscopy

See Wilson and Bullen’s ‘Introduction to scanning probe microscopy’ [17].

AFM provides a three-dimensional profile of the surface on the nanoscale, by measuring forces between a sharp probe (<10 nm) and the surface at a very short distance (0.2–10 nm probe–sample separation). The probe is supported on a flexible cantilever. The AFM tip ‘gently’ touches the surface and records the small force between the probe and the surface.

The probe is placed on the end of a cantilever (which one can think of as a spring). The amount of force between the probe and the surface is dependent on the spring constant (stiffness) of the
cantilever and the distance between the probe and the sample surface. This force can be described using Hooke’s law:

$$ F = -kx $$

(5.10)

where $F$ is force, $k$ is the spring constant and $x$ is the cantilever deflection.

If the spring constant of the cantilever (typically ~0.1–1 N m$^{-1}$) is less than the surface, the cantilever bends and the deflection is monitored. This typically results in forces ranging from nanonewtons to micronewtons in the open air.

Figure 5.10 shows tapping-mode AFM images of (a) NF-PES-10 (Osmonics) and (b) Desal 5DL (Nadir) nanofiltration membranes [18]. One can see that NF-PES-10 is a very smooth membrane and Desal 5DL is a very rough membrane.

![Figure 5.10 Tapping-mode AFM images of (a) NF-PES-10 and (b) Desal 5DL. Note that the X and Y dimensions are both 3 μm, while the Z-scale is 200 nm.](image)
5.1.8 Infrared Spectroscopy

IR spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types, such as gases, liquids and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification [24].

The IR absorption spectra of the untreated cellulose nitrate membrane and the membrane treated with an ammonium hydrogen sulfide solution are shown in Figure 5.11. The characteristic absorption bands at 3400 cm\(^{-1}\), 1060 cm\(^{-1}\), 2900 cm\(^{-1}\), 1640 cm\(^{-1}\) and 1365 cm\(^{-1}\) shown in the resulting spectra are assigned to the hydroxyl group, the C─OH stretching vibration, C─H stretching vibration, hydroxyl overtone and CH respectively. The characteristic absorption bands of the untreated membrane at 1650 cm\(^{-1}\), 1275 cm\(^{-1}\) and 830 cm\(^{-1}\) are due to the asymmetric NO\(_2\) stretching vibration, the symmetric NO\(_2\) stretching vibration, and the O─H stretching vibration respectively. The strong absorption peaks due to the nitrate have disappeared completely in the spectrum of the treated membrane. It is seen from these spectra that the cellulose nitrate membrane is reduced completely to cellulose membrane.

The permeation rates and permeation fractions of cellulose nitrate membranes and cellulose membranes were determined using pure water and 1.0% aqueous solutions of seven kinds of poly(ethylene glycol) having different molecular weights as feed solute. The operating pressure was 200 mmHg, the feed flow rate was 200 mL min\(^{-1}\) and the operating temperature was 38 °C. The experimental results obtained are summarized in Table 5.2, which also includes the relative viscosity of the feed solution.

![Figure 5.11 IR spectra of cellulose nitrate before and after ammonium hydrogen sulfide treatment.](image-url)
From Table 5.2 it can be seen that all permeation rates decrease with an increase in molecular weight of the feed solute and depend upon the viscosity of the feed solution. The permeation rates of cellulose membrane are always greater than those of cellulose nitrate membrane. The permeation fractions of cellulose membrane are 100% in all systems having molecular weights in the range from 200 to 20 000. However, in cellulose nitrate membrane, just a little separation begins with the system of poly(ethylene glycol) 1000 and the permeation fractions are 0% in systems of poly(ethylene glycol) 6000 and 20 000. From these results, it is seen that there is a rather large difference between the permeation characteristics of cellulose nitrate membranes and cellulose membranes. The ammonium hydrogen sulfide reagent is known to reduce cellulose nitrate without disrupting the cellulose chain. Therefore, it may be presumed that the conformation of the main cellulose chains in these two polymer membranes is almost the same. The difference between the permeation characteristics of these membranes depends upon the substituent groups on the pyrane rings in the cellulose chain. By converting the nitrate groups to hydroxyl groups, the resulting membrane becomes more hydrophilic. Therefore, the affinity between the membrane substrate and the feed solution increases, and consequently the permeation rate and the permeation fraction will increase. A slight enlargement of the void space accompanied by the conversion of —ONO₂ groups to —OH groups will also effect an increase of the permeation rate and the permeation fraction [20].

### Table 5.2 Effect of solute in feed solution permeation characteristics through cellulose nitrate and cellulose membranes.

<table>
<thead>
<tr>
<th>Relative feed viscosity</th>
<th>Cellulose nitrate membrane</th>
<th>Cellulose membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Permeation rate (mL cm⁻² s⁻¹) × 10⁴</td>
<td>Permeation fraction (%)</td>
</tr>
<tr>
<td>Pure water</td>
<td>1.000</td>
<td>7.29</td>
</tr>
<tr>
<td>PEG 200</td>
<td>1.028</td>
<td>4.78</td>
</tr>
<tr>
<td>PEG 400</td>
<td>1.043</td>
<td>2.80</td>
</tr>
<tr>
<td>PEG 600</td>
<td>1.046</td>
<td>1.87</td>
</tr>
<tr>
<td>PEG 1000</td>
<td>1.055</td>
<td>1.65</td>
</tr>
<tr>
<td>PEG 4000</td>
<td>1.107</td>
<td>0.54</td>
</tr>
<tr>
<td>PEG 6000</td>
<td>1.202</td>
<td>0.2</td>
</tr>
<tr>
<td>PEG 20 000</td>
<td>1.431</td>
<td>0.08</td>
</tr>
</tbody>
</table>

5.1.9 Fourier-Transform Infrared Spectroscopy


FTIR spectroscopy is a technique that is used to obtain an IR spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time. FTIR has made dispersive IR spectrometers all but obsolete (except sometimes in the near IR), opening up new applications of IR spectroscopy.
Belfer et al. reported on surface modification structure of commercial polyethersulfone (PES) ultrafiltration membrane using attenuated total reflectance (ATR) FTIR spectroscopy [21]. Figure 5.12 shows ATR-FTIR spectra of the PES membrane (a) as received (the bands that were removed by washing, are marked with arrows) and (b) after washing with water.

According to the spectra obtained, Millipore PES membranes are composed solely of PES. Spectral inspection of the ‘as-received’ PES membrane revealed the presence of preservatives (a very strong band at 3400 cm$^{-1}$ and three bands at 1650, 1040 and 920 cm$^{-1}$) (Figure 5.12a). The preservatives were washed out with water (complete disappearance of the aforementioned bands – Figure 5.12b). After washing, the membranes underwent a drying procedure, but water removal was not complete, even under vacuum drying at room temperature for several days. The water–EtOH exchange procedure

![Figure 5.12 ATR-FTIR spectra of the Millipore PES membrane: (a) as received (the bands that were removed by washing are marked with arrows); (b) after washing with water.](image-url)
was then applied. Finally, the degree of ‘cleanness’ was monitored by the disappearance of the strong aliphatic CH stretch near 2900 cm\(^{-1}\), which does not belong to PES.

In general, it is well known that the highly reactive alkoxy groups of silane coupling agents can easily be formed by the self-assembly of a monolayer membrane with hydroxy groups on the solid surface. Using this trimethylmethoxysilane (TMS) modification it can be expected that the surface of P(BMA-co-VTES)/TEOS hybrid membrane becomes hydrophobic.

FTIR spectra of the untreated P(BMA-co-VTES)/TEOS hybrid membrane and a TMS-modified P(BMA-co-VTES)/TEOS hybrid membrane with a TEOS content of 125 mol% are shown in Figure 5.13 [22].

In the FTIR spectrum of the TMS-modified hybrid membrane, a decrease in the absorption peaks at 3500 cm\(^{-1}\) was observed because of silanol groups and hydrogen bonds. The absorption peak at about 1700 cm\(^{-1}\) in the untreated P(BMA-co-VTES)/TEOS hybrid membrane disappeared in the TMS-modified P(BMA-co-VTES)/TEOS hybrid membrane. These results suggest that the residual silanol groups in the former membrane were modified by TMS, and, consequently, the latter membrane became more hydrophobic [23,24]. This discussion was supported by the fact that the contact angles for water of the untreated and TMS-modified P(BMA-co-VTES)/TEOS hybrid membrane were 98° and 104° respectively with a TEOS content of 125 mol%.

5.1.10 X-Ray Photoelectron Spectroscopy or Electron Spectroscopy for Chemical Analysis

See http://www.eag.com/xps-esca/.

XPS (also known as ESCA) is the most widely used surface analysis technique because of its relative simplicity in use and data interpretation. X-rays excite the electrons of the sample atoms and if their binding energy is lower than the X-ray energy they will be emitted from the parent atom as a
photoelectron. Only the photoelectrons at the extreme outer surface (10–100 Å) can escape the sample surface, making this a surface analysis technique. A quartz crystal focuses the X-ray beam into a small spot on the sample surface. The spot size on SEAL Laboratories’ X-ray photoelectron spectrometer can be varied from 150 to 1000 μm in diameter. When the X-ray hits the sample surface it excites the sample electrons. If the sample electrons have a binding energy less than the X-ray energy (1486 eV) they will jump out of the sample atom. Most of these electrons are reabsorbed by the sample, but the electrons emitted from atoms near the sample surface (10–100 Å) can escape the sample surface. This depth is approximately 20 atomic layers. XPS analysis not only provides elemental information, but because the technique is detecting the binding energy of emitted electrons it can also provide some chemical bonding information. Depending on what elements the parent atom is bound to, the binding energy of the emitted photoelectrons may shift slightly. The instrument is sensitive enough to detect these electron energy shifts and use them to determine what chemical compounds are present.

The performance of polyamide composite reverse osmosis (RO) membranes is essentially determined by a dense skin layer several hundred nanometres thick. Improved understanding of this critical thin layer will likely advance our understanding and control of membrane fouling and trace organics rejection. Tang et al. [25] carried out XPS, ATR-FTIR, TEM measurements and streaming potential analysis to characterize commercial fully aromatic polyamide RO membranes. By using these techniques together in a systematic way, the presence of an aliphatic coating layer rich in –COH groups was confirmed for some commercial RO membranes. While the uncoated RO membranes had surface elemental compositions (measured by XPS) very close to the predicted values for polyamides based on the classical interfacial polymerization chemistry of trimesoyl chloride and 1,3-benzenediamine (m-phenylene-diamine), the coated membranes showed higher oxygen and lower nitrogen content. The typical layered structures (a polyamide layer on top of a polysulfone layer) and the rough ridge-and-valley features were clearly visible in TEM micrographs. For a coated membrane, a light-coloured coating layer (lack of electron density) was visible, especially when a stained humic acid foulant layer was present to increase the contrast between the coating and the background. An intense OH stretching peak in conjunction with new aliphatic C–H stretching peaks were observed in ATR-FTIR spectra for coated membranes, where the aromatic =C–H stretching peak normally present for uncoated membranes was overwhelmed. High-resolution XPS scans on carbon 1 s peaks confirmed the presence of alcoholic –COH groups in the coating layer, where an additional peak with a binding energy shift of 1.5 eV was identified in addition to the two peaks present for uncoated membranes: 284.6 eV (aliphatic and aromatic carbon atoms) and –287.8 eV (carboxylic and amide bond carbon atoms). The measured zeta potential values of the coated membranes were significantly less negative than those of the uncoated ones, suggesting that the coating layer is likely neutral.

XPS is a highly surface-sensitive technique, with the ability to measure elemental composition and chemical binding information for the top 1–5 nm depth of the surface region. The technique is able to detect all elements except hydrogen with detection limits around 0.01 monolayer or 0.1% of the total elemental concentration. The elemental compositions analysed from typical XPS spectra, normalized against the carbon 1 s peak (–284 eV) for eight membranes are summarized in Table 5.3.

In order to improve the surface properties of PTMSP membranes, surface-modified PTMSP membranes were prepared by adding a small amount of a polymer additive, which is a graft copolymer PFA-g-PDMS, consisting of poly(fluoroacrylate) (PFA) and poly(dimethylsiloxane) (PDMS), in a casting solution of PTMSP [26]. Table 5.4 summarizes the atomic ratios of the surfaces on the air and glass plate sides of the PTMSP and surface-modified PTMSP membranes determined by XPS. Table 5.4 also includes theoretical atomic ratios of PTMSP and PFA-g-PDMS. In this table, the theoretical atomic ratios mean values are calculated from the compositions of PTMSP and PFA-g-PDMS.
Figure 5.14 shows the relationship between the ratios of F/C for the surfaces on the air and glass plate sides of the PTMSP membranes modified with PFA-g-PDMS and the additional amount of PFA-g-PDMS is shown.

As can be seen from Table 5.4 and Figure 5.14, the ratios of F/C of both membrane surfaces on the air and glass plate sides of the surface-modified PTMSP membranes increased with increasing

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**Table 5.3** Elemental compositions and oxygen-to-nitrogen (O/N) ratios of eight commercial RO membranes from XPS analysis.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>O (%) ±</th>
<th>N (%) ±</th>
<th>C (%) ±</th>
<th>O/N ratio ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>XLE</td>
<td>12.6 ± 0.5</td>
<td>13.2 ± 0.7</td>
<td>74.3 ± 0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>LE</td>
<td>13.1 ± 0.9</td>
<td>12.1 ± 0.6</td>
<td>74.8 ± 0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>ESPA3</td>
<td>12.8 ± 0.8</td>
<td>12.9 ± 1.0</td>
<td>74.3 ± 1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>SWC4</td>
<td>13.2 ± 0.2</td>
<td>11.2 ± 0.8</td>
<td>75.5 ± 0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>LFC1</td>
<td>22.2 ± 1.5</td>
<td>7.4 ± 0.8</td>
<td>70.0 ± 4.1</td>
<td>3.0</td>
</tr>
<tr>
<td>LFC3</td>
<td>22.4 ± 1.1</td>
<td>7.3 ± 0.8</td>
<td>70.3 ± 1.7</td>
<td>3.1</td>
</tr>
<tr>
<td>BW30</td>
<td>29.0 ± 1.5</td>
<td>3.1 ± 1.0</td>
<td>76.9 ± 0.6</td>
<td>9.3</td>
</tr>
<tr>
<td>SW30HR</td>
<td>27.0 ± 7.4</td>
<td>5.5 ± 4.9</td>
<td>67.5 ± 2.9</td>
<td>4.9</td>
</tr>
<tr>
<td>SW30HR (N rich)</td>
<td>20.3 ± 0.9</td>
<td>10.0 ± 1.1</td>
<td>69.8 ± 0.9</td>
<td>2.0</td>
</tr>
<tr>
<td>SW30HR (N lean)</td>
<td>33.8 ± 2.5</td>
<td>1.0 ± 1.2</td>
<td>65.2 ± 2.2</td>
<td>35</td>
</tr>
</tbody>
</table>

**Theoretical values**
- Fully cross-linked: O = 12.5, N = 12.5, C = 75.0; O/N = 1.0
- Fully linear: O = 19.1, N = 9.5, C = 71.4; O/N = 2.0

**Table 5.4** Surface composition of the surface-modified PTMSP membranes determined by XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Additional amount (wt%)</th>
<th>Surface</th>
<th>F/C</th>
<th>O/C</th>
<th>Si/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMSP</td>
<td>—</td>
<td>Air</td>
<td>—</td>
<td>—</td>
<td>0.164</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>Glass</td>
<td>—</td>
<td>—</td>
<td>0.177</td>
</tr>
<tr>
<td>PTMSP with PFA-g-PDMS</td>
<td>0.1</td>
<td>Air</td>
<td>0.107</td>
<td>0.087</td>
<td>0.205</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glass</td>
<td>0.021</td>
<td>0.031</td>
<td>0.170</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>Air</td>
<td>0.137</td>
<td>0.115</td>
<td>0.184</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glass</td>
<td>0.025</td>
<td>0.071</td>
<td>0.199</td>
</tr>
<tr>
<td>PTMSP&lt;sup&gt;a&lt;/sup&gt;</td>
<td>—</td>
<td></td>
<td>—</td>
<td>—</td>
<td>0.167</td>
</tr>
<tr>
<td>PFA-g-PDMS&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.351</td>
<td></td>
<td>0.332</td>
<td>0.302</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Theoretical atomic ratios.
additional amount of PFA-g-PDMS. The ratios of F/C of the surface on the air side of the surface-modified PTMSP membranes with added PFA-g-PDMS, however, were considerably higher than those of the surface on the glass plate side. These XPS results support the localization of PFA-g-PDMS on the air side of the surface-modified PTMSP membranes, as suggested in the contact-angle measurements for water. When the ratio of F/C (0.137) of the surface on the air side of the PTMSP membrane modified with 0.1 wt% of PFA-g-PDMS is compared with the theoretical ratio of F/C (0.351) for PFA-g-PDMS, it is found that the addition of only 0.1 wt% of PFA-g-PDMS to the PTMSP casting solution can modify about 40% of the surface of the PTMSP membrane.

From the results of the contact angle for water and XPS measurements of the surfaces of the PTMSP membranes modified with PFA-g-PDMS, it is presumed that the structure of the surface-modified PTMSP membranes is as shown in Figure 5.15. In this figure an illustration of represents a molecule of PFA-g-PDMS as a polymer additive, and the parts and in the molecule correspond to PFA and PDMS in the graft copolymer respectively. PFA-g-PDMS that is added to improve the surface of the PTMSP membrane is mainly localized to the surface on the air side of the modified PTMSP membranes, and the PFA part in PFA-g-PDMS appears on the surface of the air side and the PDMS part integrates with the PTMSP membrane matrix.

### 5.1.11 Wide-Angle X-Ray Scattering or Wide-Angle X-Ray Diffraction

WAXS or WAXD [27] is an X-ray diffraction [28] technique that is often used to determine the crystalline structure of polymers. This technique specifically refers to the analysis of Bragg peaks scattered to wide angles, which (by Bragg’s law) implies that they are caused by sub-nanometre-sized structures.

WAXS is the same technique as SAXS, only the distance from sample to the detector is shorter and thus diffraction maxima at larger angles are observed. Depending on the measurement instrument used it is possible to do WAXS and SAXS in a single run.

![Figure 5.14](image.png)  
**Figure 5.14** Ratios of fluorine/carbon (F/C) for the surfaces on the air and glass plate sides of the modified PTMSP membranes with PFA-g-PDMS as a function of the additional amount of PFA-g-PDMS.

![Figure 5.15](image.png)  
**Figure 5.15** Structure of the PTMSP membrane modified with PFA-g-PDMS of the polymer additive. is a molecule of PFA-g-PDMS as polymer additive.
The technique is a time-honoured, but a somewhat out-of-favour, technique for the determination of degree of crystallinity of polymer samples. The diffraction pattern generated allows one to determine the chemical composition or phase composition of the film, the texture of the film (preferred alignment of crystallites), the crystallite size and the presence of film stress. According to this method, the sample is scanned in a wide-angle X-ray goniometer, and the scattering intensity is plotted as a function of the $2\theta$ angle. X-ray diffraction is a nondestructive method of characterization of solid materials. When X-rays are directed in solids they will scatter in predictable patterns based upon the internal structure of the solid. A crystalline solid consists of regularly spaced atoms (electrons) that can be described by imaginary planes. The distance between these planes is called the $d$-spacing. The intensity of the $d$-spacing pattern is directly proportional to the number of electrons (atoms) that are found in the imaginary planes. Every crystalline solid will have a unique pattern of $d$-spacings (known as the powder pattern), which is a ‘fingerprint’ for that solid. In fact, solids with the same chemical composition but different phases can be identified by their pattern of $d$-spacings.

WAXD of poly(vinylidene fluoride) (PVDF) and PVDF nanocomposite membranes prepared using water as the nonsolvent is shown in Figure 5.16 [29].

It can be seen that the major peaks in both membranes correspond to the $\alpha$-form of PVDF and remain largely unchanged upon the incorporation of the MWNTs. The difference in crystal structure obtained as a function of nonsolvent can be attributed to the fact that EtOH gives rise to a relatively slow rate of polymer coagulation for PVDF, whereas water as the nonsolvent results in rapid coagulation of PVDF [30–33]. Upon addition of EtOH, solid–liquid demixing occurs in the crystallizable segments of the polymer, which enables polymer crystallization to take place due to slow precipitation of the polymer [32]. In the case of water, the rate of polymer precipitation is very fast, leading to a relatively fast rate of crystallization, which should result in a lowered degree of crystallinity [33–35]. The principle reason that the rate of precipitation increases for the water–PVDF system should be associated with the rapid rate of interdiffusion of the solvent and the nonsolvent [33]. It is interesting to note that the nanocomposite membranes prepared using water as the nonsolvent

![Figure 5.16](image_url) **Figure 5.16** WAXD of PVDF and PVDF nanocomposite membranes prepared using water as the nonsolvent. (a) 5% multi-wall carbon nanotube–PVDF membrane; (b) PVDF membrane.
did not exhibit the β-phase (Figure 5.16), which can again be related to the slow coagulation rate with EtOH.

Park et al. [36] fabricated novel Nafion/hydroxyapatite (HA) composite membrane with high crystallinity to suppress methanol crossover for direct methanol fuel cell applications. In this study, water and methanol diffusivity were evaluated through a water–methanol sorption/desorption test and methanol permeation experiments. It was shown that the water–methanol diffusivity and methanol crossover for the composite membranes decrease as HA increases. Structural variation was investigated with wide-angle X-ray. As a result, it was found that the crystallinity of composite membranes increases with HA, whereas water uptake content decreases gradually (see Table 5.5). Methanol permeability using a diffusion cell reduced in the composite membranes, suggesting that high crystallinity and low water uptake of composite membrane result in the suppression of methanol crossover due to the incorporation of HA into Nafion structure.

The WAXD measurements were mainly performed for the crystalline diffraction in poly(vinyl alcohol) (PVA) membranes. Table 5.6 summarizes the diffraction angle of the crystalline peak 2θ and the spacing d (Å) of the unannealed PVA membrane and the annealed PVA–TEOS hybrid membrane containing TEOS 25 wt%, which was annealed at 130 °C for 24 h. The annealed PVA–TEOS hybrid membrane had a large d spacing value at the crystalline peak. This suggests that the noncrystalline region in PVA became more dense by introducing TEOS and by annealing to encourage the polycondensation reaction in the membrane. This change in the noncrystalline region of PVA affected the PVA molecule chains, and changed the rougher crystalline region. This idea is supported by the measurements of the membrane density.

The WAXD measurements concluded that the noncrystalline region, where the partitioning of an aqueous ethanol solution occurred, became denser by introducing the TEOS and by annealing to encourage the polycondensation reaction [37].

### Table 5.5 Crystallinity and water uptake contents for PTFE, cast Nafion, C1, C2, C3 composite membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>PTFE</th>
<th>Cast Nafion</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA (%)</td>
<td></td>
<td></td>
<td>2.5</td>
<td>5.0</td>
<td>7.5</td>
</tr>
<tr>
<td>Average crystallinity (Xcr, %)</td>
<td>64</td>
<td>28</td>
<td>31.5</td>
<td>36</td>
<td>38</td>
</tr>
<tr>
<td>Standard deviation (%)</td>
<td>1.6</td>
<td>1.5</td>
<td>2.6</td>
<td>1.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Water uptake content (%)</td>
<td>—</td>
<td>31</td>
<td>26</td>
<td>21</td>
<td>18</td>
</tr>
</tbody>
</table>

### Table 5.6 WAXD date of PVA and PVA–TEOS hybrid membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>2θ</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA crystalline, unannealed</td>
<td>19.86</td>
<td>4.467</td>
</tr>
<tr>
<td>PVA–TEOS (25 wt%) anneal at 130 °C for 24 h, crystalline</td>
<td>19.76</td>
<td>4.489</td>
</tr>
</tbody>
</table>
5.1.12 Small-Angle Neutron Scattering


SANS is an experimental technique that uses elastic neutron scattering at small scattering angles to investigate the structure of various substances at a mesoscopic scale of about 1–100 nm. SANS is in many respects very similar to SAXS; both techniques are jointly referred to as small-angle scattering. Advantages of SANS over SAXS are its sensitivity to light elements, the possibility of isotope labelling and the strong scattering by magnetic moments.

The structure of Nafion-117 perfluorosulfonate ionomer membranes was investigated with SANS techniques [38]. Structural changes induced by the swelling of the membranes with water, alcohols and dipolar, aprotic solvents were monitored at solvent-swelling levels ranging from approximately 2 vol.% to greater than 50 vol.%. Membranes swollen up to approximately 50 vol.% solvent exhibited two scattering maxima: one known to be associated with ionic regions of the membrane structure and one known to be associated with correlation distances between crystalline regions in the membrane structure. The positions of both maxima shifted toward lower scattering vector values as the solvent content in the membrane increased. The shift in the position of both maxima was linearly related to the solvent volume fraction in the membrane. The Bragg spacings corresponding to both the ionic-feature scattering maximum and the crystalline-feature scattering maximum were plotted versus the solvent volume fraction in the membranes, and the data fit with linear regression. The slopes associated with the curves of the spacing versus the solvent volume fraction were greater for the crystalline-feature spacing than for the ionic-feature spacing for all solvents other than water; this was indicative of preferential segregation of nonaqueous solvents into regions of the structure not directly associated with the ionic scattering maximum.

The microstructure of plasticized poly(vinyl chloride) (PVC) membranes in the dry state and during the process of soaking in heavy water was studied by SANS [39]. Inhomogeneities were found in the dry membrane. The membrane structure is well described by a polydisperse hard-sphere model. The mean diameter of the dispersed spherical inhomogeneities is ~6 nm, which is smaller than the estimated dimension of a single statistically curled PVC polymer chain in the membrane. The values of the best-fit parameters and their change with membrane composition suggest that the particles consist of unplasticized PVC, probably in the crystalline state. The type of plasticizer, the plasticizer content and the addition of a lipophilic salt were found to influence the water uptake significantly. Water uptake did not change the microstructure due to the original (i.e. dry state) inhomogeneities in the membranes.

The structure of gradient-porous (asymmetric) membranes based on polyamide imide at different conditions of their formation was investigated using SANS by Kul’velis et al. [40]. It was shown that the membranes consist of rigid porous networks with well-defined interfaces between the polymer and the pores. It has been found that there are differences in the packings of structural elements of porous membranes – spherical pores with radii from 4 to 100 nm – depending on the membrane preformation time, drying regime and the presence of fullerene C_{60} for modifying the mechanical and selective properties of membranes. The membranes also contain larger pores of micrometre sizes. Differences in the rates of saturation of membranes with water and their limiting swelling ratios are found, which can be explained by the structure of the dense layers of membranes (skin layer) and their different hydrophilicities (depending on the fullerene content).

5.1.13 Positron Annihilation Spectroscopy or Positron Annihilation Lifetime Spectroscopy

PAS [41], or sometimes specifically referred to as PALS, is a nondestructive spectroscopy technique to study voids and defects in solids [42]. The technique operates on the principle that a positron or positronium will annihilate through interaction with electrons. This annihilation releases $\gamma$-rays that can be detected; the time between emission of positrons from a radioactive source and detection of $\gamma$-rays due to annihilation corresponds to the lifetime of the positron or positronium. When positrons are injected into a solid body they interact in some manner with the electrons in that species. For solids containing free electrons (such as metals or semiconductors), the implanted positrons annihilate rapidly unless voids such as vacancy defects are present. If voids are available, positrons will reside in them and annihilate less rapidly than in the bulk of the material, on timescales up to $\sim$1 ns. For insulators, such as polymers or zeolites, implanted positrons interact with electrons in the material to form positronium. Pore structure in insulators can be determined using the quantum mechanical Tao–Eldrup model and extensions thereof. By changing the temperature at which a sample is analysed, the pore structure can be fit to a model where positronium is confined in one, two or three dimensions. However, interconnected pores result in averaged lifetimes that cannot distinguish between smooth channels or channels having smaller, open, peripheral pores due to energetically favoured positronium diffusion from small to larger pores.

PALS has tremendous potential as a powerful tool for quantifying the types and densities of defects in solids. Following the injection of positrons into a solid material, the positrons pair-annihilate at a rate depending on the density of electrons near the injection site. If there are lattice vacancy or dislocation defects (voids) near the injection site, the positrons are attracted to these areas, which have lower electron densities and thus give rise to longer positron lifetimes. For conductor-type materials (metals) with many free electrons, the positron lifetimes can be quite short in defect-free regions (e.g. $\sim$100 ps) and considerably longer in defect regions (e.g. $\sim$200 ps). In the analysis of a lifetime decay spectrum acquired by PALS, the relative intensities of the various lifetime contributions that make up the spectrum can be extracted, giving access to the density of defects near the injection site. Furthermore, if the timing resolution of the PALS system is precise enough, and the event statistics in the lifetime decay distributions are large enough, then information about the density of various types of defects could be extracted.

PALS has been developed as a useful tool for probing the microscopic structure of a variety of polymeric materials. Free-volume size, fractional free volume and size distribution have been reported by many research groups using the PALS technique [43–52].

PALS and molecular dynamics simulation analyses were adopted for an in-depth understanding at the molecular scale of the variation in the fine-structure of polyamide active layers of thin-film composite (TFC) membranes in the dry or the wet condition [53]. The interfacial polymerization reaction between 1,3-diaminopropane (DAPE) and succinyl chloride (SCC) or between DAPE and $\text{trans-3,6}$-endomethylene-1,2,3,6-tetrahydrophthaloyl chloride (tNBDC) on the surface of a modified polyacrylonitrile (mPAN) membrane was carried out to fabricate DAPE–SCC–mPAN or DAPE–tNBDC–mPAN TFC membranes. PALS and molecular dynamics simulation experimental results were highly consistent with each other.

The data on the effect of the molecular structure of the polyamide active layer in dry and wet states on $\tau_3$ and $I_3$ values are given in Table 5.7. A 90 wt% aqueous EtOH solution was used as the liquid to wet the membrane. In the dry state, the spaces in the cube show only the free accessible volume in the unit cell. Compared with the polyamide active layers in the wet state, those in the dry state show a more compact structure with less free volume between the surrounding polymer chains. Apparently, the polyamide active layers are swollen by the aqueous EtOH solution. The theoretical results of the image analysis from molecular dynamics simulation are in good agreement with the experimental results on the positron annihilation lifetime from PALS.
5.1.14 Contact Angle


The contact angle is the angle, conventionally measured through the liquid, where a liquid–vapour interface meets a solid surface. It quantifies the wettability of a solid surface by a liquid via the Young equation. A given system of solid, liquid and vapour at a given temperature and pressure has a unique equilibrium contact angle. However, in practice contact-angle hysteresis is observed, ranging from the so-called advancing (maximal) contact angle to the receding (minimal) contact angle. The equilibrium contact is within those values, and can be calculated from them. The equilibrium contact angle reflects the relative strength of the liquid, solid and vapour molecular interaction.

In general, methylene iodide and water are used respectively as the measurement liquid for contact angle measurement of membranes consisting of hydrophilic polymers (e.g. PVA and chitosan) or hydrophobic polymers (e.g. PDMS and PTMSP). These contact angles are determined by the advancing contact angle $\theta_a$ and the receding contact angle $\theta_b$:

$$\theta = \cos^{-1}\left(\cos \theta_a + \cos \theta_b\right)$$

(5.11)

When we want to know the surface free energy of the membrane, it can be easily calculated from the contact angles of water and a nonsolvent for a membrane with Equation 5.12, which was proposed by Owens and Wendt [64–68]:

$$\frac{(1 + \cos \theta) \gamma_1}{2} = \left(\gamma_s^{d} \gamma_1^{d}\right)^{1/2} + \left(\gamma_s^{p} \gamma_1^{p}\right)^{1/2}$$

(5.12)

$$\gamma_s = \gamma_s^{d} + \gamma_s^{p}$$

(5.13)

where $\gamma_s$ and $\gamma_1$ are the surface free energy of the solid and the liquid, and $\gamma_s^{d}$, $\gamma_1^{d}$, $\gamma_s^{p}$ and $\gamma_1^{p}$ are the dispersion force components and polar force components of the surface free energy of the solid and the liquid respectively. The dispersion force component and polar force component of the surface free energy of water are 21.8 erg cm$^{-2}$ and 51.0 erg cm$^{-2}$ respectively, and those of formamide are 39.5 erg cm$^{-2}$ and 18.7 erg cm$^{-2}$ respectively [59,60].

Figure 5.17 shows the effects of the molar ratio of the carboxylate and ammonium groups on the contact angle for methylene iodide at the surface of the q-Chito–PEO acid polion complex/PES composite membranes [61]. Because the contact angles were measured using methylene iodide, a higher value indicates that the membrane surface is more hydrophilic. When the q-Chito was cross-linked...
with PEO acids, the contact angle increased with both an increasing PEO acid content in the polyion complex membranes and an increasing molecular weight of PEO acid. These results suggest that the membrane surface gradually became hydrophilic with the introduction of a hydrophilic cross-linker, PEO acid, and that the hydrophilicity of the membrane increased with both an increase in the PEO acid content and an increase in the molecular weight of PEO acid.

Contact-angle measurement was conducted to determine surface hydrophilicity of RO membranes with the intention of predicting membrane performance or fouling potential [62]. Most researchers of membrane technology have used contact angles without considering effective factors for contact-angle measurement, such as measurement time, drop volume and membrane sample preparation. In fact, significantly different contact angles are reported even on the same RO membrane. In this study, contact angles were measured by the sessile drop method and captive bubble method and were compared with various conditions such as measurement time, drop volume, membrane sample preparation and liquid type in the commercialized RO membranes. As a result, the sessile drop method showed unreliable contact angles, which varied dramatically with the preparation conditions. On the other hand, the captive bubble method, which represents conditions closer to the real RO membrane process, showed reproducible contact angles. For the different commercially available RO membranes, similar hydrophilicity was observed. Overall, the captive bubble method appears to be a more adequate method for measuring the contact angle of RO membranes.

Rosa and de Pinho [63] proposed a new concept of contact-angle measurements by the immersed method to characterize the membrane surface. The general system of two immiscible liquids is used wherein a droplet of CCl₄ is deposited on the membrane surface immersed in an aqueous solution. When the solution is pure water, membrane hydrophilicity is evaluated. With aqueous solutions of a cationic surfactant (below its critical micelle concentration) at different pH values, membrane titration curves are obtained. From these curves they obtain the acid–base behaviour of each membrane and the pH value at which half of the membrane surface groups are ionized, pK₁/₂. This method is tested with five nanofiltration membranes, a series of three cellulose acetate membranes, CA-316, with increasing hydraulic permeabilities, and two commercial TFC membranes, CD-NF-50 of poly(trans-2,5-dimethyl)piperazin thiofurazanamide–PES and HR-98-PP of polyamide–polysulfone. The results show that the method (i) is easy to perform and avoids dynamic measurements (requires 5 min of drop deposition); (ii) is reproducible (maximal deviations of 7°); (iii) simulates multiple membrane

![Figure 5.17](image_url)  
**Figure 5.17** Effect of the molar ratio of the carboxylate and ammonium groups on the contact angle for methylene iodide on the surface of the quaternized chitosan (q-Chito)–poly(ethylene oxydiglycolic acid) (PEO acid) polyion complex/PES composite membrane: (a) PEO acid 400; (b) PEO acid 1000; (c) PEO acid 4000.
technical environments (e.g. pure water, aqueous solutions); (iv) is not affected by the presence of pores in the nanofiltration range of operation; and (v) is sensitive to membrane hydrophilicity and membrane acidity/basicity (titration curves and $pK_{1/2}$ values). Furthermore, the results show the direct effect of the annealing treatment on the acidity of the CA-316 membranes and they show the importance of the membrane chemical properties (hydrophilicity, acidity/basicity) on the membrane permeation performance.

5.1.15 Zeta Potential


The zeta potential is the electrical potential that exists at the shear plane of a particle, which is some small distance from the surface. Colloidal particles dispersed in a solution are electrically charged due to their ionic characteristics and dipolar attributes. The development of a net charge at the particle surface affects the distribution of ions in the neighbouring interfacial region, resulting in an increased concentration of counter ions (ion of charge opposite to that of the particles) close to the surface. Each particle dispersed in a solution is surrounded by oppositely charged ions called a fixed layer. Outside the fixed layer there are varying compositions of ions of opposite polarities, forming a cloud-like area. Thus, an electrical double layer is formed in the region of the particle–liquid interface. This double layer may be considered to consist of two parts: an inner region, which includes ions bound relatively strongly to the surface, and an outer, or diffuse region in which the ion distribution is determined by a balance of electrostatic forces and random thermal motion. The potential in this region, therefore, decays with the distance from the surface, until at a certain distance it becomes zero. When a voltage is applied to the solution in which particles are dispersed, particles are attracted to the electrode of the opposite polarity, accompanied by the fixed layer and part of the diffuse double layer. The potential at the boundary between this unit, that is to say at the aforementioned shear plane between the particle with its ion atmosphere and the surrounding medium, is known as the zeta potential. The zeta potential is a function of the surface charge of a particle, any adsorbed layer at the interface, and the nature and composition of the surrounding medium in which the particle is suspended.

Zeta potential can be calculated with the following equation:

$$\zeta = \left( \frac{4\pi n}{\epsilon} \right) \times U \times 300 \times 300 \times 1000 \quad (5.14)$$

where $\zeta$ is the zeta potential, $\eta$ is viscosity of solution, $\epsilon$ is dielectric constant and $U$ is $vL/V$, where $v$ (cm s$^{-1}$) is the speed of the particle, $V$ is voltage and $L$ is the distance of the electrode.

Most materials when immersed in water exhibit a zeta potential. The majority of demineralized water contaminants, including most colloids, particles, bacteria and pyrogens (bacterial fragments), are negatively charged. Filter media can be chemically modified to give them a positive zeta potential.

Martín et al. [64] analysed the zeta potential versus pH characteristics of an ultrafiltration polysulfone membrane, which will be called here PRI-PSUF. This membrane was prepared by phase inversion from casting solutions of polysulfone. The electric potential per unit pressure both through and on the membrane were evaluated for a constant $\text{Cl}^-$ concentration with a gradual substitution of protons by sodium cations. It was seen that the difference in potentials on and through the membrane is almost constant when pH is >5 when the concentration of protons is very low. This difference can be attributed to diffusion potentials appearing through the membrane due to retention. However, when the fraction of protons is high, the potentials through and on the membrane are substantially equal and very low.
In order to obtain accurate zeta potentials and the isoelectric point, the streaming potential should be measured on the membrane, when no differences in the surface and inside materials should be expected. These measurements should be conducted at relatively high concentrations of a salt with very similarly mobile anion and cation and then extrapolated to zero protons percentage. All these conditions would warrant an easy calculation of zeta potentials by the simple Smoluchowski equation (Equation 5.14).

Figure 5.18 shows the relationship between zeta potential and pH. As can be seen from these results, the zeta potential is significantly influenced by both pH and cation species.

The streaming potentials of four different types of membranes were analysed using an electrokinetic analyser. Three of the membranes are RO membranes, including an asymmetric cellulose acetate blended membrane, a fully aromatic polyamide TFC membrane, and a TFC membrane with enhanced rejection. The fourth membrane is a TFC nanofiltration membrane. The streaming potentials of the membranes were determined over a wide range of pH using test solutions of inorganic salts (sodium chloride, calcium chloride and sodium sulfate), humic acid and surfactant. Prior to the measurements of streaming potential, several steps were taken to ensure maximum repeatability of the measurements. First, templates, spacers and formers were fabricated so that variations in the location and shape of the flow channel were minimized. Second, tests were performed to determine the maximum variation in the measured value of streaming potential with different samples of the same membrane and with different equilibration times after solution adjustments. Third, based on the equilibration tests, a procedure for preparing the membranes and performing the measurements was developed.

Zeta potentials were calculated from the measured streaming potential using the Helmholtz–Smoluchowski equation. Results show that all membranes display an iso-electric point (IEP) at an acidic pH; the zeta potential is negatively charged at pH values above the IEP and is positively charged at lower pH. In general, the surface charge of the TFC RO membranes becomes more negative with increasing sodium chloride concentrations. This change is attributed to the close approach of co-ions. When calcium chloride is added to the solution, all of the membranes acquire a more positive zeta potential.
potential, most likely because of specific adsorption of the divalent cations (Ca^{2+}). On the other hand, when sodium sulfate is added to the solution, the effect of the divalent anion (SO_4^{2−}) is not as noticeable. Results for the experiments with Suwannee River humic acid show that with only a small concentration of humic acid in the solution the membranes become more negatively charged over the entire pH range (3–10). The negatively charged functional groups of the humics dominate the surface charge of the membrane. Experiments with sodium dodecyl sulfate also resulted in more negative zeta potentials over the entire pH range. This result is attributed to the negatively charged sulfate functional groups of the adsorbed surfactant molecules [65].

5.1.16 Differential Scanning Calorimetry


DSC is a thermal analysis technique that looks at how a material’s heat capacity C_p is changed by temperature. A sample of known mass is heated or cooled and the changes in its heat capacity are tracked as changes in the heat flow. This allows the detection of transitions like melts, glass transitions, phase changes and curing. Because of this flexibility, DSC is used in many industries, including pharmaceuticals, polymers, food, paper, printing, manufacturing, agriculture, semiconductors and electronics, as most materials exhibit some sort of transition. The biggest advantage of DSC is the ease and speed with which it can be used to see transitions in materials. If we work with polymeric membranes of any type, the glass transition is important to understanding that material. In liquid crystals, metals, pharmaceuticals and pure organics you can see phase changes or polymorphs and study the degree of purity in materials. If you are processing or distilling materials, knowledge of a material’s heat capacity and enthalpy changes can be used to estimate how efficiently your process is operating. For these reasons, DSC is the most common thermal analysis technique and is found in many analytical, process control, quality assurance and R&D laboratories.

Table 5.8 summarizes the molecular weights and compositions of the poly(methyl methacrylate) (PMMA)-g-PDMS, poly(ethyl methacrylate) (PEMA)-g-PDMS, and PBMA-g-PDMS graft copolymers as determined by gel-permeation chromatography and 1H nuclear magnetic resonance and the T_g values of their membranes as determined by DSC. Number-average molecular weights of PMMA-g-PDMS were in the range of 50 000–75 000, those of PEMA-g-PDMS were between 130 000 and 200 000, and those of PBMA-g-PDMS were between 120 000 and 210 000. The ratio of the weight-average molecular weight to the number-average molecular weight (M_w/M_n) of PMMA-g-PDMS was >2 and that of PEMA-g-PDMS and PBMA-g-PDMS was <2. The molecular weight distribution of PBMA-g-PDMS was very narrow. Two T_g values were observed at about +128 and −127 °C in the PMMA-g-PDMS membranes and at about +73 and −120 °C in the PEMA-g-PDMS membranes. The observation of two T_g values in the PMMA-g-PDMS and PEMA-g-PDMS membranes is attributable to the fact that the T_g values of PMMA or PEMA and PDMS homopolymers are about 128 °C or 73 °C and −120 to −127 °C respectively. The higher T_g is due to the MMA or EMA component and the lower T_g to the DMS component. The presence of these two T_g values implies that the PMMA-g-PDMS and PEMA-g-PDMS membranes had a heterogeneous structure. Therefore, it is suggested that the PMMA-g-PDMS and PEMA-g-PDMS membranes have microphase-separated structures. In PBMA-g-PDMS membranes, however, T_g values based on the BMA and DMS components were not observed. Such observations suggest that the PBMA-g-PDMS membranes do not form the microphase separation structure and that the BMA and DMS components may be miscible. On the other hand, in the PEMA-g-PDMS and PBMA-g-PDMS membranes a peak, which is not due to T_g, appeared...
at about −39 to −45 °C on the DSC curves of those membranes. This peak is not due to the second transition caused by the \( T_g \) but rather is due to the first transition, as shown in Figure 5.19 [66].

The thermal profiles of the Nafion membranes from DSC measurements are shown in Figure 5.20 [67]. DSC experiments show for all samples the expected broad endothermic peaks between 140 and 190 °C. This thermal effect is due to an order–disorder transition in the ionic domains of the Nafion polymer membrane [68]. It is known to be strongly affected by the amount of water within the membrane both in terms of transition temperature (smaller for larger water contents) and enthalpy variation (\( \Delta H \), larger for higher hydration degrees) [69]. All the membranes added with the inorganic fillers show smaller transition temperatures and larger enthalpy variations in comparison with the Nafion benchmark membrane. Thus, the addition of SnO\(_2\)-based inorganic fillers unequivocally leads to an increase of the amount of water within the composite membranes under the experimental conditions quoted here (i.e. without any control of external relative humidity). In particular, the comparison among the DSC data for the Nafion-E400 (from alcoholic hydrolysis of Sn(II)-2-ethylhexanoate), the Nafion-F110 (from the water hydrolysis of SnCl\(_4\)) and the benchmark Nafion membrane suggests that the Nafion-F110 sample keeps the larger amount of water. This is in agreement with the glass transition temperature results and with the water uptake measurements. Focusing attention on the sulfated membranes, the DSC data show contradictory trends. In particular, the Nafion-E400S (sulfated tin oxide) sample shows a decrease of the transition temperature and of

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Molecular weight(^{a)})</th>
<th>Polymer(^{b)})</th>
<th>( T_g ) (^{c)}) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>( M_n \times 10^{-5} )</td>
<td>( M_n \times 10^{-5} )</td>
<td>( M_w )</td>
</tr>
<tr>
<td>0</td>
<td>0.89</td>
<td>0.51</td>
<td>1.75</td>
</tr>
<tr>
<td>50</td>
<td>1.74</td>
<td>0.66</td>
<td>2.62</td>
</tr>
<tr>
<td>60</td>
<td>1.14</td>
<td>0.60</td>
<td>1.90</td>
</tr>
<tr>
<td>70</td>
<td>1.52</td>
<td>0.74</td>
<td>2.04</td>
</tr>
</tbody>
</table>

| EMA     | \( M_n \times 10^{-5} \) | \( M_n \times 10^{-5} \) | \( M_w \) | \( M_n \) | Mol%\(^{d)}\) Low | Middle | High |
| 0       | 2.82             | 2.21           | 1.28             | 0 | — | — | 75 |
| 10      | 1.96             | 1.36           | 1.43             | 17 | — | — | 76 |
| 30      | 2.11             | 1.46           | 1.43             | 56 | — | — | 72 |
| 50      | 1.95             | 1.95           | 1.55             | 72 | — | — | 74 |
| 60      | 1.94             | 1.94           | 1.50             | 75 | — | — | 74 |
| 70      | 2.40             | 1.69           | 1.42             | 85 | — | — | 69 |

| BMA     | \( M_n \times 10^{-5} \) | \( M_n \times 10^{-5} \) | \( M_w \) | \( M_n \) | Mol%\(^{d)}\) Low | Middle | High |
| 0       | 2.22             | 2.12           | 1.05             | 0 | — | — | 38 |
| 10      | 1.67             | 1.24           | 1.35             | 16 | — | — | 44 |
| 30      | 1.63             | 1.21           | 1.35             | 41 | — | — | 40 |
| 60      | 2.05             | 1.76           | 1.17             | 73 | — | — | 40 |
| 70      | 2.13             | 1.83           | 1.17             | 86 | — | — | 39 |

---

a) Determined by gel permeation chromatography.

b) Determined by \(^1\)H nuclear magnetic resonance.

c) Determined by DSC.

d) Mole per cent of dimethysiloxane (DMS) units in feed.
the enthalpy variation compared with the bare N-E400 membrane, whereas the Nafion-F110S (sulfated tin oxides) sample shows an increase of the transition temperature and of the enthalpy variation compared with the bare Nafion-F110 membrane.

Figure 5.19 DSC curves of the PMMA-g-PDMS, PEMA-g-PDMS and PBMA-g-PDMS membranes: (a) PMMA-g-PDMS (DMS content: 68 mol%); (b) PEMA-g-PDMS (DMS content: 75 mol%); (c) PBMA-g-PDMS (DMS content: 73 mol%).

Figure 5.20 DSC measurements of Nafion, N-E400 (from alcoholic hydrolysis of Sn(II)-2-ethyl-hexanoate), N-110 (from the water hydrolysis of SnCl₄), N-E400S (sulfated tin oxide of N-400), and N-F100S (sulfated tin oxide of N-F110) membranes.

5.1.17 Thermogravimetry

5.1.17.1 Characteristics and Applications of Thermogravimetric Analysis

1) TGA measures the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of nitrogen, helium, air, other gas or in vacuum.

2) Inorganic materials, metals, polymers and plastics, ceramics, glasses and composite materials can be analysed.

3) Temperature ranges from 25 to 900 °C routinely. The maximum temperature is 1000 °C.

4) Sample weight can range from 1 to 150 mg. Sample weights of more than 25 mg are preferred, but excellent results are sometimes obtainable on 1 mg of material.

5) Weight change sensitivity of 0.01 mg.

6) Samples can be analysed in the form of powder or small pieces, so the interior sample temperature remains close to the measured gas temperature.

7) Determines temperature and weight change of decomposition reactions, which often allows quantitative composition analysis. May be used to determine water content.

8) Can be used to measure evaporation rates, such as to measure the volatile emissions of liquid mixtures.

Novel inorganic–organic hybrid membranes containing immobilized amine–trifluoromethanesulfonimide (HTFSI) groups were explored by Yang et al. [70]. Considering the activation energy of proton transport could depend upon the distance between the active sites as well as the nature of the electrolytes, a higher density of the active functional groups was introduced into the membranes to reduce the distance among active sites. The membranes are comprised of a three-dimensional cross-linked silicon–oxygen backbone and organic amine groups. The silicon–oxygen backbone, which is stable to free radical attack, provides the proton exchange membrane with the necessary thermal/chemical/mechanical properties. The organic amine groups were doped with HTFSI to form H⁺-conducting sites. The thermal stability and proton conductivities of these novel membranes were studied using TGA and AC impedance.

Polyethylenimine (PEI) was chosen in this study because it has the highest amine density among the other polyamine polymers. Since the prepared linear PEI (cal. $M_w$ 215 k) has a soft point of ~80 °C, 3-glycidyloxypropyltrimethoxysilane (GLYMO) was used to crosslink PEI to increase its heat resistance. When mixed with PEI in alcohol solution, the epoxy ends of GLYMO covalently bonded to the amine groups of PEI, and the trimethoxysilane ends of GLYMO hydrolysed and condensed together to form inorganic silica clusters through so-called sol–gel processes, which greatly improved thermal stability of the composite membranes (Figure 5.21) [71].

The thermal stability of the polymer is a key metric to forming ionic conducting ionomers for use in a fuel cell. Fuel cell performance generally improves at elevated temperature. Operation between 40 and 120 °C is of interest. TGA was carried out on the polymers synthesized here to examine their thermal stability. The TGA curves for poly(arylene ether sulfone) (PSF), chloromethylated poly(arylene ether sulfone) (CMPSF) and PSF functionalized with benzyltrimethylammonium groups (QAPSF) are shown in Figure 5.22 [72].

![Figure 5.21 TGA of PEI polymer and GLYMO cross-linked PEI.](image-url)
The 5\% weight loss temperature for the neat PSF is 455 °C, as shown in Figure 5.22a. PSF is thermally stable because of its rigid aromatic structure. Two decomposition steps are observed in the TGA for CMPSF (Figure 5.22b). The first degradation step, from 311 to 350 °C, is attributed to the loss of chloromethyl groups. The second decomposition step, beginning at about 450 °C, corresponds to the degradation of the PSF backbone. The pendent quaternary ammonium groups have a great influence on the CMPSF thermal property. The TGA curves for QAPSF in chloride and carbonate forms are shown in Figure 5.22c and d respectively. The initial weight loss of QAPSF in chloride from 25 to 220 °C is attributed to loss of residual solvent (dimethylformamide (DMF)) and water. The second weight loss above 200 °C is due to cleavage of the quaternary ammonium groups from QAPSF. The third weight loss at temperatures greater than 380 °C is due to cleavage of the quaternary ammonium groups from QAPSF. Comparing Figure 5.22c and d, it is found that the decomposition of QAPSF in the chloride and carbonate forms is similar. However, the decomposition temperature of the quaternary ammonium groups of QAPSF with carbonate anions is at about 150 °C. This shows that quaternary ammonium groups are less stable in a dry, alkaline condition. In addition, it is interesting to note that the dehydration of QAPSF continues well above 100 °C, indicating strong hydrogen bonding of water to the amine [73].

5.1.18 Membrane Density

The density of membranes is determined by the flotation method using a single solvent or mixture of nonsolvents for the membrane [74,75].

Mecerreyes et al. [76] determined the membrane density using a flotation weight loss method in a four-decimals-precision gram precision balance.

Figure 5.23 shows the density and crystallinity of the N-alkyl chitosan membranes as a function of the degree of substitution in the N-alkyl group. The density of the membrane decreased with an increase of the degree of substitution. This result suggests that the N-alkyl chitosan membranes become rough structures when they have an increased degree of substitution. The crystallinity of the N-alkyl chitosan membranes also decreased with an increase of the degree of substitution in the N-alkyl group. The decrease in the crystallinity means roughness of the membrane [77].

The correlation crystallinity index $C_c$ was determined from the slope of the relationship

![Figure 5.22 Typical TGA curves of the polymers under nitrogen atmosphere: (a) PSF, (b) CMPSF, (c) QAPSF in chloride and (d) QAPSF in carbonate.](image)
\[ I_u - I_a = C_c (I_c - I_a) + B \]  

(5.15)

where \( I_u \) is the X-ray intensity of the unknown sample, \( I_a \) the X-ray intensity of the amorphous reference and \( I_c \) the X-ray intensity of the crystalline reference, which are determined by the measurement of WAXD of the chitosan and \( N \)-alkyl chitosan membranes, and \( B \) is the intercept on the \( y \)-axis.

### 5.1.19 Cross-link Density

The cross-link density \( \rho \) of the q-Chito–TEOS hybrid membranes was calculated from the network theory of rubber elasticity given by [78–80]

\[ \rho = \frac{E'}{3d\phi RT} \]  

(5.16)

where the elastic modulus \( E' \) is determined from measurements with a dynamic mechanical analyser under the following conditions: frequency, 1, 2, 4, 10 Hz; temperature, 40 °C; \( d \) is membrane density, \( \phi \) is the front factor (where \( \phi = 1 \)), \( R \) is the gas constant and \( T \) is the absolute temperature.

Figure 5.24 shows the relationship between the elastic modulus of the q-Chito–TEOS hybrid membrane and the TEOS content in the hybrid membrane. The elastic modulus deceased with increasing TEOS content. The cross-link density of the q-Chito–TEOS hybrid membranes expressed in Equation 5.16 was determined using the elastic modulus obtained from measurement of the dynamic viscoelasticity and the membrane density measured by the electric gravity meter. In Figure 5.24, the effect of TEOS content in q-Chito–TEOS hybrid membranes on the cross-link density of the membranes is also shown. The cross-link density also decreased with an increase in TEOS content. The decrease in the cross-link density with increasing TEOS content can be attributed to the fact that the formation of cohesive domains due to reactions between the tetrasilanol silane (TSS) molecules was more predominant than the formation of cross-linking between \( q \)-Chito and TSS molecules.
Therefore, when excess TEOS was added to the casting solution, the cross-link reaction was reduced, the elastic modulus decreased, and consequently the cross-link density also decreased [81].

### 5.1.20 Degree of Membrane Swelling

See Tarleton et al. [82].

Slow diffusion of solvents into polymer chains causes a swelling phenomenon and leads to a swollen polymeric membrane (Figure 5.25). In this case, an expansion of the polymer network is promoted because polymer–polymer interactions are greater than polymer–solvent forces and a complete dissolution of the membrane is prevented [83]. Different degrees of swelling can be achieved depending on the cross-linking, crystallinity and intermolecular forces involved. The choice of the materials and their combination can direct the swelling events and make the membrane performance addressable at the macroscopic level. Membrane swelling over an area of 1 mm$^2$ is indicated as a bulk swelling, whilst small changes in dimension are classified as a microscopic swelling and are detectable by SAXS.

Polymer membranes, which were completely dried under reduced pressure at room temperature and weighed, are immersed into feed mixtures in a sealed vessel at 40 °C. After the weight of the

---

**Figure 5.24** Effect of the TEOS content on the elastic modulus (○) and the crosslinker density (●) of q-Chito–TEOS hybrid membranes.

**Figure 5.25** Reversible expansion and shrinking of polymer chain after solvent adsorption/desorption.
membranes became constant, the membranes were taken out of the vessel, wiped quickly with filter paper and weighed. The degree of swelling (DS) of the membrane was determined from

\[
DS = \frac{W_s}{W_d}
\]

where \(W_s\) is the weight of the membrane swollen in feed mixtures and \(W_d\) is the weight of the dried membrane.

The effects of the degree of butyrylation of the butyrylcellulose (BuCell) membrane on the permeation rate, benzene concentration and degree of swelling for a benzene/cyclohexane (Bz/Chx) feed mixture (5/95 by weight) are shown in Figure 5.26. With increased degree of butyrylation, the permeation rate increased remarkably and the degree of swelling increased slightly. It is well known that swelling of polymer membranes leads to a more open membrane structure and consequently an enhancement of the diffusivity of the permeants in the polymer membranes. The increase in the permeation rate with an increase of butyrylation is due to an increase in the degree of swelling of the BuCell membranes, as shown in Figure 5.26 [84].

Improvements to an apparatus for in-situ determinations of swelling where a linear inductive probe and electronic column gauge with an overall resolution of 0.1 μm were used for measurements of seven variants of polyacrylonitrile–PDMS composite nanofiltration membranes in a range of alkane, aromatic and alcohol solvents were reported by Tarleton et al. [82]. The unswollen membranes incorporated PDMS layers between 1 and 10 μm nominal thickness and were manufactured with a radiation and/or thermal cross-linking step. The membranes tested exhibited a range of swelling dependent on the degree of cross-linking, the initial PDMS layer thickness and the type of solvent. With no applied pressure the PDMS layer on some radiation cross-linked membranes swelled as much as ~170% of the initial thickness, whilst other membranes were restricted to a maximum swelling of ~80%. When a pressure up to 2000 kPa was applied to a membrane then swelling could be reduced to ~20% of the value obtained at zero applied pressure. By vertically stacking up to three membrane samples

Figure 5.26 Effect of the degree of butyrylation on the benzene concentration in the permeate (●) and the permeation rate (○) through the BuCell membranes for a Bz/Chx mixture of 0.5 wt% benzene by pervaporation and the degree of swelling of the BuCell membranes (□) for a Bz/Chx mixture at 40 °C. The dotted line is the feed mixture composition (Bz/Chx = 0.5/99.5).
it was possible to determine the swelling of PDMS layers as thin as 1 μm, although higher imposed pressures rendered some results unreliable as the measurement resolution of the apparatus was approached. The results of the swelling experiments are contrasted with crossflow nanofiltration performance in terms of solvent flux and solute rejection.

5.1.21 Sorption Selectivity

Polymer membranes were dried completely under reduced pressure at room temperature and weighed. The dried membranes were immersed into feed mixtures consist of $x$ and $y$ in a sealed vessel at 40 °C until equilibrium was reached. A large amount of the swollen polymer membrane was placed in a container, as shown in Figure 5.27 [85].

The system in Figure 5.27 was evacuated, and the container with the swollen membranes was heated. The solution sorbed into the swollen membranes was completely desorbed under reduced pressure and was collected in a U-tube cooled with liquid nitrogen. The composition of the solutions sorbed in polymer membranes was then determined by measuring the concentration of component in the collected solution by gas chromatography. The solution composition in polymer membranes and that in the feed solution yield the sorption selectivity $\alpha_{sorp \ x/y}$:

$$\alpha_{sorp \ x/y} = \frac{M_x}{M_y} \left( \frac{F_x}{F_y} \right)$$

(5.18)

where $F_x$ and $F_y$ are the weight fractions of $x$ and $y$ respectively in the feed solution and $M_x$ and $M_y$ are those sorbed in the membrane respectively.

If the addition of tert-butylcalix[4]arene (CA) to polymer membranes is exclusively responsible for the enhancement of the affinity between benzene and CA, the benzene concentration absorbed into the various membranes should be equal. However, as can be seen in Figure 5.28, the benzene concentration in these membranes differed markedly between the various membranes. This difference in benzene concentration is dependent on differences in the affinity of the membrane matrix polymer for benzene.

As shown in other experiment results, despite the fact that CA–PMMA–b–PDMS membranes showed higher benzene permselectivity than CA–PMMA–g–PDMS membranes, the benzene

Figure 5.27 Diagram of apparatus to determine the composition of the solution absorbed in polymer membrane.
concentration in CA–PMMA-g-PDMS membranes was greater than that in the CA–PMMA-b-PDMS membranes. This difference in the affinity for benzene between the CA–PMMA-g-PDMS and the CA–PMMA-b-PDMS membranes may also be due to differences in the affinity of the polymer matrix portion for benzene [86].

Figure 5.29 shows the EtOH concentration sorbed into q-Chito–TEOS hybrid membranes immersed in an aqueous solution of 96.5 wt% EtOH (EtOH–water azeotrope) and the contact angle for chloroform as a function of the TEOS content in the hybrid membrane. The EtOH concentration sorbed into the q-Chito–TEOS hybrid membranes decreased with increasing TEOS content up to 45 mol% and then increased at higher TEOS content. The contact angle for chloroform increased with increasing TEOS content. This increase in the contact angle for chloroform, which is a hydrophobic solvent, suggests that the membrane surface of the q-Chito–TEOS hybrid membranes became more hydrophilic with an increase in the TEOS content. The decrease in the EtOH concentration sorbed in the q-Chito–TEOS hybrid membranes with increasing TEOS content up to 45 mol% is due to an
increase in the hydrophilicity of the membrane surface. This suggests that the solubility of water in the q-Chito–TEOS hybrid membrane was improved by introducing TEOS into the q-Chito molecule [81].

### 5.1.22 Burst and Tensile Strength of Membrane

Table 5.9 summarizes the characteristics of interpolymer membranes prepared from PVDF and PSA at 70 °C [87]. The PWP and the membrane characteristics are very much influenced by the casting solution composition. When the DMF content in the casting solution increases, the resulting membrane is more heterogeneous. In particular, the morphology of the surface layer side of the membrane is too different from that of the back side of the membrane to face the glass plate. This phenomenon may be caused by the fact that PSA molecules, which do not become entangled strongly with PVF2 molecules in the lower part of the casting mixture on the glass plate, are removed during water treatment and, consequently, heterogeneous membranes are formed, because PVF2 molecules are concentrated mainly at the air interface side and PSA molecules are concentrated primarily in the lower layer of the casting mixture with the evaporation loss of DMF. The differences of PWP and membrane character with the casting solution composition are due to the different dissolving forms of PVF2 and PSA molecules in the casting solutions and the different dissolution of PSA molecules in water during water treatment based on the phase separation between PVF2 and PSA molecules. From the fact that the ion-exchange capacity of the dry membrane and the swelling degree increase with DMSO content in the casting solution, it is supported that PSA contents in the resulting membranes increase and more heterogeneous phase separation occurs with an increase in DMSO. Also, the ion-exchange capacity, the swelling degree, the water content increase and the burst strength of the resulting

**Table 5.9** Characters of interpolymer membranes from PVDF and poly(polystyrene sulfonic acid) (PSA).

<table>
<thead>
<tr>
<th>Casting composition&lt;sup&gt;a)&lt;/sup&gt;</th>
<th>Solvent</th>
<th>PVF&lt;sub&gt;2&lt;/sub&gt;/PSA</th>
<th>IE&lt;sub&gt;1&lt;/sub&gt;&lt;sup&gt;b)&lt;/sup&gt;</th>
<th>IE&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c)&lt;/sup&gt;</th>
<th>SD&lt;sup&gt;d)&lt;/sup&gt; (cm&lt;sup&gt;3&lt;/sup&gt; cm&lt;sup&gt;−3&lt;/sup&gt;)</th>
<th>WC&lt;sup&gt;e)&lt;/sup&gt; (%)</th>
<th>BS&lt;sup&gt;f)&lt;/sup&gt; (kg cm&lt;sup&gt;−5&lt;/sup&gt;)</th>
<th>IC&lt;sup&gt;g)&lt;/sup&gt;</th>
<th>PWP&lt;sup&gt;h)&lt;/sup&gt; (mL cm&lt;sup&gt;−2&lt;/sup&gt; s&lt;sup&gt;−1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF/DMSO = 4/1</td>
<td>4/3</td>
<td>0.582</td>
<td>0.365</td>
<td>1.217</td>
<td>38.6</td>
<td>1.08</td>
<td>0.946</td>
<td>1.10 × 10&lt;sup&gt;−3&lt;/sup&gt; i)</td>
<td></td>
</tr>
<tr>
<td>DMF/DMSO = 1/1</td>
<td>4/3</td>
<td>0.591</td>
<td>0.335</td>
<td>1.327</td>
<td>44.9</td>
<td>0.68</td>
<td>0.746</td>
<td>8.38 × 10&lt;sup&gt;−4&lt;/sup&gt; i)</td>
<td></td>
</tr>
<tr>
<td>DMF/DMSO = 1/4</td>
<td>4/3</td>
<td>0.350</td>
<td>0.267</td>
<td>1.174</td>
<td>33.5</td>
<td>1.36</td>
<td>0.797</td>
<td>1.60 × 10&lt;sup&gt;−3&lt;/sup&gt; j)</td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>4/1</td>
<td>0.459</td>
<td>0.274</td>
<td>1.208</td>
<td>40.3</td>
<td>1.25</td>
<td>0.780</td>
<td>1.86 × 10&lt;sup&gt;−4&lt;/sup&gt; j)</td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>2/1</td>
<td>0.593</td>
<td>0.322</td>
<td>1.580</td>
<td>48.4</td>
<td>0.93</td>
<td>0.665</td>
<td>1.65 × 10&lt;sup&gt;−5&lt;/sup&gt; j)</td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>4/3</td>
<td>0.626</td>
<td>0.283</td>
<td>1.382</td>
<td>58.9</td>
<td>1.15</td>
<td>0.480</td>
<td>2.88 × 10&lt;sup&gt;−5&lt;/sup&gt; j)</td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>1/1</td>
<td>0.262</td>
<td>0.283</td>
<td>1.382</td>
<td>58.9</td>
<td>1.15</td>
<td>0.480</td>
<td>2.88 × 10&lt;sup&gt;−5&lt;/sup&gt; j)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a)</sup> PVF<sub>2</sub>/solvent = 10/90 (wt%).
<sup>b)</sup> Ion-exchange capacity of dry membrane (meq g<sup>−1</sup> of dry membrane).
<sup>c)</sup> Ion-exchange capacity of wet membrane (meq g<sup>−1</sup> of wet membrane).
<sup>d)</sup> Swelling degree of membrane.
<sup>e)</sup> Water content in membrane.
<sup>f)</sup> Burst strength of wet membrane.
<sup>g)</sup> Ion concentration in membrane.
<sup>h)</sup> Rate of pure water permeability.
<sup>i)</sup> 2 kg cm<sup>−2</sup> of operating pressure.
<sup>j</sup>) 4 kg cm<sup>−2</sup> of operating pressure.
membrane decrease as PSA content in the casting solution increases. These facts suggest that PSA contents in the resulting membranes increase with increasing PSA content in the casting solution.

In general, membrane strength is one of the key factors that influence the industrial application of polymer membranes. In addition, crystalline conformation and total crystallinity of polymer membranes are very important in determining the strength of membranes. Crystalline conformation can be converted from one form to the other by certain treatments. Liu et al. [88] studied in detail the effect of preparation methods on crystallization behaviour and tensile strength of polymer membranes and reported the following results: PVDF membranes were prepared by nonsolvent-induced phase separation (NIPS), melt spinning and the solution-cast method. The effect of preparation methods with different membrane formation mechanisms on crystallization behaviour and tensile strength of PVDF membranes was investigated. ATR-FTIR and X-ray diffraction were employed to examine the crystal form of the surface layers and the overall membranes respectively. Spherulite morphologies and thermal behaviour of the membranes were studied by polarized light optical microscopy and DSC separately. It was found that the crystallization behaviour of PVDF membranes was closely related to the preparation methods. For membranes prepared by the NIPS method, the skin layers had a mixture of α and β phases, the overall membranes were predominantly α phase, and the total crystallinity was 60.0% with no spherulites. For melt-spinning membranes, the surface layers also showed a mixture of α and β phases; the overall membranes were predominantly α phase. The total crystallinity was 48.7% with perfect spherulites. Whereas the crystallization behaviour of solution-cast membranes was related to the evaporation temperature and the additive, when the evaporation temperature was 140 °C with a soluble additive in the dope solution, obvious spherulites appeared. The crystalline morphology of PVDF exerted a great influence on the tensile strength of the membranes, which was much higher with perfect spherulites.

References


6

Fundamentals of Membrane Transport Phenomena

6.1 Thermodynamical Fundamentals for Membrane Transport

For an introduction, see, for example, Nakagaki’s ‘Fundamentals of membrane transport phenomena’ [1].

6.1.1 Thermodynamics of Membrane Transport

Typical examples of transport phenomena are heat conduction (which is the transport phenomenon of energy), the viscosity of a gas (which is the transport phenomenon of the amount of motion), and diffusion (which is a material transport phenomenon). They are a very important theme in molecular kinetics theory and typical examples in thermodynamics of irreversible processes. In this section the transport phenomena of materials are described from the viewpoint of thermodynamics of irreversible processes (thermodynamics for nonequilibrium) and applications to membrane permeation are discussed.

When two (or more) components are mixed in an irreversible process such as diffusion and membrane permeation, free energy, which represents the ability of work in a system, is decreased and entropy which cannot be taken out as a work increases. Namely, free energy degenerates but entropy of the same value is formed in the system.

When both components in a system consisting of ideal gases A and B are mixed at a constant temperature, state I is changed to state II, as shown in Figure 6.1.

Since internal energy $U$ is determined by only temperature $T$, at a constant temperature we obtain

$$\Delta U = 0$$

If some of the work that a system makes outside is $W$ and heat capacity absorbed from the external part is $Q$, consequently Equation 6.2 holds:

$$\Delta U = Q - W = 0, \quad Q = W$$

When the increases of entropy $S$ are an external increase $\Delta_e S$ and an internal increase $\Delta_i S$, $\Delta S$ is

$$\Delta S = \Delta_e S + \Delta_i S$$

However:

$$\Delta_e S = \frac{Q}{T}$$

where $T$ is absolute temperature.
As shown in Figure 6.1, when the diagram in state I consists of piston I with a semipermeable membrane which cannot permeate gas A and can permeate gas B and piston II with a semipermeable membrane which can permeate gas A and cannot permeate gas B, both components can be mixed reversibly by shifting reversibly these pistons at a constant temperature. In this time the system produces an amount of work $W$ out of the system by the piston and simultaneously heat is absorbed from outside of the system. Accompanying these phenomena, the increase of internal energy $\Delta U$ in the system is

$$\Delta U = Q - W$$  \hspace{1cm} (6.5)

On the other hand, the work $W$ done reversibly out of the system at a constant temperature equals a decreased amount of free energy in the system $\Delta F$. In a reversible process

$$\Delta S = 0$$  \hspace{1cm} (6.6)

Therefore, in reversible mixing at a constant temperature

$$\Delta S = -\frac{\Delta F}{T}$$  \hspace{1cm} (6.7)

On the other hand, when the semipermeable membranes are removed and both gases can be irreversibly mixed, the final equilibrium state II is same as that in reversible mixing. Consequently, the system does never work to out of the system. Therefore, $W = 0$ and Equation (6.8) is obtained:

$$\Delta U = 0, \quad W = 0, \quad Q = 0$$  \hspace{1cm} (6.8)

Since $\Delta S$ is a thermodynamical amount, it is determined only by the initial state and final state, regardless of the process of change, and also Equation 6.7 is held in irreversible mixing. However, since $Q$ is zero in irreversible mixing (as shown Equation 6.8), the following holds:

$$\Delta eS = \frac{Q}{T}$$  \hspace{1cm} (6.9)
Consequently:
\[
\Delta_i S = -\frac{\Delta F}{T}
\]  
(6.10)

In such irreversible mixing, it is found that the increase of internal entropy in the system corresponds to the decrease of free energy in the system.

In general, the dissipation function \( \Phi \) is represented by multiplying the entropy production rate \( \sigma \) and \( T \) together:
\[
\Phi = T \sigma = T \frac{d_i S}{d t}
\]  
(6.11)

where \( t \) is time.

\( \Phi \) is represented by the sum of the multiplication of the flux \( J_i \) by the conjugated power \( X \):
\[
\Phi = \sum_{i=1}^{n} J_i X_i
\]  
(6.12)

There is a proportion relation between \( J \) and \( X \). In general, it is as in the following equation:
\[
J = LX
\]  
(6.13)

In Fick’s law \( J \), \( X \) and \( L \) are diffusion flow, concentration gradient and diffusion coefficient respectively.

In thermodynamics of irreversible process, when \( \phi \) is represented by Equation 6.12, \( J_i \) is shown by the following linear equation:
\[
J_i = \sum_{j=1}^{n} L_{ij} X_j \quad (i = 1, 2, \cdots, n)
\]  
(6.14)

Equation 6.14 is called the phenomenological equation. \( L_{ij} \) is the phenomenological coefficient and Onsagar’s reciprocity relation is held as follows:
\[
L_{ij} = L_{ji}
\]  
(6.15)

\( X_i \), the power conjugated to \( J_i \) of component \( i \), is the negative slope of the physicochemical potential \( \mu_i \) of component \( i \):
\[
X_i = -\text{grad} \tilde{\mu}_i
\]  
(6.16)

where \( \tilde{\mu}_i \) is the sum of the chemical potential \( \mu_i \) and the physical potential \( \Phi_i \) of component \( i \):
\[
\tilde{\mu}_i = \mu_i + \phi_i = \mu_i + RT \ln a_i + \Phi_i
\]  
(6.17)

where \( \mu_i^* \) is the standard chemical potential and \( R \) is the gas constant. \( a_i \) is the activity of component \( i \) and the product of activity coefficient \( \gamma_i \) and concentration \( c_i \).

When the physical potential consisting of a binary system water \( w \) and solute \( s \) is negligible, the chemical potential difference between both sides of the membrane is \( \Delta \mu_i \), membrane thickness is \( L \) and \( \text{grad} \tilde{\mu}_i \) is replaced by \( \Delta \mu_i/L \), \( \Phi \) is as follows:
\[
\Phi = -\frac{J_w \Delta \mu_w}{L} - \frac{J_s \Delta \mu_s}{L}
\]  
(6.18)
By using pressure difference $\Delta P$ and osmosis pressure difference $\Delta \pi$ between both sides of the membrane, Equation 6.18 is rewritten as follows:

$$\Phi = -\frac{J_v \Delta P}{L} - \frac{J_D \Delta \pi}{L}$$  \hspace{1cm} (6.19)

However:

$$J_v = \bar{v}_w J_w + \bar{v}_s J_s$$  \hspace{1cm} (6.20)

$$J_D = \frac{J_s}{\bar{c}_s} - \bar{v}_w J_w = \nu_s - \nu_s$$  \hspace{1cm} (6.21)

where $J_v$ is volume flow and $J_D$ is relative rate of solute for solvent flow. But this rate in a dilute solution equals the barycentrical solute rate. $\bar{v}_w$, $\bar{v}_s$ and $c_s$ are mole volumes of water (solvent) and solute, and concentration of solute respectively.

Equation 6.19 can be rewritten as phenomenological equations in which $J_v$ and $J_D$ are a function of $\Delta P$ and $\Delta \pi$:

$$J_v = L_P \Delta P + L_{PD} \Delta \pi$$

$$J_D = L_{DP} \Delta P + L_D \Delta \pi$$  \hspace{1cm} (6.22)

But from Equation 6.15, $L_{PD} = L_{DP}$; therefore, the independent phenomenological coefficients are only $L_P$, $L_{PD}$ and $L_D$.

6.1.2 Volume Flow and Diffusion Flow

When the coefficient $L_P$ with a minus sign is the filtration coefficient $L_f$, the following equation is given:

$$L_f = -L_p = -\left(\frac{J_v}{\Delta P}\right)_{\Delta \pi = 0}$$  \hspace{1cm} (6.23)

Although volume flow $J_v$ is given in Equation 6.20, $J_v$ of a dilute solution almost equals the rate of water $\nu_w (= \bar{v}_w J_w)$, and the filtration coefficient $L_f$ is as follows:

$$L_f = -\frac{\bar{v}_w J_w}{\Delta P} = \frac{f}{L} \left(\frac{a^2}{8\eta} + \frac{\bar{v}_w D_w}{RT}\right)$$  \hspace{1cm} (6.24)

where $f$ and $a$ are the membrane coefficient [2] and the radius of the channel in the membrane respectively. Consequently, $L_f$ increases with increasing water content in the membrane.

The first term in parentheses in Equation 6.24, $a^2/8\eta$ is due to Poiseuille laminar flow when liquid of viscosity $\eta$ flows through channel of radius $a$, and the second term in parentheses is dependent on diffusion flow of water by the increase of chemical potential of water under pressure. Namely, the former is flow based on mass motion of molecules and the latter is attributed to permeation of random walk of water molecules. When pore radius is less than about 3 Å, the first term in parentheses in Equation 6.24 is negligible compared with the second. In practice, spaces between molecules which constitute the membrane play an important role as pores, and permeation molecules diffuse in these pores. In this case, interaction between permeant and membrane molecules significantly influences membrane permeability.
Concrete examples can be seen in both biomembranes and artificial membranes. In biomembranes, cell membrane polypeptide channels exist in a lipid bilayer membrane, as shown in Figures 6.2 and 6.3 [3,4].

Inorganic ions can permeate through polypeptide channels and organic molecules can pass the space between lipid molecules because the lipid layer in the biomembrane is fluid. Therefore, a more hydrophobic molecule be easily permeate through the lipid layer. Such a topical fluid membrane contributes significantly to permeability.

Similar phenomena are also observed in artificial membranes. In ultrafiltration (UF), solvent and solute can permeate by volume flow through pores of the UF membrane (see Figure 2.1 porous

---

**Figure 6.2** Model of cell membrane by Singer and Nicolson.

**Figure 6.3** Detailed model of cell membrane [3].
membrane). Therefore, in UF, for various organic liquids the flux is remarkably governed by the viscosity of the feed solution. However, since reverse osmosis (RO) membranes have a dense skin layer (see Figure 2.2b and c), water molecules can permeate through the space between the molecules making up this dense skin layer but electrolytes are rejected by this dense layer. Such an RO membrane performance is strongly dependent on the fact that the RO membrane cannot be swollen by water molecules. Interaction between water molecules and the membrane material making up this dense skin layer is significantly related to RO performance.

In a mixed system of water and organic solvents it is expected that hydrophilic or hydrophobic membranes preferentially permeate water or organic solvent respectively. However, many polymer membranes easily permeate water compared with alcohol in pervaporation (PV) \[5 – 7\]. These results are attributed to the fact that the permselectivity of a membrane depends strongly on the molecular size of the permeant. However, poly(dimethylsiloxane) (PDMS) and poly[(1-trimethylsilyl)-1-propyne] membranes are very highly hydrophobic. These membranes showed high alcohol permselectivity and high permeability in PV \[5 – 8\]. Alcohol permselectivity of PDMS membrane is due to the fact that interaction between the PDMS membrane and the alcohol molecule is very strong, and also high permselectivity is dependent on the high topical fluidity of the PDMS molecule, which is due to a low glass transition temperature \(T_g\) at which micro-Brownian motion becomes active.

The reflection coefficient \(\sigma\) is defined as follows:

\[
\sigma = \frac{L_{PD}}{L_f} = -\frac{L_{PD}}{L_p}
\]

(6.25)

The first equation in Equation 6.22 is rewritten as follows:

\[
J_v = -L_f (\Delta P - \sigma \Delta \pi)
\]

(6.26)

In an ideal semipermeable membrane that can freely permeate solute but not perfectly permeate solute, \(\sigma = 1\) and volume flow \(J_v\) is proportional to \((\Delta P - \Delta \pi)\). In a permeable membrane that can freely permeate both solvent and solute, \(\sigma = 0\), \(J_v\) is not influenced by \(\Delta \pi\) and is proportional to \(\Delta P\). On the other hand, in a completely permeable membrane in which part of the solute permeates, \(0 < \sigma < 1\), and with \(\Delta P = 0\), from Equation 6.26 we have

\[
J_v = L_f \sigma \Delta \pi \quad \Delta P = 0
\]

(6.27)

In this case, the volume flow occurs to the side of higher osmotic pressure as \(J_v\) and \(\Delta \pi\) are the same sign.

To discuss the coefficient \(L_D\), from Equations 6.21, 6.25, 6.26 and the second equation in Equation 6.22, the following can be obtained:

\[
J_s = (1 - \sigma) \bar{c}_s J_v - \omega \Delta \pi
\]

(6.28)

where \(L_D\) is contained in \(\omega\), it is represented as the following equation:

\[
\omega = -\left(\frac{J_s}{\Delta \pi}\right)_{J_v = 0} = -\bar{c}_s (L_D + \sigma^2 L_f)
\]

(6.29)

Equating the first term on the right-hand side in Equation 6.28 to \(J_s^{(V)}\) we get

\[
J_s^{(V)} = (1 - \sigma) \bar{c}_s J_v
\]

(6.30)

This equation corresponds to the flux of solute by solvent drag; then, equating the second term on the right-hand side in Equation 6.28 to \(J_s^{(m)}\), we get the equation for solute flow by solute migration:

\[
J_s^{(m)} = -\omega \Delta \pi
\]

(6.31)
Equation 6.31 is the flux of solute without flow of solvent. If we define the coefficient of membrane permeation \( P_s \) as

\[
P_s = - \frac{J_s^{(m)}}{\Delta c_s/L}
\]

then the relation between Equation 6.32 and \( \omega \) is

\[
P_s = \omega L \left( \frac{\Delta \pi}{\Delta c_s} \right) \div RT \omega L
\]

When Equation 6.28 is rewritten using Equation 6.32 and \( \Delta c_s/L \) is \( dc_s/dx \), \( J_s \) is

\[
J_s = (1 - \sigma)c_s J_v - P_s \frac{dc_s}{dx}
\]

where \( x \) is the coordinates for the normal direction of the membrane surface.

In steady state, both \( J_v \) and \( J_s \) are constant; when this equation is integrated from \( x = 0, C_s = C_s^I \) to \( x = L, C_s = C_s^{II} \), the following equation is obtained:

\[
- \frac{(1 - \sigma)L}{P_s} J_v = \ln \left[ \frac{J_s - (1 - \sigma)c_s^I J_v}{J_s - (1 - \sigma)c_s^{II} J_v} \right]
\]

Since filtrate concentration \( C_s^{II} \) is

\[
c_s^{II} = \frac{J_s}{J_v}
\]

if Equation 6.37 holds, then Equation 6.38 is given using Equation 6.35:

\[
F = \exp \left[ - \frac{(1 - \sigma)L}{P_s} J_v \right]
\]

\[
F = \frac{1}{\sigma} \frac{1 - \sigma c_s^I}{c_s^{II}}
\]

Therefore, rejection coefficient \( R \) is given by the following equations [9]:

\[
R = 1 - \frac{c_s^{II}}{c_s^I}
\]

\[
R = \left( \frac{1 - F}{1 - \sigma F} \right) \sigma
\]

Since \( F \) given in Equation 6.37 is a function of \( J_v \), rejection \( R \) is also a function of \( J_v \). Therefore, as shown in Figure 6.4, with increasing volume flow \( J_v \), rejection \( R \) approaches the reflection coefficient \( \sigma \). But when \( J_v \) is small, \( R \) becomes small because leaks due to self-diffusion of solute are not negligible.

### 6.1.3 Mobility and Diffusion Coefficient

Flux of solute without volume flow \( J_s^{(m)} \) is proportional to the slope of the physicochemical potential:

\[
J_s^{(m)} = -L_s \text{ grad } \bar{\mu}_s
\]

**Figure 6.4** Rejection coefficient \( R \) as a function of volume flow \( J_v \).
However, the value of the phenomenological coefficient $L_s$ cannot be obtained by thermodynamics. Therefore, it is required to consider molecular theory.

When the physicochemical potential $\tilde{\mu}_i$ is defined for 1 mol, the force acting on one particle (molecule, ion, etc.) $f_i$ is represented using the Avogadro number $N_A$ as follows:

$$ f_i = \left( \frac{1}{N_A} \right) \nabla \tilde{\mu}_i \tag{6.42} $$

The linear velocity of a particle $v_i$ (cm s$^{-1}$) is given using mobility $B_i$ as follows:

$$ v_i = B_i f_i = -\left( \frac{B_i}{N_A} \right) \nabla \tilde{\mu}_i \tag{6.43} $$

The flux $J_i$ (mol cm$^{-2}$ s$^{-1}$) for component $i$ of concentration $c_i$ is

$$ J_i = c_i v_i = -\left( \frac{c_i B_i}{N_A} \right) \nabla \tilde{\mu}_i \tag{6.44} $$

Using Equation 6.44 and the Boltzmann constant $k_B (= R/N_A)$:

$$ J_i = -k_B T B_i \left( \frac{\partial \ln a_i}{\partial \ln c_i} \right) \nabla c_i - \left( \frac{c_i B_i}{N_A} \right) \nabla \varphi_i \tag{6.45} $$

If the physical potential can be negligible – that is, when flux and diffusion coefficient for $\varphi_i = 0$ are $J_i$ and $D_i^0$ respectively – from Equation 6.45 the following equations are given:

$$ J_i^0 = -D_i^0 \nabla c_i \tag{6.46} $$

$$ D_i^0 = -\frac{J_i^0}{\nabla c_i} = k_B T B_i \frac{\partial \ln a_i}{\partial \ln c_i} \tag{6.47} $$

Equation 6.46 is called Fick’s first law. Fick’s second law is as follows:

$$ \frac{\partial c_i}{\partial t} = -\text{div} J_i^0 = \text{div} (D_i^0 \nabla c_i) \tag{6.48} $$

When $D_i^0$ is constant:

$$ \frac{\partial c_i}{\partial t} = D_i^0 \Delta^2 c_i \tag{6.49} $$

When the activity in Equation 6.50 is used, $D_i^0$ in Equation 6.47 is written as Equation 6.51:

$$ a_i = \gamma_i c_i \tag{6.50} $$

$$ D_i^0 = k_B T B_i \left( 1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} \right) \tag{6.51} $$

When the dependency of the activity coefficient is negligible, $D_i^0$ is given by

$$ D_i^0 = k_B T B_i \tag{6.52} $$

When the radius of spherical particle is $a_i$ and viscosity of medium is $\eta$, the mobility for this particle is represented by Stokes’ law [10] as follows:

$$ B_i = \frac{1}{6\pi \eta a_i} \tag{6.53} $$
When this equation is combined with Equation 6.52 and \( k_B = R/N_A \) is used, we get

\[
D_i^0 = \frac{RT}{6\pi\eta a_i N_A} \quad (6.54)
\]

This equation is called the Einstein equation, which was used in determination of the Avogadro number.

When the ionic valence of ion \( i \) in electrolyte is \( z_i \), electrophysical potential, \( \varphi_i \) is

\[
\varphi_i = z_i F \quad (6.55)
\]

When elementary charge is \( |e| = F/N_A \), Equation 6.45 becomes

\[
J_i = - D_i^0 \text{grad } c_i - z_i |e| c_i B_i \text{grad } c_i \quad (6.56)
\]

Consequently, the diffusion coefficient of an ion is

\[
D_i = - \frac{J_i}{\text{grad } c_i} = D_i^0 + z_i |e| c_i B_i \frac{\text{grad } E}{\text{grad } c_i} \quad (6.57)
\]

In the right-hand side of this equation, when the action direction of the concentration gradient and the electric potential gradient are reversed – that is, \( (z_i \text{grad } E/\text{grad } c_i) < 0 \) – there is a possibility of \( D_i < 0 \), and consequently reverse diffusion against the concentration gradient will be able to occur [11]. Generally, when the effects of concentration gradient (term 1) and electric potential gradient (term 2) on the right-hand side of Equation 6.57 are compared, the following occurs. As shown in Figure 6.5: (a) when the effect of term 2 is small compared with that of term 1, and ordinary permeation can be recognized in ordinary diffusion or membrane permeation as expected by Fick’s law (see curve a in Figure 6.5); (b) when the effect of term 2 is larger than that of term 1, and they are reversed in direction, reverse permeation occurs (see curve b in Figure 6.5); (c) when the effect of term 2 is larger than that of term 1, and they are in the same direction, facilitated permeation occurs in the initial stage, and after equilibrium concentration a reverse permeation furthermore occurs (see curve c in Figure 6.5) [12].

As shown in Equation 6.58, the diffusion current \( I_D \) in the steady state for all electrolytes is zero:

\[
I_D = F_A \sum_i z_i J_i = 0 \quad (6.58)
\]

Using this equation and Equation 6.56, we obtain

\[
\text{grad } E = \frac{-1}{|e| \sum_k z_i^2 c_i B_i} \sum_i z_i D_i^0 \text{grad } c_i \quad (6.59)
\]

By substituting this equation for Equation 6.57, the following equation is obtained:

\[
D_i = D_i^0 \frac{z_i c_i B_i}{\sum_k z_i^2 c_i B_k} \sum_j z_j D_j^0 \frac{\text{grad } c_j}{\text{grad } c_i} \quad (6.60)
\]
In a binary ion system consisted of cation 1 and anion 2, we have
\[ c_1 = \nu_1 c, \quad c_2 = \nu_2 c \quad (6.61) \]
where \( c \) is mole concentration of electrolyte.

Also, since the following equation holds, Equation 6.63 is given:
\[ z_1 \nu_1 = |z_2| \nu_2 \quad (6.62) \]
\[ \text{grad} E = -\frac{D_1^0 - D_2^0}{|e|(z_1 B_1 + |z_2| B_2)} \text{grad} \ln c \quad (6.63) \]

Furthermore, using the approximation \( D_1^0 = k_B T B_1 \):
\[ \text{grad} E = -\frac{RT}{F \lambda(z_1 B_1 + |z_2| B_2)} \text{grad} \ln c \quad (6.64) \]

Also, by applying same approximation to Equation 6.60, since \( D_1 = D_2 \), when they are \( D_{12} \) we have
\[ D_{12} = D_1 = D_2 = k_B T = z_1 B_1 + |z_2| B_2 \quad (6.65) \]

This equation is called the Haskell equation.

In Equation 6.64, when, for example, the mobility of the cation is higher than that of the anion, \( B_1 > B_2 \) and \( \text{grad} \ln c < 0, \text{grad} E > 0 \) holds. As shown in Figure 6.6, when ions diffuse from a concentrated solution on the left side to a dilute solution on the right side, cations and anions move fast and slow respectively, since \( B_1 > B_2 \). Consequently, positive and negative differences of electric potential ( \( \text{grad} E > 0 \) ) on the left and right sides of the diffusion layer are generated respectively. This difference of electric potential is the diffusion potential.

Consequently, the diffusion velocity of cations is slow because they are brought back, but that of anions is conversely fast. At steady state, the diffusion velocities of cations and anions are equal, as show in Equation 6.65.

From Equation 6.65, when the transport number of cations is much higher than that of anions (i.e. \( z_1 B_1 \gg |z_2| B_2 \)) we have
\[ D_{12} \cong k_B T \lambda \left( 1 + \frac{|z_2|}{z_1} \right) \quad (6.66) \]
Consequently, the diffusion coefficient $D_2$ ($=D_{12}$) of anions becomes larger than the value without diffusion potential (which is shown in Equation 6.67), as shown in Equation 6.68:

$$D_2 = k_BT_2$$  
(6.67)

$$D_{12} = k_BT_2\left(1 + \frac{z_1}{z_2}\right)D_0 > D_2$$  
(6.68)

In coloured ions such as dyes the diffusion coefficient can be directly determined [13]. In dyes with impurities or dyes containing electrolyte, such as NaCl, since anions with a high mobility, such as Cl$^-$ ion, pass, the diffusion potential is compensated. Therefore, $D_2$ in Equation 6.68 cannot be evaluated. However, in a system of pure dye it can be exactly determined. Diffusion coefficients of pure dyes are summarized in Table 6.1 [13], which also contains $D_2$ calculated by substituting the value of electrochemical mobility in the Haskell equation (6.65). Good agreements are recognized between experimental $D_2$ and calculated $D_2$.

By substituting experimental $D_2$ in Equation 6.54 the Stocke radius $a_2$ can be obtained; the apparent particle weight calculated using this $a_2$ is smaller than the formula weight.

### 6.1.4 Surface Potential and Membrane Potential

When an equilibrium is held between a solution $S$ ($S = I$ or $II$) and a membrane surface $S^*$ and electrochemical potentials $\bar{\mu}_i$ of component $i$ equal as in Figure 6.7a (see Equation 6.69) in a system of (solution $I$ | membrane $M$ | solution $II$), using Equations 6.69 and 6.70 obtained from Equations 6.17 and 6.55, Equation 6.71 is obtained:

$$\bar{\mu}_i^S = \bar{\mu}_i^{S*}$$  
(6.69)

$$\mu_i = \mu_i^0 + RT \ln a_i + z_iF\Delta E$$  
(6.70)

$$\frac{a_i^{S*}}{a_i^S} = \exp\left(-\frac{\Delta \mu_i^{S*}}{RT}\right) \exp\left(-\frac{z_iF\Delta E}{RT}\right)$$  
(6.71)

where

$$\Delta \mu_i^{S*} = \mu_i^{S*} - \mu_i^{S}$$

$$\Delta E^S = E^{S*} - E^S$$

### Table 6.1 Diffusion coefficient of pure dyes.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$D_2 \times 10^6$/cm$^2$s$^{-1}$</th>
<th>$a_2 \times 10^{10}$/m</th>
<th>Apparent particle weight/g mol$^{-1}$</th>
<th>Formula weight/g mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Congo Red</td>
<td>5.1</td>
<td>3.4</td>
<td>148</td>
<td>698</td>
</tr>
<tr>
<td>Benzopurpurine 4B</td>
<td>5.6</td>
<td>4.3</td>
<td>302</td>
<td>726</td>
</tr>
<tr>
<td>meta-Benzopurpurine</td>
<td>5.2</td>
<td>3.7</td>
<td>163</td>
<td>726</td>
</tr>
<tr>
<td>Congo Rubine</td>
<td>5.2</td>
<td>3.6</td>
<td>177</td>
<td>699</td>
</tr>
</tbody>
</table>

a) Using Equation 6.65.

b) Using Equation 6.68.
ΔE\textsuperscript{S} is the potential difference of the membrane surface. Δμ\textsubscript{i}\textsuperscript{S} is the standard chemical potential of component \(i\) on the interface. \(b_i\textsuperscript{S}\) as defined in the following equation is the distribution coefficient of component \(i\) when the solute is a nonelectrolyte (\(z_i = 0\)) in ideal solution (\(a_i = c_i\)) or the membrane is not charged (\(ΔE\textsuperscript{S} = 0\)):

\[
b_i\textsuperscript{S} = \exp\left(-\frac{Δμ_i\textsuperscript{S}}{RT}\right)
\]

(6.73)

In general solution, the distribution coefficient \(\beta_i\textsuperscript{S}\) of component \(i\) on interface \(S\) is represented as follows by applying Equation 6.50 to left side of Equation 6.71:

\[
\beta_i\textsuperscript{S} = \frac{c_i\textsuperscript{S'}}{c_i\textsuperscript{S}} = \frac{1}{g_i\textsuperscript{S}} \exp\left(-\frac{z_iF_AΔE\textsuperscript{S}}{RT}\right)
\]

(6.74)

where

\[
g_i\textsuperscript{S} = \frac{γ_i\textsuperscript{S'}}{γ_i\textsuperscript{S}}\frac{b_i\textsuperscript{S}}{\beta_i\textsuperscript{S}}
\]

(6.75)

Generally, since \(β_i\textsuperscript{S} \neq 1\), the concentration on the membrane surface changes discontinuously, as shown in Figure 6.7c.

By Equation 6.74, surface potential of the membrane \(ΔE\textsuperscript{S}\) is

\[
ΔE\textsuperscript{S} = -\frac{RT}{F_A} \ln\left(g_i\textsuperscript{S} \frac{c_i\textsuperscript{S'}}{c_i\textsuperscript{S}} \right)^{1/z_i}
\]

(6.76)

**Figure 6.7** Distribution of physicochemical potential, electrical potential \(E\), and concentration of component I \(c_i\) in the system (I | M | II).
Since the value of $\Delta E^S$ is independent of the kind of ion $i$, the flowing equation is obtained:

$$\left(\frac{g_1^S c_1^S}{c_1^S}\right)^{1/z_1} = \left(\frac{g_2^S c_2^S}{c_2^S}\right)^{1/z_2} = \cdots = \left(\frac{g_n^S c_n^S}{c_n^S}\right)^{1/z_n}$$  \hspace{1cm} (6.77)

This is the condition of the generalized Donnan equilibrium [14].

In a binary ion system consisting of cation 1 and anion 2, when Equation 6.62 and $\nu = \nu_1 + \nu_2$ are used, the following equation is obtained from Equation 6.77:

$$\left(g^S\right)^\nu (c_1^S)^{\nu_1} (c_2^S)^{\nu_2} = (c_1^S)^{\nu_1} (c_2^S)^{\nu_2}$$  \hspace{1cm} (6.78)

where

$$g^S = \left\{\left(\frac{g_1^S}{g_2^S}\right)^{\nu_1} \left(\frac{g_2^S}{g_2^S}\right)^{\nu_2} \right\}^{1/\nu}$$  \hspace{1cm} (6.79)

When $g^S$ is unity in this equation, Equation 7.78 is the equation of the Donnan equilibrium. In a 1 : 1 electrolyte system, since conditions of $C_1^S = C_2^S = C^S$, $\nu_1 = \nu_2 = 1$, $\nu = 2$ hold, Equation 6.78 is rewritten as

$$(g^S)^2 c_1^{ss} c_2^{ss} = (c^S)^2$$  \hspace{1cm} (6.80)

By applying the condition of electrical neutrality as in Equation 6.81 to this equation, Equation 6.82 is obtained:

$$c_1^{ss} - c_2^{ss} + \theta^S = 0$$  \hspace{1cm} (6.81)

$$\frac{c_1^{ss}}{c^S} = \sqrt{\left(\theta^S\right)^2 + 1 - \theta^S}$$  \hspace{1cm} (6.82)

$$\frac{c_2^{ss}}{c^S} = \sqrt{\left(\theta^S\right)^2 + 1 + \theta^S}$$

where

$$\theta^S = \frac{g^S \theta^S}{2 c^S}$$  \hspace{1cm} (6.83)

Here, when the concentration ratio $r$ is $c^I/c^II$, and $c^I = rc$ and $c^II = c$ hold, and furthermore if $g^S$ and $\theta^S$ are constant and $g^I = g^II = g$ and $\theta^I = \theta^II = \theta$, we have

$$\theta^I = \frac{\theta}{r}, \theta^II = \theta$$  \hspace{1cm} (6.84)

The potential difference $\Delta E$ between solutions across a membrane is called the membrane potential. As shown in Figure 6.7b, if the potential difference between solution I of the high concentration side and solution II of the low concentration side is the membrane potential $\Delta E$ [15–17], we have

$$\Delta E = E^I - E^II$$  \hspace{1cm} (6.85)

This equals the sum of the difference between the two surface potential $\Delta E^I$ and $\Delta E^II$ and diffusion potential $\Delta E_{dif}$:

$$\Delta E = \Delta E_{surf} + \Delta E_{dif} \hspace{1cm} (6.86)$$
The difference of surface potential $\Delta E_{\text{surf}}$ is given using Equation 6.76 as follows:

$$
\Delta E_{\text{surf}} = \frac{RT}{z_i F_A} \ln \left( \frac{g_i^1 c_i^{1^*}}{g_i^1 c_i^{2^*}} \right)
$$

(6.87)

The diffusion potential $\Delta E_{\text{dif}}$ can be obtained by integrating Equation 6.59. When coordinates of the normal direction of membrane $x$ and grad are substituted by $\partial/\partial x$, Equation 6.59 is rewritten using approximation of $D_i^0 = k_B T B_i$ as follows:

$$
\frac{\partial E}{\partial x} = -\frac{RT}{F_A} \sum_j z_j B_j \left( \frac{\partial c_j}{\partial x} \right)
$$

(6.88)

$L$ is the membrane thickness, and when Equation 6.88 is integrated from $(x = 0, c_j = c_j^{1^*}, E = E^{1^*})$ to $(x = L, c_j = c_j^{2^*}, E = E^{2^*})$, the following equation is obtained and can determine the diffusion potential:

$$
\Delta E_{\text{dif}} = - \int_{E^{1^*}}^{E^{2^*}} \frac{\partial E}{\partial x} \, dx
$$

(6.89)

Henderson [18,19] gave the following equation by assuming that the composition of the solution in a certain position in the diffusion layer corresponds to a mixed ratio $\delta$ of solution $1^*$ and $2^*$ at both ends of the diffusion layer:

$$
c_j = (1 - \delta)c_j^{1^*} + \delta c_j^{2^*}
$$

(6.90)

Parameter $\delta$ does not need to be proportional to coordinates $x$ but it is assumed that $\delta$ is the same for all ions.

Consequently, the following equation is given for all $j$:

$$
\frac{\partial c_j}{\partial x} = (c_j^{2^*} - c_j^{1^*}) \frac{\partial \delta}{\partial x}
$$

(6.91)

If the diffusion potential obtained under this assumption is Henderson’s diffusion potential $\Delta E_H$, from Equation 6.89 we have

$$
\Delta E_H = - \int_0^1 \frac{\partial E}{\partial x} \, d\delta
$$

(6.92)

By applying Equations 6.88 and 6.91 to Equation 6.92, Henderson’s equation is obtained as follows:

$$
\Delta E_H = \frac{RT}{F_A} \sum_i z_i B_i \left( c_i^{1^*} - c_i^{1^*} \right) \ln \frac{\sum z_i^2 B_i c_i^{1^*}}{\sum z_i^2 B_i c_i^{2^*}}
$$

(6.93)

The membrane potential $\Delta E(H)$ used in Equation 6.93 becomes

$$
\Delta E(H) = \Delta E_{\text{surf}} + \Delta E_H
$$

(6.94)

In a binary ion system containing only 1:1 electrolyte consisting of cation 1 and anion 2, when membrane charge is constant and $\theta^1 = \theta^2 = \theta$, from electrical neutrality in Equation 6.81 the following equation is given:

$$
c_1^{1^*} - c_1^{2^*} = c_2^{1^*} - c_2^{2^*}
$$

(6.95)
Consequently, Equation 6.93 becomes

\[
\Delta E_H = \frac{RT}{F_A} \left( \frac{B_1 c_{1s}^{+} + B_2 c_{2s}^{+}}{B_1 c_{1s}^{+} + B_2 c_{2s}^{+}} \right) \ln \left( \frac{B_1 c_{1s}^{+}}{c_{1s}^{+}} \right) + \frac{B_2 c_{2s}^{+}}{c_{2s}^{+}} \ln \left( \frac{B_2 c_{2s}^{+}}{c_{2s}^{+}} \right) \quad (6.96)
\]

When the concentration ratio \( c^I/c^{II} \) and \( r \) in Equation 6.84 are kept constant and \( c \) is changed, since the effect of the membrane charge in high concentration is small and the following relationships hold, Equation 6.98 is obtained:

\[
c_1^{S^*} \doteq c_2^{S^*}, \quad c_1^{s^*} / c_2^{s^*} \doteq r \quad (c \gg |\theta|) \quad (6.97)
\]

\[
\Delta E_H \doteq -\frac{RT}{F_A} \left( \frac{B_1 - B_2}{B_1 + B_2} \right) \ln r \quad (c \gg |\theta|) \quad (6.98)
\]

Also, when \( g_i \) is constant and \( g_i^I = g_i^{II} \) in Equation 6.87, Equation 6.99 is given and the membrane potential in Equation 6.94 almost equals the diffusion potential \( \Delta E_H \):

\[
\Delta E_{surf} \doteq 0 \quad (c \gg |\theta|) \quad (6.99)
\]

On the other hand, the effect of membrane charge is remarkable in low concentration, co-ion \( c \) does not approximately enter the membrane and anti-ion \( g \) almost neutralizes the membrane charge. Therefore, we arrive at Equation 6.100, and consequently the diffusion potential of Equation 6.96 is given as Equation 6.101:

\[
c_{c}^{S^*} \doteq 0, \quad c_{g}^{S^*} \doteq |\theta| \quad (c \ll |\theta|) \quad (6.100)
\]

\[
\Delta E_H \doteq 0 \quad (c \ll |\theta|) \quad (6.101)
\]

Also, different to the surface potential in Equation 6.87, since the ionic valence of anti-ion \( z_i \) is given opposite sign to the membrane charge and the \( \ln \) term becomes \( \ln r \), the following equation results:

\[
\Delta E_{surf} \doteq \pm \left( \frac{RT}{F_A} \right) \ln r \quad (c \gg |\theta|) \quad (6.102)
\]

where the plus/minus sign is the same sign as the membrane charge.

From the aforementioned result, the relationship between the membrane potential \( \Delta E \) and concentration \( c \) is shown in Figure 6.8. At high concentration, the membrane potential almost equals the diffusion potential. As shown in Figure 6.6, the plus/minus is plus when the mobility of the anion is larger than that of the cation, and minus when the mobility of the cation is larger than that of the anion, and the transport number of the ions in the membrane can be obtained using Equation 6.98. At low concentration, the membrane potential almost equals the difference of surface potential; this value is given in Equation 6.102. When \( r > 1 \) the plus and minus of the membrane potential is identical with the membrane charge. This result can be attributed to the fact that membrane permeation of the co-ion is hindered and the high concentration side is charged with the same sign as the membrane. On the other hand, value of \( |\theta| \) can be obtained from concentration in which membrane potential suddenly changes. That is, \( c_{i}^{S^*} \) in Equation 6.82 is substituted for Equations 6.87 and 6.96; furthermore, when those are substituted for
Equation 6.94, a theoretical curve is obtained and value of parameter $|\theta|$ can be determined by comparing the experimental and theoretical values.

### 6.1.5 Distribution Coefficient and Membrane Permeability Coefficient

The flux of membrane permeability $J_i^*$ by diffusion of component $i$ is given by approximating the concentration gradient $\Delta c_i^*$ as

$$J_i^* = -fD_i^* \frac{\Delta c_i^*}{L}$$

where

$$\Delta c_i^* = c_i^\text{II} - c_i^\text{I}$$

Consequently, since $\Delta c_i = c_i^\text{II} - c_i^\text{I}$ for Equation 6.32, the membrane permeability coefficient $P_i$ in Equation 6.32 is as follows:

$$P_i = -\frac{J_i^*}{\Delta c_i/L} = fD_i^* \frac{\Delta c_i^*}{\Delta c_i}$$

When the distribution coefficient $\beta_i^S$ in Equation 6.74 is used in Equation 6.105 we obtain

$$P_i = fD_i^* (\beta_i^\text{I} c_i^\text{I} - \beta_i^\text{II} c_i^\text{II})$$

Consequently, when the membrane is symmetric and $\beta_i^\text{I} = \beta_i^\text{II} = \beta_i$, we have

$$P_i = f \beta_i D_i^*$$

Membrane permeability coefficient $P_i$ increases with increasing distribution coefficient.

In permeation of charged membrane of 1:1 electrolyte consist of cation 1 and anion 2, $\beta_1^S$ is not equal $\beta_2^S$ as can be seen from Equation 6.82 obtained from the Donnan equilibrium. This fact is supported from that $\beta_g > 1$ and $\beta_c < 1$ (where $g^* \approx 1$) can be held, since the counter ion $g^*$ is incorporated into the membrane but the co-ion $c^*$ is rejected by the membrane. When the membrane is symmetric and the elations $g^\text{I} = g^\text{II} = g$ and $\theta^\text{I} = \theta^\text{II} = \theta$ are held, the value of $\Delta c_i^*/\Delta c_i$ required in Equation 6.105 is equal in both cation $(i = 1)$ and anion $(i = 2)$. Therefore, when this value is $\beta$, using Equations 6.82, 6.83 and 6.84, we arrive at the following equation:

$$\beta = \frac{\Delta c_1^*}{\Delta c_1} = \frac{\Delta c_2^*}{\Delta c_2} = \frac{\sqrt{\theta^2 + r^2} - \sqrt{\theta^2 + 1}}{g(r-1)}$$

When the value $\beta$ as electrolyte concentration is high and $c \gg |\theta|_i$, then

$$\beta = \frac{1}{g}$$

On the other hand, when its concentration is low and $c \ll |\theta|_i$, then

$$\beta = 0 \quad (\theta \to \infty)$$

The permeability of electrolyte through the charged membrane decreases with decreasing electrolyte concentration, as shown in Figure 6.9 [20]. Therefore, the charge density of the membrane $\theta$ can be determined from concentration at the sudden decrease of permeation coefficient of the membrane and is in agreement with that determined from the concentration change in electrical potential of the
membrane ΔE. Such a lowering of the permeability of the electrolyte is dependent on the electrostatic repulsion between the co-ion and membrane charge.

\[ \langle c \rangle = \frac{c^I + c^{II}}{2} = \frac{c(r + 1)}{2} \]  

(6.111)

When

\[ \langle \theta \rangle = \frac{g \theta}{2 \langle c \rangle} = \frac{2}{r + 1} \]  

(6.112)

is substituted for \( \theta \) in Equation 6.84, and the fact that \( \beta \to 1/g \) as \( \theta \to 0 \) in Equation 6.108 is also used, the following equation results:

\[
\frac{P}{P_\infty} = g\beta = \frac{\langle |\theta| \rangle (r + 1)}{2(r - 1)} \left[ \sqrt{1 + \frac{4r^2}{(r + 1)^2 \theta^2}} - \sqrt{1 + \frac{4}{(r + 1)^2 \theta^2}} \right]
\]  

(6.113)

When \( \langle c \rangle \) is used on the abscissa as in Figure 6.9, the value of \( P/P_\infty \) changes very much whether \( r \to 1 \) or \( r \to \infty \). If Equation 6.113 is developed in the low concentration region (1/\( \langle |\theta| \rangle \) small), then

\[
\frac{P}{P_\infty} = \frac{1}{\langle |\theta| \rangle} \left[ 1 - \frac{r^2 + 1}{(r + 1)^2 \langle \theta \rangle^2} \right]
\]  

(6.114)

By approximating term 1 on the right-hand side of Equation 6.114, the following equation is obtained:

\[
\frac{P}{P_\infty} = \frac{1}{\langle |\theta| \rangle} \quad (|\theta| \gg 1)
\]  

(6.115)

This is shown as a broken line in Figure 6.9.

In the aforementioned handling, it was approximated that flux of diffusion \( J^* \) is proportional to the average concentration gradient in the membrane as shown in Equation 6.103. Therefore, also in diffusion in the membrane the effect of diffusion potential must be considered. We return to Equation 6.56 and consider again.

If the membrane coefficient \( f \) is considered and grad \( E \) in Equation 6.59 is substituted, Equation 6.56 is rewritten as follows:

\[
\frac{J}{f} = -D_i^0 \text{grad} c_i - z_i |e| c_i B_i \text{grad} E
\]  

(6.116)

In a binary ion system consisting of cation 1 and anion 2, from conditions of electrical neutrality as shown in Equation 6.81, the following equation is obtained:

\[
z_1 \frac{\partial c_1}{\partial x} + z_2 \frac{\partial c_2}{\partial x} = 0
\]  

(6.117)

Furthermore, Equation 6.59 is given as the following equation:

\[
\frac{\partial E}{\partial x} = -\frac{RT}{F_A} \frac{z_1 (B_1 - B_2)}{z_1^2 c_1 B_1 + z_2^2 c_2 B_2} \frac{\partial c_1}{\partial x}
\]  

(6.118)
When this equation is substituted into Equation 6.116 and \( D_1^0 = k_B T B_1 \) is approximated, we obtain
\[
\frac{J_1}{f} = -k_B T B_1 B_2 \frac{\partial c_1}{\partial x} \tag{6.119}
\]

And corresponding to Equation (6.81) we use
\[
|z_2| c_2 = z_1 c_1 + \theta \tag{6.120}
\]

In Equation 6.119, if \( f = 1 \) and \( q = 0 \), the Haskell equation (6.65) is obtained.
Using \( D_{12} \) in Equation 6.65, the following equation is obtained:
\[
\frac{J_1}{f} = -D_{12} \frac{\partial c_1}{\partial x} \left[ 1 + \frac{\tau \theta}{(z_1/|z_2| + 1)c_1 + (1/z_1 - \tau)\theta} \right] \tag{6.121}
\]
where
\[
\tau = \frac{t_1 - t_2}{|z_2|} = \frac{B_1 - B_2}{z_1 B_1 + |z_2| B_2} \tag{6.122}
\]

In a steady state \( J_1 \) is constant and when Equation 6.121 is integrated from \( x = 0, c_1 = c_1^{I*} \) to \( x = L, c_1 = c_1^{II*} \), the following equation is obtained:
\[
\frac{J_1 L}{f} = -D_{12} (c_1^{II*} - c_1^{I*}) \rho
\]
\[
\rho = 1 + \frac{|z_2| \tau \theta}{(z_1 + |z_2|)(c_1^{II*} - c_1^{I*})} \ln \left[ \frac{z_1 + |z_2|}{|z_2|} \frac{c_1^{II*} + \left( \frac{1}{z_1} - \tau \theta \right)}{\frac{z_1 + |z_2|}{|z_2|} c_1^{I*} + \left( \frac{1}{z_1} - \tau \theta \right)} \right] \tag{6.123}
\]

In 1:1 electrolyte \( (z_1 = |z_2| = 1) \), the following equation is obtained using Equations 6.82, 6.83 and 6.84.
\[
\frac{J_1 L}{f} = D_{12} \frac{c}{g} \left( \sqrt{\theta^2 + r^2} - \sqrt{\theta^2 + 1} \right) \rho
\]
\[
\rho = 1 + \frac{\tau \theta}{\sqrt{\theta^2 + r^2} - \sqrt{\theta^2 + r^2} - \tau \theta} \ln \left( \frac{\sqrt{\theta^2 + r^2} - \tau \theta}{\sqrt{\theta^2 + 1} - \tau \theta} \right) \tag{6.124}
\]

If concentration \( c \) is infinite \( (c \to \infty) \) and flux in \( \theta \to 0 \) is \( J_1^0 \), \( \rho \) is 1, we obtain the following equation:
\[
\frac{J_1^0}{f} = D_{12} \frac{c}{g} (r - 1) \tag{6.125}
\]

When Equation 6.126 holds, Equation 6.127 is given:
\[
R_f = \frac{P}{P_\infty} = \frac{J_1}{J_1^0} = b \rho \tag{6.126}
\]
\[
b = \frac{\sqrt{\theta^2 + r^2} - \sqrt{\theta^2 + 1}}{r - 1} \tag{6.127}
\]

If \( \beta_0 \) is for \( \beta \) in Equation 6.108 as \( \theta = 0 \), the following equation is given like Equation 6.113:
\[
b = \frac{\beta}{\beta_0} = g \beta \tag{6.128}
\]
When $c$ is co-ion and $g$ is counter ion for $\rho$ and $\tau_0$ is defined as follows, Equation 6.130 is given:

$$
\tau_0 = \frac{B_c - B_g}{z_c B_c + z_g B_g}
$$

(6.129)

$$
\tau\theta = \tau_0|\theta|
$$

(6.130)

$\rho$ is as follows:

$$
\rho = 1 + \frac{\tau_0|\theta|}{\sqrt{\theta^2 + r^2 - \sqrt{\theta^2 + 1}} \ln \left( \frac{\sqrt{\theta^2 + r^2 - \tau_0|\theta|}}{\sqrt{\theta^2 + 1 - \tau_0|\theta|}} \right)}
$$

(6.131)

Figure 6.10 shows the theoretical curves of $P/P_\infty$ for $r = 2$. The curve for $\tau_0 = 0$ in this figure corresponds to the curve for $r = 2$ in Figure 6.9.

As can be seen from Figure 6.10, when $\tau_0$ is positive (i.e. transport number of co-ion is high) a maximum point appears before membrane permeability coefficient degrades with decreasing concentration [21].

When the membrane is asymmetric or conditions in membrane permeation are asymmetrical, the relations in Equation 6.132) hold, and Equation 6.133 is given:

$$
\beta^I_i \neq \beta^{II}_i \quad \text{and} \quad c^I_i = c^{II}_i
$$

(6.132)

$$
\frac{\beta^{II}_i}{\beta^I_i} > \frac{c^I_i}{c^{II}_i}
$$

(6.133)

In this case, $P_i$ in Equation 6.106 is negative and reverse permeation occurs. This is due to the fact that the concentration gradient in the membrane is reversed in direction, which is expected from the concentration difference for solution I and solution II, as shown in Figure 6.11 [2,22–24]. In this manner, conditions in which reverse permeation as active transport occurs are the following two cases: (1) membrane is asymmetric and characteristic of surface and back side of membrane is different, or (2) characteristics of solution I and solution II in symmetric membrane are different (e.g. pH).

In practice, the lipid bilayer membrane in a biomembrane such as a cell membrane has an asymmetric structure that consists of a higher hydrophilic lipid layer in the molecular membrane in the outer side and a higher hydrophobic lipid layer in the molecular membrane in the inner part. On the other hand, in a liquid membrane that contains an acidulous chelate compound in organic solvent, since metal ions are transported from higher pH to lower pH because partition of chelated metal ions to the liquid membrane is depressed at low pH, it is
well known that mobile [23,25–28] and fixed [23,29–34] carrier membranes can concentrate metal ions by such a reverse permeation. In such reverse permeation, reactions as shown in Figure 6.12 on the interface in each membrane side occur. That is, metal ion $M^+$ is transported from the low concentration side to high concentration by a concentration gradient of $H^+$ ions.

### 6.2 Solution-Diffusion Model

#### 6.2.1 Fundamentals of Solution-Diffusion

Gas diffusion through nonporous membranes is a concentration-gradient-driven process, which is generally well described by Fick’s first law [35]:

$$J = -D V c$$

(6.134)

where $D$ is the diffusion coefficient and $c$ refers to the local gas or penetrant concentration. For unidirectional diffusion through a flat membrane, Equation 6.134 can be written for species $i$ as [35]

$$J_i = -D_i(c_i) \frac{dc_i}{dx}$$

(6.135)

where $D_i(c_i)$ indicates that the diffusion coefficient can be dependent on the local composition of penetrant $i$.

The permeability coefficient is defined in terms of the steady-state flux $J_i$ and the pressure or fugacity driving force $\Delta p_i$ or normalized by the membrane thickness $l$:

$$P_i = \frac{J_i}{\Delta f_i l}$$

(6.136)

The common unit of $P_i$ is the Barrer, $10^{-10}$ cm$^2$ (STP) cm cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$.

Substitution of the expression for steady-state flux (Equation 6.135) into Equation 6.136 yields

$$P_i = \frac{-D_i(c_i)dc_i}{dx} \frac{l}{\Delta f_i}$$

(6.137)

where $\Delta f_i$ refers to the difference in fugacity for a given species at the upstream conditions ($x = 0$) and at the downstream conditions ($x = l$), and $dc_i/dx$ is the local concentration gradient at a given position.
in the membrane. The product of $D_i(c_i)$ and $dc_i/dx$ must be a constant at each point in a flat membrane, since the steady-state permeability is constant for fixed upstream and downstream conditions [36]. For the special case in which the concentration of penetrant is zero at the downstream face of the membrane, Equation 6.137 can be rearranged and integrated for the appropriate boundary conditions [37]; namely:

$$\int_0^l \frac{P_i}{l} \, dx = \int_{C_{d}}^{C_i} \frac{D_i(c_i)}{f'_i - f''_i} \, dc_i$$  \hspace{1cm} (6.138)$$

This equation can be rearranged to the form

$$P_i = \frac{1}{f'_i - f''_i} \int_{f''_i}^{f'_i} [D_i(c_i)] \frac{df_i}{dc_i}$$  \hspace{1cm} (6.139)$$

Thus, Equation 6.139 indicates that permeability is a function of the product of kinetic and thermodynamic factors. While the fugacity driving force used in these equations is more thermodynamically correct, pressure is used in many of the following equations. For many permanent gases at moderate pressures ($\leq 50$ atm), the difference between pressure and fugacity is small.

A more common way of expressing Equation 6.139 is by the relation

$$P_i = D_i S_i$$  \hspace{1cm} (6.140)$$

where $D_i$ and $S_i$ are the diffusivity and solubility coefficients respectively for component $i$. The quantity $S_i$ is thermodynamic in nature and is affected by polymer–penetrant interactions as well as excess interchain gaps in glassy polymers. The average diffusion coefficient $D_i$ is kinetic in nature and largely determined by polymer–penetrant dynamics. Typically, the permeability and solubility are measured independently, and the diffusion coefficient is calculated by Equation 6.140. In this case, the diffusion coefficient is an average measure of the penetrant diffusivity in the membrane at the upstream and downstream concentrations.

The ability of the membrane to separate gases is characterized by the separation factor

$$\alpha_{ij} = \frac{y_i / y_j}{x_i / x_j}$$  \hspace{1cm} (6.141)$$

where $y_i, x_i$ and $y_j, x_j$ refer to the mole fraction of components $i$ and $j$ in the product and feed streams respectively.

When the downstream pressure is negligible compared with the upstream pressure, the separation factor is determined by

$$\alpha_{ij}^* = \frac{P_i}{P_i}$$  \hspace{1cm} (6.142)$$

For the special case in which the absolute downstream pressure is close to zero, the above ratio of permeabilities is referred to as the ‘ideal’ separation factor and is so denoted by an asterisk. In the absence of plasticizing effects due to high levels of penetrant sorption, the separation factor for a mixed gas case $\alpha_{ij}$ can be closely approximated by a ratio of pure gas permeabilities for the individual components $i$ and $j$.

For cases in which the downstream pressure cannot be ignored, the true separation factor defined by Equation 6.141 is related to the ratio of the permeability coefficients by [36,37]:

$$\alpha_{ij} = \alpha_{ij,inh} \left[ \frac{x_i (\alpha_{ij} - 1) + 1 - r \alpha_{ij}}{x_i (\alpha_{ij} - 1) + 1 - r} \right]$$  \hspace{1cm} (6.143)$$
where

\[ \alpha_{ij, inh} = \frac{P_i}{P_i} \]  

(6.144)

and \( r \) is the ratio of the downstream and upstream pressures \( \left( \frac{P''}{P'} \right) \). For permeation experiments for which the downstream pressure is essentially zero, \( r \) is zero and Equation 6.143 is equivalent to Equation 6.142.

Also, a useful way to gain a better understanding of how the membrane material forms the separation is by dividing the separation factor into its diffusivity and solubility components. If Equation 6.139 is substituted into Equation 6.142 the ideal separation factor can be expressed as [37]

\[ \alpha_{ij}^* = \left( \frac{D_i}{D_j} \right) \left( \frac{S_i}{S_j} \right) \]  

(6.145)

\[ \alpha_{ij}^* = \left( \frac{\text{mobility}}{\text{selectivity}} \right) \left( \frac{\text{solubility}}{\text{selectivity}} \right) \]  

(6.146)

By understanding how molecular structure within a polymer family affects the two components of the separation factor, we can conceivably optimize the polymer structure for a desired gas separation. Recently, significant advances have been made in the understanding of how polymer structure (especially for glassy polymers) affects the separation ability of materials.

### 6.2.2 Solution-Diffusion Model

See Wijmans and Baker’s ‘The solution-diffusion model: a unified approach to membrane permeation’ [40].

The starting point for the mathematical description of permeation in all membranes is the proposition, solidly based in thermodynamics, that the driving forces of pressure, temperature, concentration and electromotive force are interrelated and that the overall driving force producing movement of a permeant \( i \) is the gradient in its chemical potential \( \mu_i \). Thus, the flux \( J_i \) (g cm\(^{-2}\) s\(^{-1}\)) is described by the simple equation

\[ J_i = \frac{c_i}{v_i} = c_i U_i \frac{d\mu_i}{dx} \]  

(6.147)

where \( d\mu_i/dx \) is the gradient in chemical potential of component \( i \) and \( U_i \) is a coefficient of proportionality (not necessarily constant) linking the chemical potential driving force \( d\mu_i/dx \) with \( v_i \), the velocity of component \( i \). When this velocity is multiplied by the concentration of component \( i \) molecules \( c_i \), the result is the flux of component \( i \).

All the common driving forces, such as gradients of concentration, pressure, temperature and electromotive force, can be reduced to a chemical potential gradient, and their effect on flux expressed by this equation. This approach is extremely useful, because many processes involve more than one driving force; for example, pressure and concentration in RO. Restricting ourselves to driving forces generated by concentration and pressure gradients, the chemical potential is written as

\[ d\mu_i = RT \frac{d\ln(\gamma_i n_i)}{\gamma_i} + \nu_i dp \]  

(6.148)

where \( n_i \) is the mole fraction (mol mol\(^{-1}\)) of component \( i \), \( \gamma_i \) is the activity coefficient linking concentration with activity, \( p \) is the pressure and \( \nu_i \) is the partial molar volume of component \( i \).
In incompressible phases, such as a liquid or a solid membrane, volume does not change appreciably with pressure. Integrating Equation 6.148 with respect to concentration and pressure then gives

\[ \mu_i = \mu_i^0 + RT \ln(\gamma_i n_i) + \nu_i (p - p_i^0) \]  

(6.149)

where \( \mu_i^0 \) is the chemical potential of pure \( i \) at a reference pressure \( p_i^0 \).

In compressible gases, the molar volume changes with pressure; using the ideal gas laws and integrating Equation 6.148 then gives

\[ \mu_i = \mu_i^0 + RT \ln(\gamma_i n_i) + \nu_i \left( \frac{p}{p_i^0} \right) \]  

(6.150)

To ensure that the reference chemical potential \( \mu_i^0 \) is identical in Equations 6.147 and 6.148, the reference pressure, \( p_i^0 \) is defined as the saturation vapour pressure \( p_{\text{sat}} \) of pure component \( i \). Equations 6.147 and 6.148 can then be rewritten for incompressible liquids and the membrane phase as

\[ \mu_i = \mu_i^0 + RT \ln(\gamma_i n_i) + \nu_i (p - p_{\text{sat}}) \]  

(6.151)

and for compressible gases as

\[ \mu_i = \mu_i^0 + RT \ln(\gamma_i n_i) + RT \ln \left( \frac{p}{p_{\text{sat}}} \right) \]  

(6.152)

A number of assumptions must be made to define any model of permeation. Usually, the first assumption is that the fluids on either side of the membrane are in equilibrium with the membrane material at the interface. This assumption means that there is a continuous gradient in chemical potential from one side of the membrane to the other. It is implicit in this assumption that the rates of absorption and desorption at the membrane interface are much higher than the rate of diffusion through the membrane. This appears to be the case in almost all membrane processes, but may fail, for example, in transport processes involving chemical reactions, such as facilitated transport, or in diffusion of gases through metals, where interfacial absorption can be slow.

The second assumption concerns the way this chemical potential across the membrane is expressed within the membrane. The solution-diffusion and pore-flow models differ in the way the chemical potential gradient is expressed [40–45].

The solution-diffusion model assumes that the pressure within a membrane is uniform and that the chemical potential gradient of a permeant across the membrane is represented only as a concentration gradient. The pore-flow model assumes that the permeant concentration within a membrane is uniform and that the chemical potential gradient across the membrane is represented only as a pressure gradient.

The consequences of these two assumptions are illustrated in Figure 6.13, which compares pressure-driven permeation of a one-component solution by solution-diffusion and by pore-flow. In both models, the difference in pressure across the membrane \( (p^0 - p_{\text{sat}}) \) produces a gradient in chemical potential according to Equations 6.151 and 6.152. In the pore-flow model, the pressure difference produces a smooth gradient in pressure through the membrane, but the solvent concentration remains constant within the membrane. The solution-diffusion model, on the other hand, assumes that when a pressure is applied across a dense membrane the pressure everywhere within the membrane is constant at the high-pressure value. This assumes, in effect, that solution-diffusion membranes transmit pressure in the same way as liquids. Consequently, the pressure difference across the membranes is represented as a concentration gradient within the membrane, with Equations 6.148 and 6.149 providing the mathematical link between pressure and concentration.
Consider the pore-flow model first. Combining Equations 6.148 and 6.149 in the absence of a concentration gradient in the membrane gives

$$J_i = c_i U_i v_i \frac{dp}{dv}$$

Equation 6.153

This equation can be integrated across the membrane to give Darcy’s law:

$$J_i = k (p^0 - p_i)$$

Equation 6.154

where $k$ is the Darcy’s law coefficient, equal to $U_i v_i$, and $l$ is the membrane thickness.

In the solution-diffusion model, the pressure within the membrane is constant at the high-pressure value $p^0$ and the gradient in chemical potential across the membrane is expressed as a smooth gradient in permeant activity ($\gamma_i n_i$). The flow that occurs down this gradient is again expressed by combining Equations 6.148 and 6.149, but this time in the absence of a pressure gradient, to give

$$J_i = -RT c_i U_i \left[ \frac{d(\gamma_i n_i)}{dx} \right]$$

Equation 6.155

In Equation 6.155, the gradient of component $i$ across the membrane is given as a gradient in mole fraction of component $i$. Equation 6.155 can be written in a more practical form using the term for concentration $c_i$ (g cm$^{-3}$), defined as

$$c_i = m_i \rho n_i$$

Equation 6.156

where $m_i$ (g mol$^{-1}$) is the molecular weight of $i$ and $\rho$ is the molar density (total number of moles per cubic centimetre). Equation 6.155 then becomes
\[ J_i = \frac{-RTU_i}{\gamma_i} \left[ \frac{d(\gamma_i n_i)}{dx} \right] \]  

(6.157)

This has the same form as Fick's law, where the term \( RTU_i \) is replaced by the diffusion coefficient \( D_i \). Assuming the activity coefficient \( \gamma_i \) is constant, then

\[ J_i = -D \frac{dc_i}{dx} \]  

(6.158)

Integrating Equation 6.158 over the thickness of the membrane gives

\[ J_i = \frac{D_i (c_i^0 - c_i^l)}{l} \]  

(6.159)

In the derivations that follow, we will use Equation 6.159 repeatedly, making the implicit assumption that the ideal form of Fick’s law is valid; that is, the diffusion coefficient \( D_i \) is a constant, independent of concentration. This simplifying assumption is invalid where swelling and plasticization of the membrane by absorbed permeate occurs. These effects do not change the fundamental process involved, but concentration-dependent diffusion and sorption effects must then be used to accurately describe membrane transport.

### 6.3 Pore Flow

#### 6.3.1 Pore-Flow Model

No equivalent unified theory (like Fick’s law) that is different from the solution-diffusion model as mentioned above is proposed for transport in microporous membranes in UF and microfiltration but not RO. However, the adaptation limit of pore-flow theory is not clear because the boundary between them is not definite.

Microporous membranes have different pore structures and their separation mechanisms differ significantly. The materials from which these membranes are made also differ, ranging from hydrophobic polyethylene and polysulfone to hydrophilic poly(vinyl alcohol) and cellulose acetate. When the pore diameter is larger than the diameter of permeant and a pressure difference exists across the membrane, bulk or convective flow through pores occurs. Such flow is undesirable because separation of the components in the feed does not occur, as shown in Figure 6.14a. When a concentration or partial pressure difference exists across the membrane for the various components, the components will diffuse at different rates through the pores, resulting in some separation, as shown in Figure 6.14b. When the pores are of the order of molecular size for some of the components in the feed mixture, the diffusion of those components will be restricted (hindered), resulting in enhanced separation. Molecules of size larger than the pores will be prevented altogether from diffusing through the pores (Figure 6.14c). This is often called sieving. A special case exists for gas diffusion where the pore size and/or pressure is such that the mean free path (defined as the average distance traversed by gas molecules between collisions) of the molecules is greater than the pore diameter. This is so-called Knudsen diffusion (http://www.separationprocesses.com/Membrane/MT_Chp05b.htm).

Stable pores are assumed to be present inside the membrane, and the driving force for transport is the pressure gradient across the membrane. Assuming a system at constant temperature where there are no external forces except pressure, one can derive from the Stefan–Maxwell equations [47] the following equations describing the total volumetric flux through a membrane.
- Hagen–Poiseuille equation – if the membrane is assumed composed of more or less cylindrical pores:

\[ N_v = -\frac{d_{\text{pore}}^2}{32\eta\tau} \frac{\Delta p}{(\varepsilon/\tau)} \]  

(6.160)

- Carman–Kozeny equation – if the membrane consists of a packed bed of particles:

\[ N_v = -\frac{d_{\text{pore}}^2}{180(1-\varepsilon)^2\eta} \frac{\varepsilon^3}{\tau} \Delta p \]  

(6.161)

The use of pore flow to describe transport in organic solvent nanofiltration (OSN) is common in the literature. Robinson et al. [48] reported that their experimental data for the permeation of \(n\)-alkanes, \(i\)-alkanes and cyclic compounds in a PDMS composite OSN membrane were consistent with the Hagen–Poiseuille pore-flow model of Equation 6.163. Whu et al. [49] also suggested this pore-flow model to explain the compaction and rejection behaviour of Koch MPF series commercial OSN membranes. Van der Bruggen et al. [50] described OSN rejection curves with log-normal pore size distributions in the commercially available membranes tested. Bhanushali et al. [51] suggested that a pore-flow model including an interaction parameter between the membrane and the permeating species could qualitatively describe OSN rejection data. Finally, Machado and Semiat [52] developed a resistances-in-series model and proposed that solvent transport through the MPF 50 membrane consists of three main steps: (1) transfer of the solvent into the top active layer, which is characterized by surface resistance, (2) viscous flow through nanofiltration (NF) pores and (3) viscous flow through support layer pores, all expressed by viscous resistances; that is:

\[ N_v = \frac{\Delta p}{R_s^0 + R_{\mu}^1 + R_{\mu}^2} \]  

(6.162)

where \(R_s^0\), \(R_{\mu}^1\) and \(R_{\mu}^2\) are the surface resistance and viscous resistances through NF active layer and support layers respectively. The surface resistance is proportional to surface tension difference.
between the solvent and the OSN top layer, and viscous resistances are proportional to solvent viscosity [53].

### 6.3.2 Knudsen Diffusion


Knudsen diffusion is where the characteristic dimension of the flow space is of the same or smaller order of magnitude as the mean free path ([http://en.wikipedia.org/wiki/Knudsen_flow](http://en.wikipedia.org/wiki/Knudsen_flow)).

For a gas passing through small holes in a thin wall in the Knudsen flow regime, the number of molecules that pass through a hole is proportional to the pressure of the gas and inversely proportional to its molecular weight. It is therefore possible to effect a partial separation of a mixture of gases if the components have different molecular weights. The technique is used to separate isotopic mixtures, such as uranium, using porous membranes [54]. It has also been successfully demonstrated for use in hydrogen production, as a technique for separating hydrogen from the gaseous product mixture created when water is heated at high temperatures using solar or other energy sources [55].

Knudsen diffusion is described by the Einstein relation as follows:

\[
D_s(c) = \lim_{t \to \infty} \frac{1}{6NT} \left\langle \sum_{i=1}^{N} |r_i(t) - r_i(0)|^2 \right\rangle
\] (6.163)

where \(D_s\) is the self-diffusion coefficient, which depends on the concentration \(c\); \(t\) is time, \(N\) is the total number of particles in the system and \(r_i\) is the position vector of particle \(i\). Knudsen diffusion occurs when the mean free path is relatively long compared with the pore size, so the molecules collide frequently with the pore wall. Knudsen diffusion is dominant for pores that range in diameter between 2 and 50 nm [56].

Knudsen diffusion is a means of diffusion that occurs when the scale length of a system is comparable to or smaller than the mean free path of the particles involved; for example, in a long pore with a narrow diameter (2–50 nm) because molecules frequently collide with the pore wall ([http://en.wikipedia.org/wiki/Knudsen_diffusion](http://en.wikipedia.org/wiki/Knudsen_diffusion)).

Consider the diffusion of gas molecules through very small capillary pores. If the pore diameter is smaller than the mean free path of the diffusing gas molecules and the density of the gas is low, the gas molecules collide with the pore walls more frequently than with each other. This process is known as Knudsen flow or Knudsen diffusion.

The Knudsen number is a good measure of the relative importance of Knudsen diffusion. A Knudsen number much greater than one indicates Knudsen diffusion is important. In practice, Knudsen diffusion applies only to gases, because the mean free path for molecules in the liquid state is very small, typically near the diameter of the molecule itself.

The diffusivity for Knudsen diffusion is obtained from the self-diffusion coefficient derived from the kinetic theory of gases:

\[
D_{AA} = \frac{\lambda \mu}{3} = \frac{\lambda}{3} \sqrt{\frac{8k_BT}{\pi M_A}}
\] (6.164)

or for diffusivity of species \(j\) in a mixture:

\[
D_j = \frac{8r_a}{3} \sqrt{\frac{RT}{2\pi M_j}}
\] (6.165)
For Knudsen diffusion, path length $\lambda$ is replaced with pore diameter $d_{\text{pore}}$, as species A is now more likely to collide with the pore wall as opposed to another molecule. The Knudsen diffusivity for diffusing species A, $D_{KA}$, is thus

$$D_{KA} = \frac{d_{\text{pore}}}{3} u = \frac{d_{\text{pore}}}{3} \sqrt{\frac{8R_g T}{\pi M_A}}$$

(6.166)

where $R_g$ is the gas constant ($8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$ in SI units), molecular weight $M_A$ is expressed in units of kilograms per mole and temperature $T$ has units of kelvin. Knudsen diffusivity $D_K$ thus depends on the pore diameter, species molecular weight and temperature.

Generally, the Knudsen process is significant only at low pressure and small pore diameter. However there may be instances where both Knudsen diffusion and molecular diffusion $D_{AB}$ are important. The effective diffusivity of species A in a binary mixture of A and B, $D_{Ae}$, is determined by

$$\frac{1}{D_{Ae}} = \frac{1 - \alpha y_A}{D_{AB}} + \frac{1}{D_{KA}}$$

(6.167)

where

$$\alpha = 1 + \frac{N_B}{N_A}$$

(6.168)

For cases where $\alpha = 0$ ($N_A = -N_B$), or where $Y_A$ is close to zero, the equation reduces to

$$\frac{1}{D_{Ae}} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}}$$

(6.169)

### 6.3.3 Surface Diffusion

#### 6.3.3.1 Fundamentals of Surface Diffusion

The diffusion behaviour of component $i$ in normal bulk solid state is expressed by Fick’s first law as follows:

$$J_i = -D \text{ grad } C_i$$

(6.170)

where $J_i$ (component m$^{-2}$ s$^{-1}$) is the permeation rate of component $i$, $C_i$ (component m$^{-3}$) is the concentration of diffused component $i$, and $D$ (m$^2$ s$^{-1}$) is the diffusion coefficient.

The behaviour of a component on the surface surroundings of a solid is different from that inside the solid. However, the diffusion of a component on the surface of a solid can be defined by Fick’s law.

As shown in Figure 6.15, we image a solid in which the concentration of a component is changed only in the $x$ direction. In this case, the diffusion amount in the $x$ direction is expressed as

$$J = -\frac{dC}{dx} \int_0^L D(y) dy$$

(6.171)

The diffusion coefficient is generally defined as a function of the depth direction $y$ of a solid.

In Figure 6.15, if the component in the solid is homogeneous from the interface at $y = 0$ to the interface at $y = L$, the diffusion amount in the $x$ direction is

$$J^B = -D_B \left(\frac{dC}{dx}\right) L$$

(6.172)
where \( D_B \) is the diffusion coefficient in a homogeneous solid. The permeation rate \( J^S \) by the diffusion via a surface is defined as

\[
J^S = \frac{1}{2} (J - J^B)
\]  

(6.173)

From Equations 6.171, 6.172 and 6.173, \( J^S \) by the diffusion via a surface is

\[
J^S = -\frac{1}{2} \left( \frac{dC}{dx} \right) \int_0^L [D(y)D_B] dy
\]  

(6.174)

When the diffusion coefficient of the surface is \( D_S (\text{m}^2 \text{s}^{-1}) \) and the thickness of the surface layer is \( \delta \), the integral term in Equation 6.174 is \( 2D_S\delta \). Namely, the following equation is given [7]:

\[
J^S = -\frac{1}{2} \left( \frac{dC}{dx} \right) 2D_S\delta = -D_S \left( \frac{dC}{dx} \right) \delta
\]  

(6.175)

Surface diffusion is used to explain a type of pore diffusion in which solutes adsorb on the surface of the pore and hop from one site to another through interactions between the surface and molecules [57].

Dr Richard W. Baker explained a surface diffusion phenomenon clearly using Figure 6.16 [57].

Surface adsorption and diffusion add a second contribution to gas permeation that can occur in small-pore-diameter membranes. This phenomenon is shown schematically in Figure 6.16. Adsorption onto the walls of the small pores becomes noticeable when the pore diameter drops below about 100 Å. At this pore diameter the surface area of the pore walls is in the range 100 m\(^2\) cm\(^{-3}\) of material. Significant amounts of gas then adsorb onto the pore walls, particularly if the gas is condensable. Often the amount of gas sorbed on the pore walls is much greater than the amount of nonsorbed gas. Sorbed gas molecules are mobile and can move by a process of surface diffusion through the membrane according to a Fick’s law type.

### 6.3.3.2 Microporous Membrane and Surface Transport

A full treatment of microporous membrane transport by site hopping is found in the literature [58,59] and is summarized below. This treatment is also applicable to the case of surface transport by diffusion hopping on the pore walls of meso- and macroporous structures.

The limited microstructural definition of current membranes justifies the use of a simple competitive Langmuir chemical potential for species \( l \) in the membrane phase:

\[
\mu_{l,m} = \mu_{l,m}^0 + RT \ln \frac{\theta_l}{1 - \theta_l}
\]  

(6.176)

Since there is little evidence for surface transfer limitations, membrane concentrations at the feed and permeate side can be derived from \( \mu_{l,g} = \mu_{l,m} \) to obtain the Langmuir isotherm:

\[
\frac{\theta_{l,f,p}}{1 - \theta_{l,f,p}} = \frac{P_{l,f/p}}{P_0} \exp \left( \frac{\mu_{l,g}^0 - \mu_{l,m}^0}{RT} \right) = \frac{P_{l,f/p}}{P_0} \exp \left( -\frac{\Delta s_l^0}{R} \right) \exp \left( \frac{\Delta h_l^0}{RT} \right)
\]  

(6.177)
A high sorption affinity is obtained when the molecule actually fits in the structure and if that is the case, it has an energetically favourable interaction with the membrane material \( (\Delta h_l^0 < 0) \). The occurrence of size exclusion is mathematically equivalent to \( \Delta h_l^0 < 0 \). The molecule’s mobility \( b \) is determined by the hopping activation barrier and the availability of vacant neighbouring sites. Membrane separation for a binary mixture can be obtained by calculating individual fluxes from diagonal Onsager transport equations. The most generic expression for a quasi-homogeneous Langmuir lattice is

\[
 j_l = -\tilde{f}_{L,1} b_l^0 e^{\theta_{11}^c} \nabla \theta_{11} + \theta_{11} \nabla \theta_{12} \tag{6.178}
\]

Expressions, similar to Equation 6.178, can be obtained for other (numbers of) components. Effects of grain boundaries and orientational tortuosity in polycrystalline zeolites may require additional correction factors. In the absence of correlation effects, \( b_l \) can be written as

\[
 b_l = b_l^0 (1 - \theta) b_l^0 = b_l^0 \exp \left( -\frac{\mu_l^h}{RT} \right) \tag{6.179}
\]
The nonequilibrium correlation factor $0 < f_{L,1} < 1$ provides a correction for the oversimplification in Equation 6.179 that zero neighbouring sites is always statistically distributed. Generally, $f_{L,1}$ is close to one but can become very small for mobile molecules with low $\theta$ that percolate on a micropore network that is also occupied by slower molecules with high $\theta$ [60]. This leads to the distinction of two types of microporous or surface diffusion separation:

- **Type 1** Both molecules have little affinity and hence $\theta \to 0$. This type of behaviour is often found for small gas molecules, low pressures and high temperatures. It results in significant simplification of Equation 6.178, so that $a_{l1,l2} = a_{l1,l2}^0$ in the absence of external mass transfer limitations.

- **Type 2** One of the molecules has a much higher affinity (and hence lower mobility). It may occupy $>50\%$ of the sites and form a percolative network, nearly impermeable for the other molecule.

Most studies of microporous amorphous silica membranes assume, implicitly or supported by experiments, the occurrence of type 1 behaviour. Studies of zeolite membranes, however, often consider separation of hydrocarbons with a much higher affinity and take the possibility of type 2 behaviour into account. Type 2 behaviour can also be expected with CO$_2$ and H$_2$O separation with amorphous silica membranes and may actually lead to preferential transport of these molecules. For single gas and type 1 permeation on a Langmuir lattice, any $\theta_l$ and normal gradients

\[
j_l = -b_l^0 \theta_l c_{tot} RT \nabla \theta_l = -D_l \nabla c_l
\]

which is Fick’s first law with the chemical diffusion coefficient $D_l = b_l^0 RT$, independent of $\theta$. For type 1 behaviour $\theta \to 0$ so that Equation 6.177 simplifies to the Henry isotherm, which means that it can easily be combined with Equations 6.179) and 6.180 to obtain for each component

\[
f_{j1} = \frac{j_l}{p_{l,j} - p_{l,p}} = \frac{b_l^0 \theta_l c_{tot} RT}{p^0 X} \exp \left( - \frac{\Delta s_l^0}{R} \right) \exp \left( \frac{\Delta h_l^0 - \mu_l^0}{RT} \right)
\]

Molecules in micropores can be considered as being captured in a potential well with depth approximately equal to $\Delta h_l^0$. This means that the activation energy that is needed for hopping to a neighbouring site has a magnitude similar to $\Delta h_l^0$. The result is that, contrary to what is the case for dense membranes, single gas and type 1 microporous membranes generally exhibit fairly weak temperature dependence of Equation 6.181. A slight increase with $T$ of permeance at low $p$ is found for most light gases. On the other hand, $f_{CO_2}$, for which the Henry approximation may not apply, shows a slight decrease with $T$. The apparent thermal activation $\exp(-u^0/RT)$ of these permeances has little direct physical meaning. A positive $u^0$ is an indication of dominant microporous membrane transport. A negative $u^0$, however, may be difficult to distinguish from similar behaviour for transport in meso- and macropores [62].

**References**


7

Phenomena during Membrane Permeation and Separation

7.1 Concentration Polarization

When a membrane is used for a separation, the concentration of any species being removed is higher near the membrane surface than it is in the bulk of the stream. This condition is known as concentration polarization and exists in all ultrafiltration and reverse osmosis (RO) separations. The result of concentration polarization is the formation of a boundary layer of substantially high concentration of substances being removed by the membrane. The thickness of the layer and its concentration depend on the mass of transfer conditions that exist in the membrane system. Membrane flux and feed flow velocity are both important in controlling the thickness and the concentration in the boundary layer. The boundary layer impedes the flow of water through the membrane, and the high concentration of species in the boundary layer produces a permeate of inferior quality in ultrafiltration applications; relatively high fluid velocities are maintained along the membrane surface to reduce the concentration polarization effect.

In membrane separation processes there is a concentration gradient near the membrane interface due to the build-up of the retained compounds. This effect is called ‘concentration polarization’. It increases with increasing permeate flux, which reduces the driving force for permeation, resulting in a lower flux and a less selective separation.

In membrane separation of liquids, \( J_i \) represents the flux of the retained component \( i \) through the membrane, while \( J \) represents the total membrane flux (see Figure 7.1). At steady state and one-dimensional transport (in the \( z \)-direction) \( J \) also equals the overall convective flux in the direction of the membrane. From a simple mass balance assuming Fick’s diffusion law to be valid, the following equation is given:

\[
J_i = -D_i \left( \frac{dC_i}{dz} \right) + C_i J \tag{7.1}
\]

Term 1 on the right-hand side of Equation 7.1 represents the back-diffusion of component \( i \) into the bulk liquid phase, and term 2 is the total convective flux of \( i \) toward the membrane. Because \( J_i/J \) is the concentration \( C_{pi} \) of \( i \) in the permeate, which is constant at steady state, Equation 7.1 can be integrated between the boundaries

- \( z = 0 \), concentration of \( i \) at the interface of the membrane and the bulk solution
- \( z = -\delta \), the concentration of \( i \) in the bulk phase
where $\delta$ is the laminar diffusion layer:

$$\frac{C_{mi} - C_{pi}}{C_{bi} - C_{pi}} = \exp\left(\frac{J_i}{k_i}\right)$$

in which $k_i = D_i/\delta$ is the mass transfer coefficient. Correspondingly, such an equation can be derived for eventual concentration polarization effects at the permeate side of the membrane. According to Equation 7.2, the concentration of the retained component at the membrane interface increases with respect to its concentration in the bulk phase if the ratio of the total flux and the mass transfer coefficient increases, thus reducing the concentration gradient across the membrane of the component to be separated, and hence its flux. This unfavourable effect of concentration polarization can be reduced by increasing the mass transfer coefficient. The latter can be achieved by maintaining a high flow rate of the liquid phase along the membrane surface and by applying turbulence promoters (spacers) between the membranes. For gases it is convenient in Equation 7.1 to express the concentrations in mole fractions. If, furthermore, we express the fluxes in volume rates at standard pressure $P_0$, this equation transforms into

$$J_i = -\left(\frac{P}{P_0}\right)D\left(\frac{d_x}{dz}\right) + x_i J$$

(7.3)

where $P$ is the feed (bulk) pressure and $D$ the mutual diffusivity of the gas mixture. According to the kinetic gas theory of ideal gas mixtures, $D$ is independent of concentration and inversely proportional to the pressure. Therefore:

$$\frac{P}{P_0}D = D_0 = \text{constant}$$

(7.4)

The flux of an ideal gas $i$ through a membrane of permeability $K_i$ is expressed by

$$J_i = K_i(P x_{0i} - P y_{0i})$$

(7.5)

where $p$ denotes permeate pressure, and $x_{0i}$ and $y_{0i}$ are the mole fractions of $i$ at the membrane interfaces with the bulk and permeate respectively.

The following equation can be derived [1] from Equations 7.3, 7.4 and 7.5:

$$x_i = Y_i \left\{ 1 + \left[ \frac{J}{K_i(P - p)} - 1 \right] \left( 1 - \frac{p}{P} \right) \exp\left( -\frac{J}{b_1} \right) \right\} - \frac{p}{P} (Y_i - y_i) \exp\left( -\frac{J}{b_1} - \frac{J}{b_2} \right)$$

(7.6)
where \( x_i (y_i) \) is the concentration of \( i \) in the bulk phase, \( Y_i \) is the local permeate concentration of \( i \), and \( b_1 = D_0/\delta_1 \) and \( b_2 = D_0/\delta_2 \) are the back diffusion factor at the bulk and permeate sides respectively.

Equation 7.6 relates the local permeate concentration to the bulk permeate and concentration, depending on permeation conditions and membrane properties. It predicts optimum separation if the back diffusion factor (which in essence represents a kind of mass transfer coefficient) \( b \gg J \), while the selectivity ceases if \( b \ll J \).

The second term on the right-hand side of Equation 7.6 represents a contribution to the mode of membrane operation. For counter-current flow of permeate and retentate it predicts increasing selectivity, and for co-current flow reduced selectivity. Calculations show that these effects are maximum for low-selectivity membranes combined with a relatively high back diffusion factor. For crossflow, which in fact corresponds to the conditions where \( b \ll J \), the second term vanishes. The latter mode of operation occurs in all presently available gas modules, due to the presence of a porous support, which causes significant mass-transfer limitations [2].

### 7.1.1 State of Boundary Layer on Membrane Surface

In membrane permeation, a phenomenon called concentration polarization occurs, in which a solute rejected by the membrane in the interfacial neighbourhood (boundary layer) between the membrane and the solution on the high-pressure side is accumulated. In particular, this effect is not negligible in ultrafiltration and RO.

In ultrafiltration, the flux of water through the membrane decreases because a gel layer is formed on the membrane surface, and in RO the osmotic pressure in the interfacial neighbourhood is increased by a decrease in the effective pressure difference, and consequently the flux also decreases.

In membrane separation processes, concentration polarization refers to the emergence of concentration gradients at a membrane–solution interface resulting from selective transfer of some species through the membrane under the effect of transmembrane driving forces [3]. Generally, the cause of concentration polarization is the ability of a membrane to transport some species more readily than others (which is the membrane permselectivity): the retained species are concentrated at the upstream membrane surface, while the concentration of transported species decreases, as shown in Figure 7.2. Thus, the concentration polarization phenomenon is inherent to all types of membrane separation.

![Figure 7.2](image-url) Component 1 is rejected and component 2 is permeated.
processes. In the cases of gas separation, pervaporation, RO, nanofiltration (NF), ultrafiltration and microfiltration separations, the concentration profile has a higher level of solute nearest to the upstream membrane surface compared with the more or less well-mixed bulk fluid far from the membrane surface. In the case of dialysis and electrodialysis, the concentrations of selectively transported dissolved species are reduced at the upstream membrane surface compared with the bulk solution (http://en.wikipedia.org/wiki/Concentration_polarization).

### 7.1.2 Concentration Polarization in Gas Separation

Mass transfer coefficients on the surface of a porous glass membrane were obtained from separation tests of an H$_2$–CO mixture. These data agree with the correlation presented by Ghosh and Upadhyay for mass transfer on an impermeable wall [4]. In addition, the effects of the selectivity of the membrane and bulk composition on the concentration polarization phenomenon are discussed and the limiting permeability, which is affected by the polarization, is represented as a function of mass transfer coefficient [5].

A mathematical model was established successfully to analyse the gas separation concentration polarization, which becomes an important problem due to the rapid development of membranes, especially the increase of permeation rate. The influences of membrane performance and operation parameters on concentration polarization were studied in terms of permeation fluxes of the more and the less permeable gases and separation factor. Sample calculations were presented for the two typical gas separation applications, hydrogen recovery and air separation, with shell-side feed in a hollow-fibre module. The permeation rate was found to be a dominating factor in affecting concentration polarization, while the influences of separation factor were found to be significant initially and to level off gradually. Increasing feed gas velocity leads to a decrease in the concentration polarization. Operation pressures effect is limited and the composition of feed gas shows no effect. The range in which concentration polarization is significant has been identified by studying the combined effects of the permeation rate, separation factor and feed gas velocity. Concentration polarization is important for process analysis and design when the permeation rate of the more permeable gas is greater than $1 \times 10^{-4}$ cm$^3$ (STP) cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$ (100 GPU) [6].

Hara et al. [7] studied hydrogen separation from binary gas mixtures, Ar–H$_2$ and CO–H$_2$, using a double-tube type of palladium membrane reactor (PMR) and analysed by solving mathematical models taking into account mixing diffusion of hydrogen in the radial direction of the catalyst-packed bed. The experiment showed that carbon monoxide prevented hydrogen permeation through the membrane at temperatures less than 280 °C. The decline in hydrogen permeation could be estimated by solving a model describing the concentration polarization and the hindrance by carbon monoxide. Furthermore, the mathematical models were applied to analyse methanol decomposition in the same PMR, showing that a drop in hydrogen permeation due to both the factors had a significant influence on the performance of the PMR.

Nemmanni and Suggala [8] developed a one-dimensional mathematical model to analyse the concentration polarization phenomenon for the separation of gas mixtures in composite hollow-fibre membranes. An analytical expression was developed for determining the interfacial concentration at the interface of dense and porous support layers. Further, the model accounted for the non-ideality of the gas mixture. Both co-current and counter-current flow configurations for the separation of hydrogen from a three-component mixture were studied. The effects of feed-side pressure and velocity, as well as permeability, on concentration polarization were probed. It is apparent from this study that the concentration polarization phenomenon significantly affects the separation efficiency at higher permeability values.
7.1.3 Concentration Polarization in Pervaporation

A vibrating membrane module currently marketed for filtration applications was evaluated for the separation of volatile organic compounds (VOCs) from aqueous solutions by pervaporation. Preliminary screening experiments with three VOCs, three silicone membranes, and in the presence and absence of a surfactant were performed to determine if further consideration of the vibrating module for a field demonstration project was warranted. The primary process variables studied were vibrational amplitude and liquid flow rate. The vibrations greatly reduced concentration polarization in the system, as inferred from an order of magnitude increase in the overall mass transport coefficient. Mass transfer coefficients for the vibrating module compared favourably with those for traditional spiral-wound modules [9].

Huang et al. [10] fabricated ethylene propylene diene monomer rubber membranes in thin-film composite form to separate an aroma compound, ethyl butyrate, from water and studied the effects of operating parameters on the pervaporation performance. A resistance-in-series model was applied to the pervaporation results to estimate the transport of the permeant. The partial flux of ethyl butyrate increased with the feed concentration. It was also found that the total flux decreased with increasing permeate pressure, whereas the organic flux increased. The effect of concentration polarization on the pervaporation performance was observed with changes in the feed flow rate. It was observed that the overall mass transfer coefficient was a function of the feed flow rate at fixed feed concentration.

Lui et al. [11] applied pervaporation as an innovative membrane-based separation technology for VOC removal from contaminated groundwater. Concentration polarization is a process phenomenon occurring in pervaporation and several other membrane-based separation technologies. Concentration polarization, defined as concentration gradient of permeating solute between the bulk and the region near the membrane surface, becomes a limiting factor in pervaporation separations using high-performance membrane materials in VOC removal operations. Thus, the ability to predict the impact of concentration polarization upon process performance is highly desirable in process design and optimization. A mathematical model was developed to illustrate the interplay between concentration polarization and process performance in pervaporation operation of VOC removal in a membrane channel with rectangular cross-section. By incorporating pervaporative mass transfer, laminar hydrodynamics and boundary-layer theory, the model was built to allow theoretical analysis of the sensitivity of flow velocity, feed concentration and concentration polarization index upon the transmembrane flux and longitudinal mass flow.

The effect of the concentration boundary layer on the membrane separation is well known and intensively discussed in the literature. In most of these studies, the effect of the membrane layer on the separation is missing. Recently, some papers have been published that take into account both the concentration polarization layer and the membrane layer on the membrane separation by means of pervaporation. These papers use mostly the resistance-in-series model and try to incorporate the effect of the boundary-layer’s Peclet number as well. These models do not make possible the direct calculation of the separation characteristics (e.g. the enrichment or the polarization modulus). A coupled model of concentration polarization and diffusion transport through the membrane was developed which enables the direct prediction of the concentration distribution in both layers and other important separation properties as enrichment, polarization modulus, and so on. The calculated data were compared with the experimental ones taken from the literature. The excellent agreement between the measured and predicted data proves that the equations developed are suitable to describe the pervaporation process or to predict its effectiveness. Also demonstrated was the strong effect of the membrane properties on the concentration distribution of both layers and on the mass transfer rate, and consequently on the separation efficiency [12].
The increase of the diffusion coefficient, due to its concentration dependency, can strongly increase the mass transfer rate through the membrane. Accordingly, the negative effect of the mass transfer resistance of the polarization layer can essentially be increased on the separation efficiency, especially in the case of low solute concentration in the feed phase. This effect can also exist at high solute concentration at extremely high pervaporation rate, as illustrated by a case study. The simultaneous effect of the concentration polarization and membrane layers was discussed in the case of an exponentially or linearly concentration-dependent diffusion coefficient. Mass transfer rate, enrichment and the polarization modulus were expressed in implicit, closed mathematical equations involving the transport parameters of the two layers. There was discussion about how the increasing diffusion coefficient affects the concentration distribution in the polarization and the membrane layers, and because of this the mass transfer rate, enrichment or the polarization modulus (indicating the effect of the polarization layer). It is shown how strongly the dimensionless plasticizing coefficient can decrease the polarization modulus and can affect the concentration distribution in the polarization and the membrane layers as well as the ratio of the diffusion dependent mass transfer rate compared with that without plasticizing effect. This case study illustrates the effect of the external mass transfer resistance on the mass transfer rate and on the concentration distribution in the case of a high value plasticization coefficient [13].

7.1.4 Concentration Polarization in Reverse Osmosis

Johnson and Acrivos [14] investigated concentration polarization in the desalination of salt water by RO for the case in which the desalination membrane is a vertical flat plate. An expression for the concentration of salt at the surface of this membrane is obtained by expanding the solution of the governing laminar boundary layer equation for natural convection about the leading edge of the plate. This expression, together with an equation for the membrane concentration at large distances from the leading edge, can be used then to predict the polarization effect at any point along the membrane.

Benito et al. [15] investigated and modelled the effect of feed water flow rate on the concentration polarization of magnesium sulfate, sodium chloride and sodium selenate in RO spiral-wound elements. Experiments were performed with 40" long and 2.5" diameter spiral-wound elements tested with feed solutions of the single electrolyte magnesium sulfate, and a mixture of sodium chloride and sodium selenate as major and trace components respectively. The feed flow rates investigated ranged from 1.12 to 13.5 L min$^{-1}$, corresponding to Reynolds numbers $Re$ from 25 to 300. The element was modelled by dividing it into $n$ identical sub-elements, each separated into two compartments, feed channel and product water carrier, by the RO membrane. The feed channel compartment of each sub-element was assumed to be an ideal continuous-flow stirred tank reactor. Model predictions correlated generally well with experimental observations. Predicted product water flow rates and solute concentrations were within 12% and 24% respectively of the corresponding experimental values.

A dimensionless governing equation was formulated for a crossflow RO process in which the local variation of concentration polarization was rigorously considered. It was shown in this formulation that the crossflow RO process could be fully characterized with a single dimensionless parameter. The coupling between permeate flux and concentration polarization was properly solved and a closed-form analytical solution was obtained. This analytical solution enabled a convenient investigation of concentration polarization in the RO process. The significance of local variation of concentration polarization was demonstrated, and the operations of RO under various conditions were simulated and investigated with the newly developed model [16].

Nowadays, there is an attempt to develop new membrane separation cells to minimize the concentration polarization phenomenon. An efficient contact between the fluid and the membrane is...
fundamental to reach this objective. The hydrodynamic characteristics of a liquid jet impinging perpendicularly on a flat and round-shaped membrane was explored by Miranda and Campos [17]. The jet flow was confined by a conical wall extended from the jet nozzle to a short distance above the membrane. The momentum and mass transport equations in laminar regime were solved numerically by a finite-difference scheme. The solution depends on \( Re \) and Schmidt (\( Sc \)) numbers and on two new dimensionless groups: \( \Pi_v \) and \( \Pi_{\pi_0} \). \( \Pi_v \) represents the ratio between the permeate velocity through a non-polarized membrane surface and the average jet velocity at the cell inlet, and \( \Pi_{\pi_0} \) the ratio between the osmotic pressure over a non-polarized membrane surface and the static pressure difference across the membrane. The concentration polarization was investigated for wide ranges of values of these groups, and new indexes were defined to quantify the polarization level. For increasing values of \( Re, Sc \) and \( \Pi_v \), the polarization level and the concentration at the membrane surface increase. The polarization level increases for increasing values of \( \Pi_{\pi_0} \), but the concentration at the membrane surface tends to the bulk concentration. The suction effects on the velocity profiles in the layer over the membrane were also analysed. A compact module of jet cells was proposed.

Accurate prediction of concentration polarization phenomena is critical for properly designing RO processes because it enhances trans-membrane osmotic pressure and solute passage, as well as surface fouling and scaling phenomena. The objective of the study by Kim and Hoeck [18] was to compare available analytical concentration polarization models with a more rigorous numerical concentration polarization model and experimental concentration polarization data. A numerical concentration polarization model was developed to enable local description of permeate flux and solute rejection in crossflow RO separations. Predictions of channel-averaged water flux and salt rejection by the developed numerical model, the classical film theory model and a recently proposed analytical model were compared with well-controlled laboratory-scale experimental data. At operating conditions relevant to practical RO applications, film theory and the numerical model accurately predicted channel-averaged experimental permeate flux and salt rejection data, while the more recent analytical model did not. Predictions of local concentration polarization, permeate flux and solute rejection by film theory and the numerical model also agreed well for realistic ranges of RO process operating conditions.

Wang and Tarabara [19] determined the concentration of rejected salt at the membrane surface when colloidal particles deposited on the membrane were determined experimentally based on measured salt permeability constant. This approach allowed for a clear identification of individual contributions of concentration polarization and colloidal fouling to the permeate flux decline. The observed transient behaviour of permeate flux, salt rejection, mass of deposited colloids and effective porosity of the deposited layer unequivocally pointed to the importance of the two-way coupling between salt concentration polarization and colloidal deposition. After the initial increase in the effective porosity of the fractal colloidal deposit, the porosity reached a maximum, and then gradually decreased to a steady-state value that depended strongly on the solution ionic strength. Both the resistance of the colloidal deposit and osmotic pressure, which could be enhanced in the presence of colloids, contributed significantly to the permeate flux decline. A short-term increase in salt rejection was observed upon introduction of colloidal particles into the feed in the absence of a membrane channel spacer. This increase could be sustained over the long term in the presence of spacers and was attributed to the depolarization of the salt boundary layer due to the local mixing by the concentrated flowing layer of colloidal particles.

Chong et al. [20] reported a sodium chloride tracer response technique to determine the effect of fouling on concentration polarization level in an RO system operated in the constant flux mode. Colloidal silica and alginic acid were used as model fouling agents. It was found that the formation of the ‘unstirred’ fouling layer greatly exacerbated the concentration polarization level in RO separations,
with a more pronounced effect at high flux operation. The results suggested that operation at high flux could significantly reduce the apparent permeability, but that this is through a dramatic increase in concentration polarization and consequent loss in driving force via the enhanced osmotic pressure rather than through an additional hydraulic resistance. The study also shows that the sodium chloride tracer response technique is a promising technique that can be applied as a non-invasive tool to detect and monitor fouling development in RO.

7.1.5 Concentration Polarization in Nanofiltration

In predicting the NF process, concentration polarization should be seriously considered. Since many empirical expressions for the mass transport in the concentration polarization layer are reported, it seems difficult to choose a proper one. Yang et al. [21] discussed the concentration polarization development along the bulk flow direction in crossflow NF using a theoretical model, and then compared the differences of the concerned empirical expressions for the mass transport across the concentration polarization layer. The differences that the expressions caused were also presented with the NF experiment of the dilute PEG 600 solution. The empirical expressions and Schock–Hickey model were coupled to fit the experiment result. In the regressions of Schock–Hickey model parameters, the pressure loss along the bulk flow channel and the bulk concentration variation were both considered. It was found that the concentration polarization along the bulk flow direction increased greatly before the boundary layer was fully developed. However, the polarization degree within a mesh length of 0.003 m was not serious. On the other hand, the empirical correlations gave sharply different concentration polarization degrees. Schock and Hickey’s expressions gave a comparatively close mass transport coefficient only when the bulk flow rate was around 0.15 m s\(^{-1}\). Eriksson’s expression showed that the concentration polarization in the spiral-wound element was not serious only if the bulk flow rate was not much less than 0.1 m s\(^{-1}\). The results suggested that Eriksson’s expression was still the best choice for the polarization correction, while the other candidates seemed to overestimate the polarization.

A coupled model of concentration polarization and pore transport of multicomponent salt mixtures in crossflow NF rigorously predicts local variations of ionic concentrations, flux and individual ion rejections along a rectangular crossflow filtration channel by a coupled solution of the convective–diffusion and extended Nernst–Planck equations. Coupling the pore transport model with the multicomponent convective–diffusion equation in the concentration polarization layer provides a comprehensive understanding of the interplay between concentration polarization and salt rejection. The coupled model is used to predict the local variations of ion rejection, permeate flux and mixture composition in a rectangular crossflow filtration channel for three-component salt mixtures. The total membrane surface concentration of the ions and the ratio of different ions in the mixture (salt ratio) can change considerably along a crossflow filtration channel, and, consequently, cause remarkable variations in intrinsic ion rejections with axial position in the channel [22].

Geraldes and Afonso [23] developed a simple and accurate model for predicting the concentration polarization index in the NF/RO of dilute multi-ionic solutions. On the grounds of this model, the total flux of the ion \(i\) at the feed-solution–membrane interface consists of the sum of the diffusion, convection and migration fluxes, the former of which is determined by conventional mass-transfer correlations duly corrected to take into account the permeation through the membrane (suction effect). The coupling of the ionic fluxes is enforced by the electroneutrality requirement at the feed-solution–membrane interface. The model developed dispenses with the arbitrary assumption of the thickness of a film layer in the vicinity of the membrane surface. Assessing the accuracy/validity of this model with multi-ionic solutions would be rather harsh; thus, the model accuracy and ranges of
validity were ascertained for a benchmark case: NF/RO of single salt solutions. The model predicts approximate concentration polarization indexes of the salts $A^+B^-$, $A^{+2}B^{2-}$ and $A^{+3}B^{3-}$ (or $A^{2-}B^{-2}$ and $A^{3-}B^{-3}$) with positive deviations lower than 10% with respect to the benchmark concentration polarization index for ion diffusivity ratios $D_1/D_2$ (or $D_2/D_1$) in the range 0.16–5.5 and $\phi \equiv J_v/k_c < 3$, where $J_v$ is the permeation flux and $k_c$ is the mass-transfer coefficient of the salt for vanishing mass-transfer rates at impermeable walls. The main assumption of the model – the individual mass-transfer coefficients of the ions are independent of each other – appears to hold in a broad range of conditions, for single salt solutions. The model developed was expeditiously applied to predict the concentration polarization in the NF of solutions containing $Na^+$, $Cl^-$ and a dye $^3-$ (experimental data of [24] and its predictions are in fair agreement with the predictions of the extended Nernst–Planck equations in the film layer of the ‘slowest’ ion).

Morão et al. [25] determined the flow structure and solute concentration distribution in an NF/RO plate-and-frame module with radial thin feed channels that have considerable entrance and outlet effects by computational fluid dynamics (CFD). Simulations were performed for binary aqueous solutions, Re in the range 64–570 (based on the channel height) and Sc between 450 and 8900. The CFD simulations showed that both the velocity field and the solute concentration distribution exhibit important three-dimensional effects, and at rather low $Re$ ($\geq 118$) flow instabilities start to appear in the entrance/outlet regions. However, those instabilities do not affect significantly the average concentration polarization on the membrane surfaces up to the maximum $Re$ simulated (570). The friction factors predicted by CFD were in agreement with the corresponding experimental values for the range of $Re$ investigated. The simulations allowed the determination of a mass-transfer correlation at vanishing mass-transfer rates and a correlation for mass-transfer correction factor. The mass-transfer correlation obtained at vanishing mass-transfer rates was compared with the ones available in the literature as well as with the Sherwood numbers determined by the velocity variation method, using diluted aqueous solutions of glycerol. It was also found that a generalized mass-transfer correction factor correlation for high mass-transfer rates, previously developed for membrane modules with two-dimensional configurations, is still valid to predict the average concentration polarization in the module investigated.

De carried out steady-state modelling of NF of a textile effluent [26]. The model comprised three distinct parts. Film theory was used to account for the solute transport outside the membrane surface within the mass-transfer boundary layer. An osmotic pressure model and a solution-diffusion model were used to quantify the solvent and solute flux through the porous membrane. The osmotic pressure model was modified by incorporating adsorption of dyes onto the membrane surface. The system had three components; namely, Cibacron black and Cibacron red and the salt as sodium chloride. The model had three parameters; namely, solute permeability of two dyes and sodium chloride through the membrane. These parameters were estimated by comparing the calculated and experimental data of permeate flux and permeate concentration. It was observed that membrane hydraulic resistance and the resistance due to concentration boundary layer were more significant. The calculated permeate flux was within ±20% of the experimental data. Values of resistance due to adsorption of dyes onto the membrane surface were calculated to be about 2–3% of total resistance, and those due to the concentration boundary layer were about 47%.

One of the major difficulties for the prediction of separation performances in the case of multi-ionic mixtures NF lies in the description of the concentration polarization phenomenon. The usual models available in the literature do not take account of the polarization phenomenon or only describe it cursorily. Very few studies dedicated to the understanding and the specific description of the concentration polarization phenomenon are available in the literature, and a two-dimensional multi-ionic model describing the layer heterogeneity along the membrane length has yet to be proposed. The
model used in the work of Déon et al. [27], called the pore and polarization transport model, allows an accurate description of the concentration polarization layer occurring during the filtration of multi-ionic solutions by taking account of the radial electromigrative transport in the layer, the turbulence, as well as the axial heterogeneity. In this context, their paper aims at proposing a numerical investigation of the influence of operating conditions on the behaviour of the polarization layer occurring in the membrane vicinity. The input parameters governing the transport through the membrane had been assessed in a previous study in the same experimental conditions, so that only the polarization layer was investigated here. The proposed model, which was previously validated on experimental observed rejection curves, was then used to understand how operating conditions, such as applied pressure, feed flow rate or divalent ion proportion, govern the polarization phenomenon. For this purpose, concentration and thickness axial profiles along the membrane length and radial profiles within the polarization layer were investigated for various conditions. Finally, the impact of the type of divalent ion and the number of ions was also studied on various mixtures.

7.1.6 Concentration Polarization in Ultrafiltration

Concentration polarization, the accumulation of retained solute next to an ultrafiltering membrane, elevates osmotic pressure above that which would exist in the absence of polarization. For ultrafiltration in a cylindrical tube, use of the radially averaged solute concentration results in an underestimate of osmotic pressure, yielding an effective hydraulic permeability \( k \) less than the actual membrane hydraulic permeability \( k_m \). The extent to which \( k \) and \( k_m \) might differ in an ultrafiltering capillary has been examined theoretically by solution of the momentum and species transport equations for idealized capillaries with and without erythrocytes. For diameters, flow velocities, protein concentrations and diffusivities, and ultrafiltration pressures representative of the rat glomerular capillary network, the results indicate that the effects of polarization are substantial without erythrocytes (\( k / k_m = 0.7 \)) and persist, but to a lesser extent, with erythrocytes (\( k / k_m = 0.9 \)), the reduction in polarization in the latter case being due to enhanced plasma mixing. In accord with recent experimental findings in rats, \( k \) is found to be relatively insensitive to changes in glomerular plasma flow rate [28].

Yeh and Cheng [29] applied the concentration polarization model to analyse the permeate flux of hollow-fibre membrane ultrafiltration. Comparison of theoretical prediction with experimental data was made under various transmembrane pressures, feed velocities and solution concentrations. Both theoretical prediction and experimental results show that average permeate flux increases as transmembrane pressure or feed velocity increases, but decreases when solution concentration increases.

Flux reductions experienced during ultrafiltration are due either to concentration polarization or fouling. It is usually difficult to distinguish between these two phenomena, but by using a turbulence-promoting module it is possible to determine the reversibility of a flux reduction, and thus distinguish between concentration polarization and fouling. By using a turbulence-promoting module, it is also possible to distinguish between different cases of fouling. In a paper by Jönsson, fouling caused by the deposition of material at the surface of the membrane was illustrated by results from tests with a silica sol, and fouling due to interactions in the membrane matrix was illustrated by results from ultrafiltration of a low-molecular organic solute [30].

Jönsson et al. [31] developed a theoretical model that describes ultrafiltration of nonionic surfactants. The model takes into account the fact that surfactants start to aggregate and form micelles at the critical micelle concentration. The model can be used to predict the performance of the membrane if the transport properties inside and at the membrane surface as well as the surfactant association behaviour are known. Three hydrophilic ultrafiltration membranes, made of regenerated cellulose, were used in the investigation. The cut-offs of the membranes were 10,000, 20,000, and
30,000 Da. The surfactant used in the investigation was the nonionic surfactant Triton X-100. The influence of the concentration of surfactant, transmembrane pressure and pure water flux were studied theoretically and experimentally. From the results presented in this work it can be concluded that the calculated values are in good agreement with experimental data.

Sarkar et al. [32] studied the effects of an externally applied electric field during crossflow ultrafiltration of synthetic juice (mixture of sucrose and pectin) and measured the gel thicknesses optically. The introduction of the electric field was found to be quite effective in enhancing the permeate flux due to the electrophoresis of the gel forming pectin molecules away from the membrane surface. A model based on gel layer theory was proposed and numerically solved to quantify the flux and growth of the gel layer thickness. The gel layer thickness was also measured with high-resolution video microscopy and successfully compared with results from the numerical solution of the model under various operating conditions.

The pressure distribution across a polarized layer forming during the ultrafiltration of macromolecular solutions depends on the physicochemical properties of the ultrafiltered molecule. Theoretical and experimental studies are in disagreement over the nature of this pressure profile: some predict a constant pressure distribution, while others predict a non-zero pressure gradient. The objective of Zhang and Ethier [33] was to gain insight into this issue by directly measuring both the pressure distribution and concentration profile in a hyaluronan concentration polarization layer during a model dead-end ultrafiltration experiment. A steady-state polarized layer was created by pumping solvent at a constant flow rate through a hyaluronan matrix in a specially designed filtration cell. Polymer concentration and concentration gradient were measured using a laser-based refractometric technique. For the purposes of their study the filtration cell incorporated an in-dwelling miniature pressure transducer that traversed the polarized layer and measured pressures. Polarized layer concentration profiles were similar to those previously reported. They measured a small, but non-zero, pressure drop of 7.9 mmHg across the polarized layer (95% confidence interval: 6.6–9.3 mmHg), which can be compared with the approximately 400 mmHg pressure drop across the ultrafiltration membrane. The measured change in polarized layer pressure was of the same order as that predicted theoretically. The pressure profile across a hyaluronan polarized layer is non-constant, likely due to solute–solute interactions within the polarized layer. Such effects may be most pronounced for long-chain random coiling macromolecules. Further modelling of transport in such long-chain polymer matrices should take such effects into account.

Adsorption has been found to be significant in ultrafiltration by a mixed matrix membrane. Removal of very low molecular weight solutes compared with the molecular weight cut-off of the membrane is facilitated by adsorption. A model of adsorption coupled with concentration polarization was presented by Gekas et al. [34] based on a mathematical approach developed from first principles. However, extensive modifications were included in theoretical development, including those suggested by Ruiz-Beviá et al. [35]. The developed model captured the rejection dynamics with the help of a retention factor. The model equations were solved under the framework of boundary-layer analysis, using the integral approach. The effects of the adsorption isotherm and the different parameters affecting the system performance were also investigated. Further, experimental validation of the model results with two different mixed matrix ultrafiltration studies was also elucidated [36].

### 7.1.7 Concentration Polarization in Microfiltration

Crossflow filtration with microporous membranes is increasingly used in the separation and concentration of particulate suspensions. Existing models for the filtrate flux are inadequate for correlating experimental observations and are based on contradictory physical mechanisms. Zydney and
Colton [37] proposed that the flux is limited by the formation of a dynamic concentration polarization boundary layer consisting of a high concentration of retained particles. A simple model is developed incorporating a shear-enhanced diffusivity of the large particles which arises from mutually induced velocity fields in the shear flow of the concentrated suspension. Predictions of the model agree well with experimental data for a variety of particulate suspensions. The model provides both a fundamental understanding of the physical phenomena governing flux and a rational basis for design of improved crossflow filters.

Crossflow microfiltration (CMF) is increasingly used for the separation and concentration of suspended microparticles, bacteria and emulsion droplets. The suspensions to be filtered flow parallel to the membrane. Thereby, the thickness of a filter cake is limited, so that a constant filtrate flux can be reached over a long period of time.

Theoretical models for the description of the process and the calculation of flux values are based, like models for ultrafiltration, on the concept of concentration polarization. The basis of such a model is the mass balance for the retained components and the description of a back-transport from the membrane into the bulk stream. Two different mechanisms and the corresponding laws are used in the literature to describe this back-transport: (a) laws of diffusion and (b) laws of hydrodynamics.

These two main models were presented by Schulz and Ripperger using examples and were evaluated with regard to their appropriate use and limitations. The laws of diffusion were inadequate for the mechanism in CMF. Therefore, a simple model on the basis of hydrodynamic considerations was developed, and resulted in an expression for flux [38].

Song and Elimelech [39] developed a novel theory for concentration polarization of non-interacting particles in crossflow filtration systems. This theory reveals that the extent of concentration polarization and the behaviour of the permeate flux are characterized by an important dimensionless filtration number \( N_F = \frac{4 \pi a_p^3 \Delta P}{3kT} \). There is a critical value of the filtration number for a given suspension and operational conditions. When the filtration number is smaller than the critical value, a polarization layer exists directly over the membrane surface and the wall particle concentration is determined by the pressure and temperature. At higher filtration numbers, a cake layer of retained particles forms between the polarization layer and the membrane surface. Mathematical models are constructed for both cases and analytical solutions for the permeate flux are derived. An increase in permeate flux with increasing pressure is predicted for all operational conditions.

The increase in mass transfer coefficient with increase in suction volume flux was successfully quantified. Two virus strains Q\( \beta \) and MS2 were filtered with a 0.1 μm pore size tubular membrane made out of Al\( _2 \)O\( _3 \) in the crossflow mode. The rejection results were obtained for various permeation velocities and at different crossflow velocities in the turbulent flow region. The mass transfer coefficient obtained from the experimental results using the velocity variation method showed an increase in mass transfer with increasing volume flux rate. The mass transfer values calculated based on the Deissler equation, which is based on Sherwood number correlation, did not account for this variation of flux but gave a constant mass transfer rate for the entire flux range. Hence, based on the suction effect on boundary layer, a modification was proposed to the Deissler equation for the calculation of mass transfer coefficient. The mass transfer coefficients obtained with the modified Deissler equation showed a good agreement with the experimentally obtained mass transfer values [40].

Kromkamp et al. [41] proposed a new computer simulation model for suspension flow in microfiltration systems. In this model, the diffusion of the suspended microparticles is governed by the mechanism of shear-induced migration. Using an Euler–Euler approach, hydrodynamics and convection–diffusion are simultaneously resolved according to the lattice Boltzmann method. The new suspension flow model allows the complete solution of the flow field (including calculation of the actual local shear rate) in systems with complex geometries and the application of a pressure gradient over
the feed flow channel as well as over the membrane. The cake layer dimensions and permeability were explicitly taken into account. For a simple crossflow system, a comparison was made between the new suspension flow model and existing models. The more realistic approach of the suspension flow model was found to be especially significant for the calculation of the cake layer profile at the beginning and the end of the membrane. Also, the effect of narrowing of the flow channel by cake formation on the suspension flow pattern (at a constant pressure gradient over the flow channel) was more realistically predicted. Finally, some examples were presented of the concentration polarization and cake layer formation in microfiltration systems with more complex geometries. The newly developed suspension flow model has generic applicability as a design tool for microfiltration membranes, systems and processes. Extensions of the model to three-dimensional systems (including parallel computations), as well as adaptations of the diffusion model to anisotropic diffusivity, can be relatively easily achieved.

Zare et al. [42] studied two-dimensional CFD modelling and simulation of concentration polarization phenomenon in microfiltration of an oil–water emulsion in a narrow rectangular membrane module. The novelty of this research was in the use of an Eulerian-based multiphase method to investigate for the first time the capture of the concentration of emulsified oil droplets in different extents of membrane module. It was also shown that this new model is highly compatible with concentration polarization theory and is highly capable for determining concentration polarization profile and mass boundary-layer behaviour in different operating conditions. In this research it was proved that underdeveloped feed crossflow shows better performance in terms of membrane surface cleaning. Also, it was shown that a small portion of oil droplets accumulates at the roof of the membrane module feed channel due to gravity. The simulation results proved that for underdeveloped feed crossflows, lower feed Re induces a lower concentration polarization profile peak despite increasing the oil droplet concentration on the membrane surface and at the feed channel roof.

7.1.8 Concentration Polarization in Membrane Distillation

Kurokawa et al. [43] studied theoretically and experimentally the permeate characteristics of membrane distillation considering heat and mass transfers and concentration polarization. To understand the effect of concentration polarization, concentrated solutions of LiBr and H₂SO₄ were used as feed. The permeate flux was found to be proportional to the vapour pressure difference between the feed and cooled surface and decreased with increasing concentration because of the concentration and temperature polarization. Furthermore, when considering the heat and mass transfers and concentration polarization, the permeate flux could be estimated accurately.

Techniques of membrane distillation have been developed in the field of the desalination of seawater and the dehydration of alcohol. Kondo et al. [44] attempted the removal of solute-free water from bovine blood by membrane distillation, which has the advantages of high flux and outstanding selectivity at lower temperatures. In membrane distillation, for which the driving force is vapour pressure difference across the hydrophobic membrane, the development of temperature and concentration polarization layers on either side of microporous hydrophobic membranes leads to the decline of permeation flux because of the reduction of vapour pressure difference across the membrane. Conventional theory of heat and mass transfer was applied to transport processes in membrane distillation to clarify effects of temperature and concentration polarization on water vapour permeability for ethylene glycol solution and bovine blood. In membrane distillation with bovine blood, the resistance of the temperature polarization layer accounted for 61% of total permeation resistance at a stirring speed of 200 rpm. At a stirring speed of 1000 rpm the permeation resistance of membrane accounted for 52% of total permeation resistance. Destruction of the temperature polarization layer and thinning of the membrane are essential for practical use.
Martínez-Díez and Vázquez-González [45] studied water transport in membrane distillation using a flat polytetrafluoroethylene membrane. Experiments were carried out with water and aqueous solutions of NaCl as feed. The effects of temperature and concentration polarization on the reduction of vapour pressure differences across the membrane with regard to the vapour pressure differences corresponding to the bulk phases which are separated by the membrane were evaluated. A coefficient which measures this reduction has been introduced. This coefficient and the temperature polarization coefficient coincide when water is used as feed, but they are more and more different when the salt concentration of feed increases. The measured flux results and the calculated polarization results are discussed for different temperatures, recirculation rates and solution concentrations.

An experimental and theoretical investigation of the influence of concentration polarization and temperature polarization on the flux and selectivity of binary aqueous mixtures of ethanol for vacuum membrane distillation processes was undertaken by Izquierdo-Gil and Jonsson [46]. Experimental results include changes of the following parameters: nature of solutions, membrane material and pore size, feed temperature and recirculation flow rate. One method was proposed in order to evaluate the concentration polarization effects from the fit of the experimental data. General models taking into account Knudsen and viscous flows were proposed, but viscous contribution was found to be negligible under their operating conditions. Therefore, theoretical fluxes were estimated using a Knudsen model, and a good agreement between them and the experimental ones was found.

Textile industries consume large amounts of water and generate highly dye-contaminated effluents. Textile wastewaters have to be treated in order to be recycled in the process or to meet legislative requirements before being discharged. The objective of the study by Banat et al. [47] was to examine the potential use of the vacuum membrane distillation process for the treatment of dyed solutions. Methylene blue (MB) was used as a model dye. Batch experiments were conducted on dilute MB-water mixtures using a tubular polypropylene membrane module. The concentration of MB dye within the feed reservoir was monitored over time. The impact of operating variables such as feed temperature, flow rate and initial dye concentration was investigated. A mathematical model incorporating temperature and concentration polarization effects was developed and validated on the experimental data.

7.1.9 Concentration Polarization in Dialysis

The effect of steady shear flow on concentration polarization of plasma proteins and lipoproteins at the luminal surface of a semipermeable vessel wall was studied experimentally using suspensions of these molecules in a cell culture medium and a semipermeable membrane dialysis tube which served as a model of an implanted vascular graft or an artery [48]. The study was carried out by flowing a cell culture medium containing fetal calf serum or bovine plasma lipoproteins or bovine albumin through a 7.5 mm diameter, 60 mm long dialysis tube in steady flow under a physiologic mean arterial perfusion pressure of 100 mmHg, and measuring the filtration velocity of water (cell culture medium) at the vessel wall, which varied as a consequence of the change in concentration of plasma protein particles at the luminal surface of the semipermeable membrane dialysis tube. It was found that for perfusates containing plasma proteins and/or lipoproteins, filtration velocity of water was the lowest in the absence of flow, and it increased or decreased as the flow rate (hence wall shear rate) increased or decreased from a certain non-zero value, indicating that surface concentration of protein particles varied reversibly as a direct function of flow rate. It was also found that at particle concentrations equivalent to those found in a culture medium containing serum at 5% by volume, plasma lipoproteins that were much smaller in number and lower in concentration but larger in size than albumin had a much larger effect on the filtration velocity of water than albumin did. These findings were very much
the same as those previously obtained with a cultured endothelial cell monolayer, strongly suggesting that the flow-dependent variation in filtration velocity of water at a vessel wall results from a physical phenomenon; that is, flow-dependent concentration polarization of low-density lipoproteins at the luminal surface of the endothelial cell monolayer.

In extracorporeal renal replacement therapies, the dialyser is not only the site at which solute removal occurs, since the extracorporeal circuit component has the largest surface area exposed to blood. Therefore, it is not surprising that interactions between blood components and the dialyser membrane influence the dialysis procedure in several ways. Based on engineering principles, fluid flow along a surface such as a membrane results in the development of a boundary layer which can influence solute removal. Furthermore, the exposure of blood to any extracorporeal artificial surface results in the activation of several pathways within the body, including those involving coagulation and complement activation. One of the by-products of this generalized activation process is protein adsorption to the membrane surface, another phenomenon that can have a significant impact on solute removal. In the article by Huang et al. [49], a detailed review of the ways in which blood–membrane interactions influence solute removal during haemodialysis and related therapies is provided. The influences of secondary membrane formation and boundary layer/concentration polarization effects on solute removal are specifically discussed. Furthermore, the importance of adsorption as a specific removal mechanism for low-molecular weight proteins by highly permeable synthetic membranes is highlighted.

The reflection coefficient of the membrane \( \sigma \) is one of the basic parameters of the polymer membrane transport. Classical methods used to determine this parameter require intensive mixing of two solutions separated by a membrane to eliminate the effects of concentration polarization. In real conditions, especially in biological systems, this requirement is challenging. Thus, concentration boundary layers, which are the essence of the phenomenon of concentration polarization, form on both sides of the membrane. The main aim of the study by Batko et al. [50] was to determine whether the value of reflection coefficient in concentration polarization conditions depends on the concentration of solutions and hydrodynamic state of concentration boundary layers. In that study, a haemodialysis membrane of cellulose acetate (Nephrophan) and aqueous glucose solutions were used. Formalism of non-equilibrium thermodynamics and Kedem–Katchalsky equations were the research tools. Derived mathematical equations describe the ratio of reflection coefficients in concentration polarization conditions \( (\sigma_S) \) and in terms of homogeneity of the solutions \( (\sigma) \). This ratio was calculated for the configuration in which the membrane was oriented horizontally. It was shown that each of the curves has a bifurcation point. Above this point, the value of the reflection coefficients depended on the concentration of the solution, the configuration of the membrane system and the hydrodynamic concentration boundary layers. Below this point, the system did not distinguish the gravitational directions. The coefficient of the haemodialysis membrane in a concentration polarization condition \( (\sigma_S) \) is dependent on both the solution concentration and the hydrodynamic state of the concentration boundary layers. The value of this coefficient is largest in the state of forced convection, lower in the natural convection state and lowest in the diffusive state. The equations obtained may be relevant to the interpretation of membrane transport processes in conditions where the assumption of homogeneity of the solution is difficult to implement.

### 7.1.10 Concentration Polarization in Electrodialysis

Sata et al. [51] studied the behaviour of the diffusion boundary layer in electrodialysis using ion-exchange membranes, mainly a cation-exchange membrane, by means of six different measurements: (1) the determination of the current–voltage curve or the current–(voltage/current) curve; (2) the
relation of the pH change of the solution to the current density; (3) the relation of the charge retention – that is, the sum of the diffusion potential and the membrane potential generated from the concentration gradient across the membrane immediately after the current is shut off – to the current density; (4) the time required to reach a constant current value (namely, to obtain a stationary diffusion boundary layer) when a constant voltage is supplied to the system, versus the current density; (5) the change in the transport number of the counter-ion in the membrane with the current density; and (6) the relation of the permselectivity between sodium ions and potassium ions to the current density. The interrelation among these results was also examined. The quantity of hydrogen ions or hydroxide ions passing through the membrane increases abruptly at a current density lower than that at which the concentration at the membrane–solution interface in the desalting side attains its minimum. It was newly observed that the results of all the measurements, except for the pH change of the solution, show abnormal phenomena at a current density about twice the limiting current density.

Interfacial concentration values derived from overpotential measurements on the cation-exchange membrane AMF C 100 were considered in relation to the corresponding current–voltage curves [52]. The concentration in the depleted layer was found to reach a limiting value as a function of current density which is still large compared with the H⁺ and OH⁻ ion concentration. The pH shift and the cation transport number were also determined as a function of current density. It appeared that water splitting did not contribute significantly to the conductivity in the high polarization regime and could not be correlated with the constant value of the interfacial concentration, nor with the additional conductivity that appears beyond the limiting current density.

Rubinstein [53] reported the theory of the effect of concentration polarization under direct current upon the counter-ion selectivity of an ion-exchange electrodialysis membrane. The equilibrium selectivity is induced by the differing uptake of the counter-ions by the membrane, owing to the difference in their distribution coefficients between the membrane and solution phases. The numerical calculations are supplemented by an asymptotic analysis for a certain range of bulk concentrations and distribution coefficients, which provides an analytical expression for the dependence of selectivity on the electric current in the entire current range.

Shaposhnik et al. [54] studied the concentration polarization of ion-exchange membranes in a wide range of current densities by the three-frequency laser interferometry method. The concentration and temperature fields of solutions involved in electrodialysis of sodium chloride were measured simultaneously. The proposed method makes it possible to measure absolute values of local concentrations of acids and bases that form during irreversible dissociation of water molecules at the solution–membrane interfaces following an increase in the current density above the limiting value. According to an analysis of the concentration and temperature distributions in an electrodialyser channel, maximum variations in the measured quantities occur near the interface. Dependences of the near-membrane concentrations and temperatures on the current density were compared with the voltammogram. The comparison showed that reaching the limiting current density sharply accelerates the nonequilibrium dissociation of water molecules and increases the temperature.

Tanaka [55] evaluated ionic fluxes, current density, solution velocity and potential gradient in the boundary layer using the NaCl concentration distribution observed by measuring the refraction index in a boundary layer in an unforced flowing state in a desalting cell. Solution velocity was divided into the terms of electro-osmosis, concentration-osmosis and natural convection. The greater part of the solution velocity was due to natural convection, which is a horizontal component of ascending flow produced by the decrease in the solution density near the membrane surface in the boundary layer. Ionic fluxes and current density were divided into the terms of diffusion, migration and convection. Na⁺ ion transport in the boundary layer on the desalting surface of a cation-exchange membrane was suppressed due to the lower mobility of Na⁺ ions. Furthermore, water dissociation was strongly
restricted on the surface of the cation-exchange membrane. Accordingly, Na\(^+\) ion transport on the surface of the cation-exchange membrane placed in a diluted NaCl solution was promoted at the limiting current density by the increase of boundary-layer thickness, the solution velocity in the boundary layer and the intensity of NaCl concentration oscillation on the membrane surface. In this circumstance, ionic transport due to the convection fluxes, which do not carry an electrical current, converted to migration fluxes and carried an electrical current. In this instance, diffusion fluxes did not support an electrical current because of lower mobility of Na\(^+\) ions compared with that of Cl\(^-\) ions. On the other hand, Cl\(^-\) ion transport in the boundary layer on the desalting surface of the anion-exchange membrane was not suppressed because of the greater mobility of Cl\(^-\) ions. Furthermore, water dissociation was not strongly restricted on the anion-exchange membrane. Accordingly, phenomena like the increase of the boundary-layer thickness and the solution velocity observed in the boundary layer on the cation-exchange membrane did not occur on the anion-exchange membrane. On the anion-exchange membrane, convection fluxes were converted to diffusion fluxes and carry an electrical current. In this instance, migration fluxes did not support an electrical current because the contribution of diffusion fluxes is sufficiently effective. The potential gradient was divided into the terms of ohmic potential and diffusion potential. The ohmic potential gradient on the cation-exchange membrane was positive, and that on the anion-exchange membrane was negative. The diffusion potential gradient was positive on both the cation-exchange membrane and the anion-exchange membrane.

7.2 Membrane Fouling

See http://www.lenntech.com/membrane-fouling.htm and the paper by Mallubhotla et al. [56].

7.2.1 Cause of Membrane Fouling

During ultrafiltration and microfiltration a decline in flux is observed, which is caused by concentration and fouling. Concentration polarization is the accumulation of solutes (particles) at the membrane surface as a result of the transmembrane pressure. This phenomenon is reversible and causes the flux to decline in the first seconds of the filtration process [57]. As a result of accumulation near the membrane, particles (solute) might precipitate onto the membrane surface to cause membrane fouling, which is a collective term for phenomena that cause a long-term flux decline. Some of these phenomena are cake layer formation on top of the membrane, pore blocking, pore narrowing, adsorption, particle deposition, and so on, which are often irreversible phenomena [58].

Membrane fouling is defined as a process resulting in performance loss due to the deposition of suspended or dissolved substances on external surfaces, at pore openings or within the internal structure of a membrane [59]. It is a very complex phenomenon that depends on many factors: different fouling mechanisms, such as internal fouling, pore blocking, pore narrowing and surface fouling by the formation of a cake layer, as shown in Figure 7.3 [58].

Fouling is caused by various deposits on the membrane surface, external and internal. Fouling results in irreversible drop in performance due to increased hydraulic resistance and fouling-enhanced polarization.

Mechanisms of fouling, especially in porous membranes, are very diverse. Fouling may be colloidal, inorganic (scaling by sparingly soluble salts, silica) and organic (e.g. by natural organic matter [60] or dissolved organic matter [61]) for each pressure-driven membrane process, as shown in Figure 7.4.
In many cases all types of fouling occur simultaneously, producing a synergistic effect. The main approaches to deal with fouling are technological (imposing flux limits, pretreatment, antiscalants, cleaning), but development of low-fouling membranes is gaining popularity.

Hydrophobic membranes are in general more stable but also more prone to fouling than hydrophilic ones. This motivates attempts to modify membrane surface, which may improve anti-fouling properties without impairing other, beneficial characteristics [62].
7.2.2 Control of Membrane Fouling

See Franken’s ‘Prevention and control of membrane fouling: practical implications and examining recent innovations’ [63].

Resistances during filtration process, concentration polarization, and membrane fouling such as colloidal fouling, organic fouling, scaling, and biofouling cause flux decline and consequently the membrane performance is lowered. The prevention of membrane fouling is a very important subject to demonstrate outstanding membrane performance in practical membrane separation technique. Table 7.1 summarizes some prevention methods for membrane fouling.

Table 7.1 Control of membrane fouling.

| Membrane cleaning | Four variables: cleaning agent, mechanical action, temperature and time |
| Cleaning strategies | How to identify the type of membrane fouling? |
| Cleaning strategies | Fouulant type and phenomena |
| Cleaning strategies | Cleaning schedule |
| Cleaning strategies | Membrane autopsy |
| Reduced-fouling strategies | PolyAn® – modification of polymer surfaces |
| Reduced-fouling strategies | Functionalized surfaces for anti-fouling applications |
| Reduced-fouling strategies | Affinity materials for life science |
| Reduced-fouling strategies | Molecular surface engineering |
| Reduced-fouling strategies | LU Wageningen – C3M coating |
| Reduced-fouling strategies | Complex coacervate core micelle (C3M) |
| Reduced-fouling strategies | Coating of RO membranes |
| Reduced-fouling strategies | Evaluation of the physically attached coating |
| Fouling control by mechanical means | In-line coagulation |
| Fouling control by mechanical means | Critical flux |
| Fouling control by mechanical means | Crossflow |
| Fouling control by mechanical means | Rotation-enhanced membrane separation |
| Fouling control by mechanical means | Cross-rotation filtration |
| Fouling control by mechanical means | Rotating membranes |
| Fouling control by mechanical means | Vibration enhanced membrane separation |
| Fouling control by mechanical means | Principle of vibration-enhanced membrane filtration V-SEP |
| Fouling control by mechanical means | Back-flush/backwash/(dynamic) back-pulsing |
| Fouling control by mechanical means | Cleaning with air |
| Fouling control by mechanical means | Application of air in membrane filtration |
| Fouling control by mechanical means | AiRO – air–water for the control of particulate fouling |

a) A company specialized in chemical modification of polymer surfaces.

References


Dialysis

8.1 Diffusion Dialysis

See section 2.4 in Introduction to Practical Biochemistry [1].

Dialysis is the transport of a solute through a membrane under the influence of a difference in the solute activities of the solutions separated by the membrane [2]. In dialysis, solute separation is induced by the difference in solute diffusion transport within a membrane matrix. A diffusible small solute such as an electrolyte or acid is passed through a membrane and dialysed from a solution containing non-diffusable large molecules.

In 1861, dialysis was first used by T. Graham with parchment paper [3]. Since then, dialysis has been widely used, primarily as a laboratory technique for the purification of small quantities of solutes using various animal membranes, collodion, Cellophane and cuprophane as the membrane. In the 1940s, dialysis was used on an industrial scale in rayon and viscose production for the recovery of caustic soda from a hemicellulose-containing solution using parchmentized cotton cloth membranes.

In the late 1950s, dialysis as a unit operation attracted attention for its industrial applications along with the development of new dialysis membranes [4]. A new synthetic dialysis membrane is a strong basic anion exchanger (tertiary amine type) with a high ion-exchange capacity (IEC), is mechanically strong and is acid resistant [5]. In dialysis, the membranes demonstrate a very high diffusion transport behaviour for an acid and enable the effective separation of an acid from its mixture [5,6].

Beginning in the 1960s, a major use of dialysis became the treatment of patients with chronic kidney disease. Then new membranes and more efficient dialysis devices for haemodialysis were developed, and subsequently many lives have been sustained through haemodialysis. In 1976, poly(vinyl alcohol) (PVA) hollow fibres were developed as new dialysis membranes [7]. These hollow-fibre dialysers are used for the recovery of alkali and the desalination of foods in industrial applications.

In 1980, new charge-mosaic membranes composed of cation and anion permeable microdomains embedded in an impermeable supporting matrix were developed. The charge-mosaic membranes have three-layer lamellar structures (thickness of each layer is 200 Å) in a regular alternating arrangement [8–10]. Since charge-mosaic membranes have respective pathways for anions and cations, they have high permeability levels for electrolytes and can be used for the dialytic or piezodialytic separation of electrolytes from mixtures of electrolytes and nonelectrolytes. Charge-mosaic membranes have shown promise, and more advances are expected in the field of membrane separation processes because of their unique transport properties [11–18].
8.1.1 Principle of Diffusion Dialysis

Diffusion dialysis is a procedure employed in a number of cases when a change in the concentration or composition of solutes is necessary. In biochemical practice, dialysis is often used to alter the concentration of salts and/or small molecules in protein solutions — usually aimed at decreasing the concentration of these solutes. However, the composition of the solution can also be changed in additional ways. Diffusion dialysis is based on diffusion during which the mobility of solute particles between two liquid spaces is restricted, mostly according to their size. In rarely used versions of dialysis, restriction of diffusion via polarity or charge is also possible. Size restriction is achieved by using a porous material, usually a semipermeable membrane called a dialysis membrane. This membrane is permeable only for particles below a certain size. In the biochemical laboratory, this membrane is mostly a tube made from transparent material, also called dialysis bag, that can be tightly closed with string at its ends, as shown in Figure 8.1. The solution with a volume $V_1$ to be dialysed is loaded into the dialysis bag. The dialysis bag is then placed into a dialysis solution with a volume $V_2$ that is stirred slowly to aid the diffusion of the subset of solutes that can be released through the bag membrane, in order to achieve equilibrium between solute concentrations in the two liquid spaces. If the difference in volume between the two spaces is large ($V_2 \gg V_1$, e.g. $V_2 = 10 \text{ L}$ and $V_1 = 0.1 \text{ L}$, more than 100-fold difference), the onset of the equilibrium will lead to a very significant dilution of the small solutes that were initially inside the bag (their concentration will change by a factor $V_1/(V_1 + V_2)$, in this case $\ll 1$), with only a slight change in the concentration of small solutes in the outside solution (by a factor $V_2/(V_1 + V_2) \approx 1$), whereas the concentration of the molecules inside the bag that cannot penetrate the membrane remains almost completely unchanged.

8.1.2 Fundamental Analysis of Diffusion Dialysis

The movement of solute and solvent molecules by the concentration difference is called diffusion, and a membrane process to separate various kinds of solutes by the diffusion through the membrane is diffusion dialysis. Diffusion dialysis requires that the diffusion rate of solute between two liquid phases separated by a membrane differs due to the kind of solute. An effective separation in diffusion dialysis can be achieved by an entirely thin membrane and higher concentration difference between two phases separated by the membrane.

Diffusion dialysis is the oldest membrane process and was applied to the separation of colloid and low molecular solute by Graham in 1861 [18]. The membranes for diffusion dialysis known for a long
time are parchment paper, Cellophane, collodion and so on, and the separation mechanism of those membranes was dependent upon the size of solute molecules. These membranes suit industrial use, including the recovery of alkali in the rayon industry, but were not used industrially because their mechanical stability is low. These circumstances changed with the development of synthetic polymer membranes for ion-exchange, reverse osmosis and ultrafiltration membranes in the 1960s.

Diffusion dialysis is inferior in transaction speed and processing capacity in comparison with a membrane process driven by power increased by reverse osmosis, nanofiltration, ultrafiltration or microfiltration.

8.1.2.1 Diffusion and Diffusion Dialysis

The diffusion process is expressed using Fick’s law. When the concentration gradient $\frac{dC_i}{dx}$ of the ingredient $i$ is in the $x$ direction, the flux (mol cm$^{-2}$ s$^{-1}$) of component $i$ is

$$J_i = -D_i \frac{dC_i}{dx} \quad (8.1)$$

where $D_i$ (m$^{-2}$ s$^{-1}$) is called diffusion coefficient.

It is necessary to return to the generalization of the transportation phenomenon to make a physical meaning of the diffusion coefficient more clear. The flux of the component $i$ is defined as the product of the mean molecular speed $v_i$ with the molar concentration $C_i$:

$$J_i = v_i C_i \quad (8.2)$$

Because the movement of this material depends on the slope of the chemical potential of component $i \mu_i$, the power per mono molecule of component $i$ $X_i$ is given by

$$X_i = -\frac{1}{N_A} \frac{d\mu_i}{dt} \quad (8.3)$$

where $N_A$ is the Avogadro number. When a coefficient of friction $f_i$ between speed $v_i$ and the power $X_i$ is set, the following relation is given, and furthermore Equation 8.5 is obtained:

$$J_i = \frac{X_i}{f_i} \quad (8.4)$$

$$J_i = -\frac{C_i}{f_i N_A} \frac{d\mu_i}{dx} \quad (8.5)$$

For an ideal solution

$$\mu_i = \mu_i^0 + RT \ln C_i \quad (8.6)$$

Consequently, the following equation is obtained:

$$J_i = -\frac{RT}{f_i N_A} \frac{dC_i}{dx} \quad (8.7)$$

By comparing Equation 8.7 with Equation 8.1, we obtain

$$D_i = \frac{RT}{f_i N_A} = -\frac{kT}{f_i} \quad (8.8)$$
where \( k = R/N_A \) (Boltzmann constant).

For an actual (nonideal) solution we have

\[
\mu_i = \mu_i^\circ + RT \ln a_i \gamma_i, \quad a_i = \gamma_i C_i
\]  

(8.9)

where \( a_i \) and \( \gamma_i \) are activity and activity coefficient respectively. Therefore, we obtain

\[
D_i = -\frac{kT}{f_i} \frac{d \ln a_i}{d \ln C_i} = -\frac{RT}{f_i} \left( 1 + \frac{C_i}{\gamma_i} + \frac{d \gamma_i}{d C_i} \right)
\]  

(8.10)

Figure 8.2 illustrates a diffusion state through a membrane when solution I and solution II across a membrane are contacted with a membrane.

When the diffusion flux is sufficiently small and the distribution of the solute in liquid–membrane interface is in a partial equilibrium state, the steady flux of diffusion is as follows:

\[
J_i = D_i \frac{C_i^I - C_i^\Pi}{l}
\]  

(8.11)

where \( C_i^I \) and \( C_i^\Pi \) show the concentration of solute in the membrane and \( l \) is membrane thickness.

The distribution of solute \( i \) in the liquid phase and membrane phase is given by the solubility coefficient as shown in Equation 8.12, and then Equation 8.11 is represented as Equation 8.13:

\[
S_i = \frac{C_i}{C_i^I}
\]  

(8.12)

\[
J_i = D_i S_i \frac{C_i^I - C_i^\Pi}{l}
\]  

(8.13)

On the other hand, the permeability coefficient \( P_i \) is defined as follows:

\[
J_i = P_i \frac{\Delta C_i}{l}
\]  

(8.14)
Consequently, the permeability coefficient $P_i$ of membrane for component $i$ is simply given by

$$P_i = D_i S_i$$  \hspace{1cm} (8.15)

This equation denotes that separation by diffusion dialysis is significantly dependent upon the difference of the solubility coefficient $S_i$ into the membrane and the diffusive coefficient $D_i$ in the membrane of permeants.

Analysis of permeation and separation through a homogeneous membrane is undertaken using the ‘solution-diffusion mechanism’ [19,20]. This solution-diffusion model is the most widely accepted explanation of transport in dialysis, reverse osmosis, gas permeation and pervaporation [21].

Since $J_i$ can be measured by a diffusion experiment, $P_i$ is determined from Equation 8.14. On the other hand, $S_i$ in Equation 8.12 also can be measured by a distribution experiment, and consequently $D_i$ can be determined from Equation 8.15.

### 8.1.2.2 Diffusion Dialysis with Crossflow

**Single-Component System** When $dS$, $K$, $C^I$, and $C^{II}$, $Q^I$, and $Q^{II}$, and $A$ are the movement velocity of solute from the feed solution side to the dialysate side, the overall transfer coefficient, the solute concentration in the feed solution side and dialysate side, the flow of feed and dialysate, and the membrane area respectively, as shown in Figure 8.3, $dS$ is represented by

$$dS = K(C^I - C^{II}) dA$$  \hspace{1cm} (8.16)

$$dS = Q^I dC = Q^{II} dC$$  \hspace{1cm} (8.17)

From Equation 8.16, the following equations are obtained:

$$\frac{Q^I}{Q^{II}} dS = \frac{Q^I}{Q^{II}} Q^I dC^{II} = Q^I dC^{II}$$  \hspace{1cm} (8.18)

$$dS - \frac{Q^I}{Q^{II}} dS = Q^I dC^I - Q^I dC^{II}$$  \hspace{1cm} (8.19)

$$dS \left(1 - \frac{Q^I}{Q^{II}} \right) = Q^I (dC^I - dC^{II}) = Q^I d(C^I - C^{II})$$  \hspace{1cm} (8.20)

Consequently, we obtain

$$dS = \frac{d(C^I - C^{II})}{1 - Q^I/Q^{II}}$$  \hspace{1cm} (8.21)
When this equation is substituted into Equation 8.16, we obtain

\[
\frac{d(C^I - C^II)}{C^I - C^II} = K \left(\frac{1}{Q^I} - \frac{1}{Q^II}\right) dA
\]  

(8.22)

When \( K \) is constant at each part in the dialysis membrane, we obtain

\[
\int_{C^I_{in} - C^I_{out}}^{C^II_{out} - C^II_{in}} \frac{d(C^I - C^II)}{C^I - C^II} = K \left(\frac{1}{Q^I} - \frac{1}{Q^II}\right) dA
\]

(8.23)

\[
\ln \left(\frac{C^II_{out} - C^II_{in}}{C^I_{in} - C^I_{out}}\right) = K \left(\frac{1}{Q^I} - \frac{1}{Q^II}\right) A
\]

(8.24)

where subscripts 'in' and 'out' denote entrance and exit of feed side and dialysate side respectively. On the other hand, upon execution of Equation 8.25 we get Equation 8.26:

\[
\frac{1}{Q^I} - \frac{1}{Q^II} = \left(\frac{C^I_{in} - C^I_{out}}{S}\right) - \left(\frac{C^II_{in} - C^II_{out}}{S}\right)
\]

(8.25)

\[
\ln \left(\frac{C^II_{out} - C^II_{in}}{C^I_{in} - C^I_{out}}\right) = K \left[\left(\frac{C^II_{out} - C^II_{in}}{S}\right) - \left(\frac{C^I_{in} - C^I_{out}}{S}\right)\right] A
\]

(8.26)

Consequently, we obtain

\[
S = K\Delta C
\]

(8.27)

where \( \Delta C \) is the logarithmic mean concentration difference of solute between both liquids.

**Binary-Component System** When solute 1 and solute 2 are contained in the feed side and the solute concentration in the dialysate side is \( C^II = 0 \), the movement velocities of each solute are as follows:

\[
dS^I_1 = K_1 \Delta C^I_1 A = K_1 C^I_1 dA = K_1 \left(\frac{S^I_1}{S_T}\right) dA
\]

(8.28)

\[
dS^I_2 = K_2 \Delta C^I_2 dA = K_2 C^I_2 dA = K_1 \left(\frac{S^II_2}{S_T}\right) dA
\]

(8.29)

The total component concentration \( S_T \) is given by

\[
S_T = S^I_1 + (r_1 - 1) (S^I_{in1} - S^I_1) + (r_2 - 1) (S^I_{in2} - S^I_2)
\]

(8.30)

where \( r_1 \) and \( r_2 \) are ratio of the transfer coefficient water and solute respectively. From Equations 8.26 and 8.27, the following equations are obtained:

\[
\frac{dS^I_1}{dS^I_2} = \frac{K_1 C^I_1}{K_2 C^I_2} = \frac{K_1 S^I_1}{K_2 S^I_2}
\]

(8.31)
\[ \frac{dS_1^l}{K_1S_1^l} = \frac{dS_2^l}{K_2S_2^l} \]  

When, from the initial value, \( S_{in1}^l \) and \( S_{in2}^l \) to \( S_1^l \) and \( S_2^l \) respectively are integrated, we obtain

\[ \frac{S_1^l}{S_{in1}^l} = \left( \frac{S_2^l}{S_{in2}^l} \right)^{K_1/K_2} \]  

When the permeabilities for solutes 1 and 2 are \( x_1 \) and \( x_2 \) respectively we obtain

\[ x_1 - 1 = (x_2 - 1)^{K_1/K_2} \]  

This equation means that the separativeness increases with an increase in ratio of overall transfer coefficient \( K_1/K_2 \).

The dialysance \( D_S \) and the clearance \( C_L \) that are the index of the performance evaluation of the haemodialysis respectively are shown by the following equations:

\[ D_S = \frac{Q_{in}^l C_{in}^l - Q_{out}^l C_{out}^l}{C_{in}^l} = \frac{Q_{out}^l C_{out}^l - Q_{in}^l C_{in}^l}{C_{in}^l} \]  

\[ C_L = \frac{Q_{in}^l C_{in}^l - Q_{out}^l C_{out}^l}{C_{in}^l - C_{in}^l} = \frac{Q_{out}^l C_{out}^l - Q_{in}^l C_{in}^l}{C_{in}^l - C_{in}^l} \]

When \( C_{in}^l = 0 \), \( D_S = C_L \).

### 8.1.3 Membranes for Diffusion Dialysis

The term dialysis was first routinely used for scientific or medical purposes in the late 1800s and early 1900s, pioneered by the work of Graham [18]. The first mass-produced manmade membranes suitable for dialysis were not available until the 1930s and were based on materials used in the food packaging industry, such as Cellophane. In the 1940s, Kolff [22] constructed the first dialyser (artificial kidney), and successfully treated patients with renal failure using dialysis across semipermeable membranes.

Today, dialysis tubing for laboratory applications comes in a variety of dimensions and molecular-weight cut-offs (MWCOs). In addition to tubing, dialysis membranes are also found in a wide range of different preformatted devices, significantly improving the performance and ease of use of dialysis.

Different dialysis tubing or flat membranes are produced and characterized as differing MWCOs ranging from 1 to 1 000 000 kDa. The MWCO determination is the result of the number and average size of the pores created during the production of the dialysis membrane. The MWCO typically refers to the smallest average molecular mass of a standard molecule that will not effectively diffuse across the membrane upon extended dialysis. Thus, a dialysis membrane with a 10k MWCO will generally retain >90% of a protein having a molecular mass of at least 10 kDa. Pore sizes typically range from ~10 to 100 Å for 1k to 50k MWCO membranes.

It is important to note that the MWCO of a membrane is not a sharply defined value. Molecules with mass near the MWCO of the membrane will diffuse across the membrane slower than molecules significantly smaller than the MWCO. In order for a molecule to rapidly diffuse across a membrane it typically needs to be at least 20–50 times smaller than the membrane’s MWCO rating. Therefore, it is not practical to try separating a 30 kDa protein from a 10 kDa protein using dialysis across a 20k-rated dialysis membrane. Dialysis tubing for laboratory use is typically made of a film of regenerated
cellulose or cellulose ester. However, dialysis membranes made of polyethersulfone (PES), etched polycarbonate or collagen are also extensively used for specific medical, food or water treatment applications (http://en.wikipedia.org/wiki/Dialysis_tubing).

Cellulose tube membrane is benzoylated to prepare membrane with a lower pore size. It is useful to separate a compound with molecular weight less than 1200 from a compound whose molecular weight is greater than 2000 (http://www.sigmaaldrich.com/catalog/product/sigma/d2272?lang=ja&region=JP).

Both natural and synthetic polymers are used as materials of diffusion dialysis membranes. Membrane materials most often used include natural cellulose, regenerated cellulose, cellulose ester, chitin and its derivatives, chitosan and its derivatives, polyacrylonitrile, poly (methyl methacrylate), polysulfone (PS), polycarbonate, polyamide, polyolefins such as polyethylene and polypropylene, and poly(vinylidene fluoride).

Cuprophane dialysis membrane is a regenerated cellulose membrane made by the cuprammonium process [23]. Nephrophane membrane is regenerated cellulose membrane made by the sodium cellulose xanthogenate process [24].

Table 8.1 summarizes various mechanical properties for cellulosic membranes. Neflex membranes in this table are fibre-reinforced cellulose membranes produced by Union Carbide. As can be seen from the data in Table 8.1, each cellulosic membrane has a characteristic properties.

More than 30 different polymers or polymer blends are used as materials for dialysis membranes. They can be categorized following the scheme of a family tree of haemodialysis membranes. The trunk represents membranes from regenerated cellulose, major branches show either synthetically modified cellulose membranes or membranes manufactured from synthetic polymers. As the latter are

<table>
<thead>
<tr>
<th>Membraneb)</th>
<th>Fracture load (kg)</th>
<th>Fracture stress (kg m&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>Fracture elongation (%)</th>
<th>Fracture modulus (kg m&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>Wet thickness (mm)</th>
<th>Burst pressure (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellophane-11</td>
<td>1.2</td>
<td>210</td>
<td>32</td>
<td>640</td>
<td>0.045</td>
<td>520–570</td>
</tr>
<tr>
<td>Cuprophane-11</td>
<td>0.7</td>
<td>290</td>
<td>26</td>
<td>1160</td>
<td>0.020</td>
<td>260–370</td>
</tr>
<tr>
<td>Nephrophane-11</td>
<td>0.5</td>
<td>100</td>
<td>22</td>
<td>422</td>
<td>0.046</td>
<td>210–260</td>
</tr>
<tr>
<td>Neflex 13-11</td>
<td>2.6</td>
<td>175</td>
<td>24</td>
<td>730</td>
<td>0.117</td>
<td>&gt;760</td>
</tr>
<tr>
<td>Neflex 14-11</td>
<td>2.4</td>
<td>160</td>
<td>21</td>
<td>750</td>
<td>0.120</td>
<td>&gt;760</td>
</tr>
<tr>
<td>Neflex 16-11</td>
<td>2.5</td>
<td>155</td>
<td>20</td>
<td>775</td>
<td>0.127</td>
<td>&gt;760</td>
</tr>
<tr>
<td>Neflex 22A-11</td>
<td>2.4</td>
<td>165</td>
<td>22</td>
<td>750</td>
<td>0.117</td>
<td>&gt;760</td>
</tr>
<tr>
<td>Cellophane-1</td>
<td>0.3</td>
<td>110</td>
<td>51</td>
<td>210</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>Nephrophane-1</td>
<td>0.2</td>
<td>30</td>
<td>46</td>
<td>70</td>
<td>0.046</td>
<td></td>
</tr>
<tr>
<td>Neflex 13-1</td>
<td>1.9</td>
<td>130</td>
<td>43</td>
<td>300</td>
<td>0.117</td>
<td></td>
</tr>
<tr>
<td>Neflex 14-1</td>
<td>2.0</td>
<td>130</td>
<td>39</td>
<td>330</td>
<td>0.120</td>
<td></td>
</tr>
<tr>
<td>Neflex 16-1</td>
<td>1.6</td>
<td>100</td>
<td>35</td>
<td>290</td>
<td>0.127</td>
<td></td>
</tr>
<tr>
<td>Neflex 22A-1</td>
<td>2.2</td>
<td>150</td>
<td>40</td>
<td>380</td>
<td>0.117</td>
<td></td>
</tr>
</tbody>
</table>

b) 11 denotes sample cut parallel to roll direction; 1 denotes sample cut perpendicular to roll direction.
standardly hydrophobic, small branches elucidate the technique on how these materials have been rendered partially or completely hydrophilic. Complications may arise when comparing membranes only following their polymer names, such as PS, polyacrylonitrile or polyamide. Owing to varying polymer compositions, membranes with the same polymer names may differ in their haemocompatibility, flux properties and adsorption characteristics. Adsorption of proteins like β2-microglobulin, fibrinogen and coagulation factors, complement proteins, or hormones like parathormon and erythropoietin are differently adsorbed by dialysis membranes, and thus adsorption contributes to the removal characteristics. Of central interest for membrane development and application is the question of how these membranes can be sterilized, as a series of patient adverse reactions has been attributed to the dialyser sterilization procedures. Apart from the cellulosic membranes Cuprophan and Hemophan, the majority of membranes cannot be sterilized by steam, as these materials degrade when exposed above their glass-point temperature [25]. The regenerated cellulose in Cellu-Sep® is derived from cotton: cotton linters are dissolved in a solution and spread into flat sheets or extruded into tubes. The material is treated with glycerine to prevent the pores from collapsing, and is then air dried at a certain temperature and pressure to form a rigid membrane. Cellu-Sep regenerated cellulose membrane has a symmetric pore structure that allows small molecules to migrate in either direction, making it ideal for experimental purposes (http://www.membrane-mfpi.com/home/tech-notes).

8.1.4 Technologies

8.1.4.1 Diffusion Dialysis

Diffusion dialysis, as shown in Figure 8.4, can transport by simple diffusion according to the concentration gradient of solutes those with a low molecular weight from a higher concentration solution side to the lower one, but not solutes with high molecular weight.

**Diffusion Dialysis by Non-charged Membrane** Regenerated cellulose membranes have been used as dialysis membranes and are particularly useful for blood dialysis membranes. In general, the regenerated cellulose membranes are prepared by the cuprammonium method and cellulose acetate method. In the former, depolymerization of cellulose molecules is very low, membrane strength is high, preparation of thin membrane is possible, and consequently permeability of the solute is high. It is found that the permeability increases with a decrease in the membrane thickness. On the other hand, regenerated cellulose membranes from the latter method could be produced by mixing a compatible plasticizer (sulforane) or a poorly compatible plasticizer (polyether) with cellulose acetate and hydrolysing with an alkaline solution. The former membranes had a high permeability but not mechanical strength. The latter membranes were excellent in both permeability and mechanical strength. Cellulose derivative membranes were prepared for haemodialysis. They were modified cellulosic hollow-fibre membranes in which positive diethylaminoethyl or negative carboxymethyl groups were introduced into the cellulose matrix [26]. Cellulose triacetate membranes with a microgradient porous structure [27] showed high haemocompatibility. Cellulosic membranes with hydrophobic benzyl groups [28], cellulose carbamate membranes [29] and cellulose membranes with rough surfaces had high platelet adhesion ratios.
and poor haemocompatibility, whereas those with smooth surfaces had low platelet adhesion ratios and better haemocompatibility [30]. Polyethylene-glycol-grafted cellulose membranes [31–36] were biocompatible in haemodialysis.

Polyion complex membranes prepared from gelation and carboxymethyl cellulose not only offered higher solute permeability than the commercial Cuprophan (cellulose) membrane but also showed suitable mechanical strength, non-toxicity and non-pyrogenicity for dialysis application [35].

Chitosan and its membranes cross-linked with glutaraldehyde had a higher permeability to K⁺, Na⁺, Mg²⁺ and Ca²⁺ whose permeability order is as follows: K⁺ > Na⁺ > Mg²⁺ > Ca²⁺. The differential scanning calorimetry thermograms of the cross-linked membranes confirmed the existence of two types of water [36]. Diffusive permeability coefficients of 15 metal ions (alkali, alkali earth and transition) were measured for water-swollen gel chitosan membranes; namely, an untreated chitosan membrane and four chitosan membranes cross-linked with glutaraldehyde of concentrations between 0.01 and 1% and coated with a protein, and also for comparison with a commercial Cuprophan membrane. The results were compared with those of non-electrolytes in terms of the capillary pore and free-volume models of solute diffusion through gel membranes. Whereas for Cuprophan the permeability coefficients of the metal ions obeyed the models, those for chitosan membranes were found lower than predicted, the largest deviation being for the transition metal ions. The order of their permeability coefficients – Cu²⁺ < Ni²⁺ < Zn²⁺ < Mn²⁺ < Pb²⁺ < Co²⁺ < Cd²⁺ < Ag⁺ – corresponded to the metal ion–chitosan affinity series, which proved that chelation of these ions by chitosan is responsible for the deviation. Mg²⁺, Ca²⁺ and Ba²⁺ ions were also found to be retained by chitosan membranes, though to a lesser degree, whereas K⁺, NH₄⁺, Na⁺ and Li⁺ ions exhibited minor deviations from the models, which was attributed to electrostatic interactions. The diffusive properties of chitosan membranes toward metal ions offer potential for protection of chitosan-based biological systems against the destructive effects of heavy metal ions [37]. Chitosan membranes were used in the study of diffusion of aqueous potassium chloride solution. Diffusion was found to be outside the Fickian regime, this deviation being correlated with possible changes in the membrane structure during the experiments as well as with the occurrence of osmosis. Permeability coefficients \( P \) of KCl through porous cellulose triacetate membranes were measured as a function of the water volume fraction \( WV \), and diffusion coefficients \( D \) were determined using solubility parameters \( K \) and a membrane thickness \( d \) from the relationship of \( P = KD/d \). \( D \) increased with an increase in \( WV \times D \) especially increases abruptly around \( WV = 0.5 \), which corresponds to 2% triethylene glycol content [38]. Adsorption and diffusion of trisulfonated azo dyes onto water-swollen cellulose membrane has been studied. Diffusion behaviour of these dyes was analysed on the basis of a parallel transport theory by surface and pore diffusion. The results could be described by the parallel diffusion model provided that adsorption was stimulated by addition of NaCl. The surface diffusivities for the parallel diffusion model were correlated by the affinity of the dyes; on the other hand, the pore diffusivities for the model were affected by aggregation of the dye depending on its structure and NaCl concentration [39]. Effects of urea on transport phenomena of sulfonated azo dyes with different aggregation constants into water-swollen cellulose membrane were studied. Addition of urea decreased equilibrium adsorption of the dyes onto cellulose and increased the surface and pore diffusivities for the parallel diffusion model of the dye with high aggregation constant [40]. The permeabilities of three kinds of solutes with similar sizes, such as anionic benzenesulfonic acid, neutral styrene glycol and cationic theophylline in the chitosan membrane, were investigated. Benzenesulfonic acid showed the highest permeability, whereas theophylline showed the lowest, although these solutes have almost the same size. This could be explained by the electrostatic attraction or repulsion between the solute and the membrane instead of the size exclusion effect. The permeabilities of benzenesulfonic acid and theophylline increased and decreased.
respectively with the decrease of pH from 7.4 to 4.0 because of the increase of the charge density of the membrane. Thus, the selectivity of benzenesulfonic acid to theophylline increased and reached about 30 at pH 4.0 [41].

By grafting PVA onto chitosan, the crystallinity could controlled and an excellent biocompatibility was yielded. The swelling ratio and permeability of ribofravin through the chitosan-g-PVA copolymer membranes decreased at pH 1.2, but increased at pH 7.4 with PVA grafting percentage. And also, the permeability of the solute was controlled by changing the degree of crystallinity and cross-linking density of copolymer membrane [42]. The effects of the kind of acid to dissolve chitosan, the chitosan concentration, the drying time of the dope solution and the kind of gelating agent on the membrane structure and performance were studied in detail. With increasing chitosan concentration the solute permeability decreased, while the selectivity of theophylline to vitamin B₁₂ increased. The membrane changed from a wholly porous structure to an asymmetric structure by an increase in the chitosan concentration. Furthermore, the use of ethanol as the gelating agent brought about a wholly porous structure with high permeability and low selectivity. The asymmetric structure and the wholly dense structure were obtained in the cases of gelating agents such as aqueous NaOH solution and dimethyl sulfoxide respectively [43].

The alkane (petroleum ether) vapour plasma technique was used to modify the surface of chitosan membranes and led to reduced hydrophilicity of the membrane surface. Mechanical properties such as tensile strength and elongation-at-break of the chitosan membranes were also improved. In particular, there was a six- to seven-fold increase in tensile strength in the wet state for the chitosan membrane treated at 93 W for 30 min. Permeation coefficients through the plasma-treated chitosan membrane for urea, creatinine and uric acid decreased by 54.0%, 83.3% and 64.7% respectively [44].

The diffusion rates of 12 non-electrolytes ranging in molecular radius between 2.5 and 14 Å through the membranes cross-linked with glutaraldehyde and coated with bovine serum albumin (BSA) were measured, and the results were interpreted in terms of the capillary pore model and free-volume model of solute diffusional transport through hydrogel membranes. Glutaraldehyde cross-linking reduced the membrane water content and consequently the membrane pore size and surface porosity, whereas further BSA coating brought about the opposite effect. The optimal chitosan membrane preparation, a compromise between the solute flux and membrane stability and durability, was obtained when the membranes were cross-linked with glutaraldehyde at concentrations between 0.01 and 0.1% (w/w) [45]. The permeabilities of drug or water vapour through sprayed ethylcellulose membranes plasticized with dibutyl sebacate decreased with increasing plasticizer concentration; on the contrary, those through cast membranes increased with increasing plasticizer concentration [46]. The membranes prepared from pectin–chitosan–hydroxypropylmethylcellulose were permeable to the model drug paracetamol. The inclusion of chitosan enhanced stability of the membranes at all physiological pH values [47]. The permeabilities of isoniazid and amitriptyline hydrochloride in chitosan membranes were investigated. Drug concentration was changed from 0.1 to 1.0%, while membrane thickness was varied from 40 to 150 μm. The drugs presented quite different permeabilities, which were related to their molecular weights; the permeabilities did not change with thickness or drug concentration for the ranges investigated [48]. When an additional amount of poly(vinyl pyrrolidone) (PVP) in the blend membranes was increased, the permeabilities increased. The permeability and diffusion of vitamin B₁₂ in the chitosan, chitosan cross-linked with glyoxal and gluteraldehyde, and chitosan–PVA membranes were studied using the ‘lag time’ technique [49].

The diffusion coefficient for both the cross-linked and blended chitosan membranes was solely dependent on the equilibrium swelling ratio of the membrane in water. The transport mechanism for vitamin B₁₂ in these chitosan membranes was consistent with the ‘pore type’. The equilibrium sorption of various sodium salts for chitosan, N-benzoylchitosan and N-octanoylchitosan membranes
was measured and was explained by a dual mechanism, consisting of partition and Langmuir sorption [50]. The mobility of anions through these membranes decreased with Stokes radius and in the order chitosan > N-benzylochitosan > N-octanoylchitosan membranes. The membranes immobilized prostaglandin E1 on heparin-modified chitosan–PVA blend membrane and improved strength properties, permeability functions for low molecular weight solutes and blood compatibility [51].

Organic–inorganic composite membranes from chitosan (Chito) and tetraethoxysilane (TEOS) were prepared [52]. Drug permeation experiments were performed in a phosphate buffer solution of pH of 2.5 and 7.5. Lidocaine-HCl, sodium salicylate and 4-acetamidophenol were selected as model drugs to examine the effect of the ionic property of the drugs on permeation behaviour. The effects of the membrane composition and the external pH on the swelling and the drug permeation behaviour of Chito–TEOS membrane could be summarized as follows: chitosan incorporated into the Chito–TEOS membrane swelled at pH 2.5, while it shrunk at pH 7.5. This behaviour was completely reversible and the membrane responded rapidly to the change in the environmental pH condition. According to the swelling behaviour, an increase in pH from 2.5 to 7.5 yielded an increase in the permeation rate of the drug because of the shrinking of the incorporated chitosan in the Chito–TEOS membrane, while a decrease in pH resulted in a low permeation rate. An optimal Chito/TEOS ratio for maximum pH sensitivity existed and the drug permeation was influenced not only by the external pH but also by the ionic interactions between the drug and the membrane.

Non-charged PVA–SiO2 hybrid membranes are prepared from the sol–gel reaction of PVA and methacryloyloxypropyltrimethoxysilane (γ-MPS) or poly(γ-MPS) [53]. As the polymerization degree increases from γ-MPS to poly(γ-MPS), the sol–gel solution becomes turbid or generates precipitation, while the silica particles formed in the hybrid membranes become smaller from 1.0–3.4 μm to 0.1–0.2 μm or disappear. The membrane tensile strength generally increases from 35 MPa to 44 MPa, while the elongation at break decreases from 318% to 141%. Three deductions are proposed according to the structure of poly(γ-MPS), membrane swelling behaviours in 65–85 °C water and 65 °C alkaline solution, and the diffusion dialysis performance.

1) As poly(γ-MPS) contains no ion-exchange groups like the multisilicon copolymer, it tends to become inhomogeneous during the sol–gel process, which reduces its crosslinking ability.
2) The membrane structure is generally stable in 65 °C water with the swelling degrees of 140–347%, but is damaged in 85 °C water or 65 °C alkaline solution.
3) Non-charged hybrid membranes can be potentially applied in the diffusion dialysis process. The dialysis coefficient of NaOH is in the range of 0.0069–0.0127 m h⁻¹, and the separation factor is in the range of 19–92. The OH⁻ ions may be transferred in the hybrid membranes through PVA-OH groups and interstices between organic and inorganic phases.

**Diffusion Dialysis by Charged Membrane**

It is well known that ion-exchange membranes developed as a diaphragm membrane in electrodialysis show an interesting selectivity in diffusion dialysis [54]. Anion-exchange membranes with cation as the fixed charge can reject cations and show permselectivity for anions. This permselectivity is due to contribution of sorption selectivity in Equation 8.15. That is, in the anion-exchange membrane the distribution of the anions into the membrane is considerably high but that of cations is very low. However, the distribution of H⁺ ions into the anion-exchange membrane is high; in particular, anion-exchange membranes which have a secondary and ternary amine as the fixed dissociation group show the high tendency. Therefore, when the anion-exchange membrane is applied as a diaphragm membrane in diffusion dialysis, the salt is rejected perfectly but the acid can pass relatively freely. Consequently, separation between the acid and salt is possible (see Figure 8.5).
Here, the generalization dialysis coefficient $U$ is defined as Equation 8.37 and the $U$ dependency of various acid–metal salt mixed solutions are summarized in Table 8.2:

$$J = U \Delta C \quad (U = P / l)$$  \hspace{1cm} (8.37)

As can be seen in Table 8.2, the ratio $U_{salt}/U_{acid}$ is $10^{-2} - 10^{-3}$. These results suggest a high selectivity and effective separation of acid and salt. Generally, the permeability of metal salt decreased with an increase in atomic value of metal ion. However, the separateness in hydrochloric acid and metal salt is low because a complex between the metal ion and chloride ion is formed.

Diffusion dialysis is used in the metal-processing industry for the regeneration of used pickling acids. It replaces the retardation process – an ion-exchange process – where high acid losses and insufficient separation of the metal salts make retardation uneconomical.

In the diffusion dialysis process, ion-exchange membranes are used in the form of a membrane stack, separating two different liquids: the used acid and demineralized water. The concentration gradient between the two solutions is the driving force of the process. The special anion-exchange membranes with positive surface charges in their polymer structure facilitate the diffusion of dissociated acid (anions) through the anion-exchange membrane, whereas the cations (metals) are retained by their positive charges. Hydrogen ions are the exception to the rule here; their slight size means that they can pass through the anion-exchange membrane together with the anions, as shown in Figure 8.5 (http://www.osmo-membrane.de/en/technology/diffusion-dialysis.html).

**Table 8.2** Generalization dialysis coefficient for acid–metal salt mixtures through anion-exchange membrane (Neosepta AFN) at 25 °C.

<table>
<thead>
<tr>
<th>Concentration (mol)</th>
<th>$U$ (mol h$^{-1}$ m$^{-2}$ mol$^{-1}$ L$^{-1}$)</th>
<th>$U_{salt}/U_{acid}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Salt</td>
<td>$U_{acid}$</td>
</tr>
<tr>
<td>HCl–NaCl</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>HCl–FeCl$_2$</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>H$_2$SO$_4$–Na$_2$SO$_4$</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>H$_2$SO$_4$–FeSO$_4$</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>HNO$_3$–Al(NO$_3$)$_3$</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>HNO$_3$–Cu(NO$_3$)$_2$</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>H$_3$PO$_4$–MgHPO$_4$</td>
<td>3.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Diagram 8.5** Recovery of acid and concentration of metal ion by diffusion dialysis through anion-exchange membrane.
Applications in the diffusion dialysis using ion-exchange membranes include the following points:

1) Recovery and purification of free acid from acidic waste liquor, such as sulfuric acid, hydrochloric acid, nitric acid and hydrofluoric acid.
2) Deacidification and purification of rare earths and so on in the aforementioned process.
3) Recovery of free acid from acidic waste liquor containing a metallic component.
4) Acid recovery treatment as a first stage in the purification of aluminium sulfate and polyaluminium chloride, and so on.
5) Recovery of waste acid from the aluminate/aluminium etching process.
6) Removal of impurities in the acidic waste liquor.

Stachera et al. [55] prepared two series of membranes by photoinitiated polymerization of 4-vinylpyridine and divinylbenzene (DVB) within the pores of polypropylene microfiltration membranes. The first series was comprised of membranes with varying mass gain and constant DVB content. The second series of membranes had similar mass gains but varying DVB content. The membranes were tested by diffusion dialysis of acid–salt solutions (HCl–NaCl/MgCl₂) in order to determine the effects of both mass gain and degree of cross-linking on dialysis coefficients and acid–salt separation. It was found for the first series of membranes that the dialysis coefficients of the acid and salts decreased and then levelled off with increasing mass gain while separation increased and then also levelled off. The second series of membranes showed a decrease in acid and salt dialysis coefficients but a dramatic increase in separation as the DVB content was increased. These results are interpreted in terms of the fixed charge concentration and the water content of the membranes. A comparison was made with a commercial diffusion dialysis membrane.

Zheleznov et al. [56] investigated the transport behaviour of five carboxylic acids of relevance in biotechnology (acetic, propionic, lactic, oxalic, citric) in diffusion dialysis and neutralization dialysis through an anion-exchange membrane. The dependence of acid anion flux on base concentration in neutralization dialysis was analysed in terms of two limiting situations (boundary-layer control and membrane control) by an empirical two-parameter flux equation in formal analogy to a Langmuir function. When coupled to a life fermenter, neutralization dialysis is a means to control the pH of the fermentation medium. By removing biotoxic acids, this improves microbial productivity, as exemplified with the Propioni system producing vitamin B₁₂ and propionic acid.

Sulfuric acid can be selectively separated from the sulfates of calcium, magnesium, sodium and potassium present in cation-exchange regeneration waste by diffusion dialysis. Studies were carried out to determine the optimum flow rate which will result in the maximum recovery of acid with minimum salt concentration [57].

A diffusion dialysis process for recovery of HF and HNO₃ from aluminium and from process solutions was evaluated. A chemical speciation model was developed to interpret the results and could predict measured F⁻ concentrations with excellent accuracy ($r^2 = 0.94$) over an ionic strength range of 0.5–6 M, an [F⁻] range of 10⁻⁵–10⁻¹ M, and in varied solution species matrices. Transfer rates of acid were related via Fick’s law to differences across the membrane in the HNO₃ or HF concentrations but were unrelated to the concentration gradients of individual ionic species (e.g. H⁺, F⁻ or NO₃⁻) [58].

Xu and Yang [59] produced a new series of anion-exchange membranes from linear engineering plastics poly(2,6-dimethyl-1,4-phenylene oxide) by conducting the processes of bromination, chloromethylation and amination. By using this series of membranes, runs of sulfuric acid recovery from titanium white waste liquor were experimentally conducted. The effects of some important factors such as IEC, content of benzyl-halogen and the relative compositions were investigated.
experimentally on the membrane dialysis process. It was found that the acid recovery rate was improved by benzyl substitution, while the selectivity improved by aryl substitution. By properly balancing them and adjusting the compositions of feed, both higher selectivity and acid recovery could be achieved.

A diffusion dialysis method using anion-exchange membrane was used to recover H$_2$SO$_4$ from waste H$_2$SO$_4$ solution produced in the diamond manufacturing process. Effects of flow rate, operation temperature and metal ion concentration on the recovery of H$_2$SO$_4$ were investigated. The recovery of H$_2$SO$_4$ increased with the concentration of H$_2$SO$_4$ and operation temperature. It also increased with the flow rate ratio of water/H$_2$SO$_4$ solution up to 1, above which no further increase was observed. The flow rate did not affect the rejection of Fe and Ni ions. About 80 of H$_2$SO$_4$ could be recovered from the waste H$_2$SO$_4$, which contained 4.5 M free H$_2$SO$_4$ at a flow rate of $0.26 \times 10^{-3}$ m$^3$ h$^{-1}$ m$^{-3}$. The concentration of recovered H$_2$SO$_4$ was 4.3 M and the total impurity was 2000 ppm. Preliminary economic evaluation revealed that the dialysis system was a highly attractive one that has payback period of only few months [60].

Ionic transport phenomena in a diffusion dialysis system consisting of a charged membrane and mixed electrolyte solutions can be predicted in terms of a simulation method based on the Nernst–Planck equation of ionic flux and the Donnan equation. The simulations show that a charged membrane can control the transport modes of just multivalent ions in two ways by changing its charge density: downhill (transport along their own concentration gradient in a system) and uphill (transport against their own concentration gradient). Hence, a charged membrane whose charge density changes in response to external stimuli can control the transport modes of the specific ions by changing the stimuli. Permeation experiments in a dialysis system consisting of mixed KCl and CaCl$_2$ solutions and a temperature-responsive membrane that has a charge density response to temperature changes showed that the membrane can control the transport modes of just Ca$^{2+}$ ions in two ways in response to temperature changes: downhill and uphill [61].

Charge-mosaic membranes represent a subset of bipolar membranes. They contain anion- and cation-permeable domains. Anions and cations can pass through the membrane without violation of microscopic electrical neutrality. Consequently, much higher rates of transport of electrolytes compared with non-electrolytes of the same size are obtained. The ability of charge-mosaic membranes to separate low molecular weight electrolytes from non-electrolytes of similar size could lead to applications such as desalination of amino acids and other organic species. Here, Grzenia et al. determined rates of CoCl$_2$ (2 : 1 electrolyte), CuSO$_4$ (2 : 2 electrolyte), NiSO$_4$ (2 : 2 electrolyte) and NiCl$_2$ (2 : 1 electrolyte) transport through a charge-mosaic membrane made of microspheres under dialysis conditions. The results were compared with literature values for transport of KCl, a monovalent 1 : 1 electrolyte. The results indicated that the mass flux of salt is the same for all four salts and for KCl. In all cases, negative osmosis was observed where the volume of the dialysate increases. At the same initial dialysand salt concentration, the volume of the dialysate compartment increased more rapidly for divalent 2 : 1 electrolytes compared with monovalent 1 : 1 and divalent 2 : 2 electrolytes tested here. The results highlight the effect of electrolyte charge on permeability for charge-mosaic membranes [62].

Gu et al. [68] developed cation-exchange multisilicon copolymers (i.e. copolymers containing pendant siloxane and $\text{--SO}_3$Na groups) from the copolymerization of sodium styrene sulfonate and $\gamma$-MPS. The copolymerization process proceeded smoothly without formation of gel. The copolymers are compatible with water and can produce transparent and homogeneous solutions when mixed with PVA, so that transparent and compact hybrid membranes are obtained. The membranes are thermally and mechanically stable, with initial decomposition temperatures of 237–273 °C, tensile strength of 9.1–26.0 MPa and elongation at break of 12.4–21.1%. The membranes have a water uptake of
30.0–54.8% and swelling degrees of 46–115% in 65 °C water, which are mainly controlled by the content of –Si(OCH₃)₃ groups in the multisilicon copolymers. Diffusion dialysis separation of NaOH–Na₂WO₄ solution indicates that the alkali dialysis coefficients are in the range of 0.010–0.011 m h⁻¹, higher than the values of commercial membrane (0.00137 m h⁻¹) and other polymer-based hybrid membranes (0.0014–0.0022 m h⁻¹). The membrane structure and properties are correlated with the ions transport mechanism, revealing interesting findings as to the influence of IEC and different functional groups on diffusion dialysis behaviour.

By changing –COOH content in poly(acrylic acid-co-γ-MPS) (poly(AA-co-γ-MPS), a series of PVA–SiO₂ cation-exchange membranes were prepared by the sol–gel processing of poly(AA-co-γ-MPS) in the presence of PVA. The membranes had initial decomposition temperature values of 236–274 °C. The tensile strength ranged from 17.4 to 44.4 MPa. The dimensional stability in length was in the range 10–25%, and the dimensional stability in area was in the range 21–56% in 65 °C water. The water content ranged from 61.2 to 81.7%, and the IEC ranged from 1.69 to 1.90 mmol g⁻¹. The effects of –COOH content on diffusion dialysis performance were also investigated for their potential applications. The membranes were tested for recovering NaOH from a mixture of NaOH–Na₂WO₄ at 25–45 °C. The dialysis coefficients of NaOH (U(OH)) were in the range 0.006–0.032 m h⁻¹, which is higher than that of the previous membranes (U(OH): 0.0015 m h⁻¹, at 25 °C). The selectivity can reach up to 36.2. The diffusion dialysis performances were correlated with the membrane structure, especially the continuous arrangement of –COOH in the poly(AA-co-γ-MPS) chain [64].

8.1.4.2 Haemodialysis

The principle of haemodialysis is the same as other methods of dialysis: it involves diffusion of solutes across a semipermeable membrane. Haemodialysis utilizes counter-current flow, where the dialysate is flowing in the opposite direction to blood flow in the extracorporeal circuit, as shown in Figure 8.6. Counter-current flow maintains the concentration gradient across the membrane at a maximum and increases the efficiency of the dialysis. The system in Figure 8.6 is called an ‘artificial kidney’. In this system the haemodialysis membrane plays a central role in the artificial kidney and is put between the blood and dialysate. Some of the urea, uric acid, creatinine, vitamin B₁₂ and β₂-microglobulin which are metabolism products of blood is removed by transportation based on concentration differences of each material between these two liquids, and water also is removed by convective flow.

Dialyser membranes come with different pore sizes. Those with smaller pore size are called ‘low-flux’ and those with larger pore sizes are called ‘high-flux’. Some larger molecules, such as

![Figure 8.6 Artificial kidney with haemodialysis.](image-url)
β2-microglobulin, are not removed at all with low-flux dialysers; lately, the trend has been to use high-flux dialysers. However, such dialysers require newer dialysis machines and high-quality dialysis solution to control the rate of fluid removal properly and to prevent backflow of dialysis solution impurities into the patient through the membrane.

Dialyser membranes used to be made primarily of cellulose (derived from cotton linter). The surface of such membranes was not very biocompatible, because exposed hydroxyl groups would activate complement in the blood passing by the membrane. Therefore, the basic, ‘unsubstituted’ cellulose membrane was modified. One change was to cover these hydroxyl groups with acetate groups (cellulose acetate); another was to mix in some compounds that would inhibit complement activation at the membrane surface (modified cellulose). The original ‘unsubstituted cellulose’ membranes are no longer in wide use, whereas cellulose acetate and modified cellulose dialysers are still used. Cellulosic membranes can be made in either low-flux or high-flux configuration, depending on their pore size.

Another group of membranes is made from synthetic materials, using polymers such as polyarylethersulfone, polyamide, PVP, polycarbonate and polyacrylonitrile. These synthetic membranes activate complement to a lesser degree than unsubstituted cellulose membranes. Synthetic membranes can be made in either low- or high-flux configuration, but most are high-flux configuration. Nanotechnology is being used in some of the most recent high-flux membranes to create a uniform pore size. The goal of high-flux membranes is to pass relatively large molecules such as β2-microglobulin (molecular weight 11,600 Da), but not to pass albumin (molecular weight ~66,400 Da). Every membrane has pores in a range of sizes. As pore size increases, some high-flux dialysers begin to let albumin pass out of the blood into the dialysate. This is thought to be undesirable, although one school of thought holds that removing some albumin may be beneficial in terms of removing protein-bound uremic toxins (http://en.wikipedia.org/wiki/Hemodialysis#Principle).

Levels of vancomycin in serum are traditionally believed to be unaffected by haemodialysis. By both in vivo and in vitro techniques, the effects of a newer, more permeable dialyser membrane on vancomycin concentrations were investigated. Six patients who were receiving vancomycin and undergoing maintenance haemodialysis with polyacrylonitrile dialyser membranes had post-dialysis levels in serum that were 63% of pre-dialysis levels; the intradialytic half-life was 5.7 h. Vancomycin concentrations in serum exiting the dialyser were 68% of those simultaneously entering the dialyser at the beginning of dialysis. When polyacrylonitrile and conventional cellulose membranes were perfused in vitro with a recirculating solution of vancomycin, the vancomycin concentrations fell to 39% and 91% respectively of the original concentration. The vancomycin concentration in the ultrafiltrate collected from the polyacrylonitrile membranes was only 23% of the original perfusate concentration. A significant decrease in the serum vancomycin concentration may occur during haemodialysis with newer high-flux dialyser membranes. It appears that vancomycin binds to polyacrylonitrile membranes; this binding does not require the presence of protein and is affected by the pH of the perfusate [65].

Transport parameters characterizing a commercial haemodialysis membrane (AH69, Hospal), with and without pretreatment with an adsorbed albumin layer, were determined as a function of the eternal sodium chloride equilibrium concentration. Measurements included membrane potential, streaming potential and electro-osmosis data. Transference numbers of cations and water were directly calculated from these data and were characteristic of high permselectivity at low ionic strength. Model-dependent parameters of the charged membrane, such as ζ potential and fixed charge density, were also calculated [66]. Morti and Zydney [67] carried out in vitro experiments using cellulose acetate (CA110 – Baxter), cellulose triacetate (CT110 – Baxter), PS (F60 – Fresenius), and acrylonitrile copolymer (AN69 – Hospal) dialysers. Clearance and sieving data were obtained with urea, vitamin B12 and dextrans as model solutes. Simulated dialysis was done using donated human plasma.
Results were analysed using membrane transport theory. Data for the CA110, CT110, and AN69 dialysers were consistent with the homogeneous structure of these membranes. The effective pore size of the AN69 membrane was 50% larger than that for the CT110 and six times larger than that for the CA110. This results in much higher clearance for the AN69, particularly for large molecular weight solutes. Results for the F60 suggest a distinct two-layer membrane structure. Quantitative estimates of the pore size of each layer were obtained using hydrodynamic analysis. The tight skin provides a large resistance to convective transport but has minimal effect on diffusion. Exposure to plasma causes a significant reduction in clearance for large solutes because of the resistance provided by a protein layer on the membrane surface. The properties of this layer depend upon the membrane and dialysis conditions. A tighter protein layer formed on the F60 membrane, causing a greater reduction in solute clearance than seen with either the AN69 or CT110 dialysers. The relative reduction in clearance was also greater at high ultrafiltration rates.

The aim of the study by Kubala et al. was to compare the effect of Hemophan® and PS membranes on the phagocyte-derived production of reactive oxygen species (ROS) as well as on neutrophil CD11b and CD62L expression in patients undergoing regular haemodialysis. The effects of haemodialysis membranes were also studied in in-vitro conditions after co-incubating them with differentiated HL-60 cells. ROS production was measured using chemiluminometric and flow cytometric methods. Expression of CD11b, CD62L and mitochondrial membrane potential were detected by monoclonal antibodies and by the JC-1 fluorescent probe respectively. Depressed ROS production was observed in patients already before dialysis. Further decrease in ROS production and an increase in CD11b expression were observed especially in patients after Hemophan haemodialysis. Decreased ROS production and increased CD11b expression were observed also after incubation of HL-60 cells with Hemophan membranes. Mitochondrial membrane potential dropped only after incubating cells with Hemophan membranes, proving its more serious adverse effects in comparison with the PS membrane. In conclusion, deleterious effects of haemodialysis on the metabolic activity of phagocytes were proved. Combining chemiluminescent and flow cytometric methods for the detection of ROS production and determining mitochondrial membrane potential can be useful tools for the analysis of material biocompatibility [68].

Exchanges through dialyser membranes aim: (i) at the removal of uraemic solutes that are retained because of renal failure (e.g. urea) and (ii) at the restoration of depleted compounds (e.g. bicarbonate) [69]. The originally used cellulosic membranes were derived from cotton and therefore termed ‘natural’. They activated complement and leukocytes, inducing an inflammatory reaction as one of the indices of ‘bioincompatibility’ [70]. Later on, chemically developed ‘synthetic’ polymers appeared to mitigate this activation [71]. Furthermore, masking hydroxyl groups, which are responsible for the complement activation with cellulosic membranes, also resulted in more biocompatibility [72]. Therefore, Cuprophan and its analogues were called ‘unmodified cellulosic’ versus the more biocompatible, later developed ‘modified/regenerated cellulosic’ membranes.

Many synthetic membranes have large pore sizes, allowing higher rates of water flux and permitting a higher ultrafiltration capacity as well as a better removal of high molecular weight ‘uraemic solutes’ than membranes with smaller pore size. Therefore, although a high ultrafiltration rate and the capacity to remove large molecules do not strictly run in parallel, large-pore membranes are mostly referred to as ‘high-flux’ membranes, in contrast to ‘low-flux’ membranes with smaller pores.

Hollow-fibre membranes for haemodialysis were prepared by Barzin et al. from PES and PVP (PES/PVP = 18/3 and 18/6 by weight) solution in N,N-dimethylacetamide by the dry wet spinning method. Hollow fibres were then heated either in hot water (95 °C for 30 min) or in air (150 °C for 5 min). These membranes were characterized by ultrafiltering dextrans of different molecular weights (200 ppm in water) at room temperature and an operating pressure of 5 psig. It was observed that
the water flux of the hollow fibre increased significantly when heat treated in water, while it decreased when heat treated in air. On the other hand, MWCO of the hollow fibre increased slightly when heat treated in water, while it decreased drastically when heat treated in air. The morphology of the surfaces of the hollow fibres was studied by atomic force microscopy (AFM) in terms of surface roughness. The roughness of both the inner and outer surfaces decreased upon heat treatment, whether heated in water or in air. The membrane heat treated in air exhibited the lowest roughness parameter. Scanning electron microscope images also showed that the surface morphology of membranes was different before and after heat treatment. Discussions were made on the basis of MWCO and AFM results. The performance data of the hollow fibre heated in air at 150 °C was found to be the most appropriate for haemodialysis application. The hollow-fibre membrane prepared from the blend ratio of PES/PVP = 18/3 showed slightly higher flux than the hollow-fibre membrane prepared from a solution with PES/PVP ratio of 18/6 [73].

Oxygen radicals have recently been attracting close attention because of their involvement in tissue damage and their close relationship to various clinical conditions. It has been suggested that haemodialysis increases oxidative stress, triggering the development of complications such as atherosclerosis and dialysis-related amyloidosis. Sasaki [74] developed a dialyser containing a highly functional PS membrane on which vitamin E had been bonded (PS–ViE). This study was undertaken to evaluate the biocompatibility of this membrane and to conduct other experiments on the membrane in vitro. Human blood was dialysed with minidialysers (300–600 cm² membrane area) made of PS–ViE, cellulose or untreated PS, and the effects of the dialysers on complements (C3a, C4a, and C5a), cytokines (IL-1β and IL-8) and granulocyte elastase as well as their antioxidative activity were investigated (n = 6). The effect of PS–ViE on complement activation and its effects on cytokines were comparable to those of PS membrane, whereas granulocyte elastase following dialysis with the PS–ViE membrane tended to be lower than that seen with PS membrane. The effects of PS–ViE-induced methaemoglobin, lipid peroxide and oxygen radicals were significantly less than those of PS membrane, indicating the antioxidative activity of PS–ViE. Vitamin-E-modified PS membrane dialysers were found to have favourable effects on the immune system and to express antithrombotic and antioxidative effects.

Haemodialytic treatment of patients with either acute or chronic renal failure has had a dramatic impact on the mortality rates of these patients. Unfortunately, this membrane-based therapy is still an incomplete renal replacement, as the mortality and morbidity of these patients remain unacceptably high. Much progress must be made to improve the biocompatibility of haemodialysis membranes as well as their hydraulic and permselective properties to remove small solutes and ‘middle molecules’ in compact cartridges. The next directions of development will leverage materials and mechanical engineering technology, including microfluidics and nanofabrication, to further improve the clearance functions of the kidney to replicate glomerular permselectivity while retaining high rates of hydraulic permeability. The extension of membrane technology to biohybrid devices utilizing progenitor/stem cells will be another substantive advance for renal replacement therapy. The ability to not only replace solute and water clearance but also active reabsorptive transport and metabolic activity will add additional benefit to the therapy of patients suffering from renal failure. This area of translational research is rich in creative opportunities to improve the unmet medical needs of patients with either chronic or acute renal failure [75].

Globally, kidney failure has consistently been a major health problem. The number of patients suffering from kidney failure is radically increasing. Some studies forecast an exponential growth in the number of kidney failure patients during the coming years. This emphasizes the importance of haemodialysis membranes. Current dialysis membranes (cellulose based and synthetic polymer membranes) have irregular pore shapes and sizes, nonuniform pore distribution and limited reusable
capability, which leads to low efficiency of toxin removal. New alumina membranes with uniform, controllable and well-structured nanoscale pores, channelled pores aligned perpendicular to the membrane plane, high porosity, high thermal and chemical resistance, and better mechanical properties are certainly preferable to currently used membranes. Determination of transport properties of alumina membranes will assist in the development of the alumina membranes for enhancing haemodialysis. Experiments were performed Attaluri et al. to evaluate hydraulic permeability, solute diffusive permeability, sieving coefficient and clearance of four solutes (urea, creatinine, vancomycin, and inulin) for alumina membrane. Based on comparison of these values against those of PES membranes, transport performance of alumina membrane was determined. Hydraulic conductivity of the alumina membrane was approximately twice that of the PES membrane, and inulin sieving coefficient for alumina membrane is approximately 21% higher than that for PES membrane. Alumina membrane has higher solute clearances and no albumin leakage, which makes it an effective replacement for current dialysis membranes [76].

8.2 Donnan Dialysis

8.2.1 Principle of Donnan Dialysis

The cation-exchange membrane becomes the wall for anionic transmission, but lets a cation go through freely. Therefore, when salt solutions having a different cation are put across a cation-exchange membrane, the exchange of the cation through a cation-exchange membrane occur. This exchange dialysis is called Donnan dialysis.

As shown in Figure 8.7, when a dilute CuSO₄ solution on the L side (cover processing solution) and concentrated H₂SO₄ solution on the R side (collection liquid) are set across a cation-exchange membrane, Cu²⁺ ions are concentrated to the R side by the Donnan dialysis of H⁺ ions and Cu²⁺ ions and consequently collected.

This characteristic of dialysis is an uphill transport and is possible as the concentration difference of H⁺ ions between both sides is kept high [77].

The concentration ratio in the steady state in this system is

\[ \frac{C_{\text{Cu}^{2+}}^L}{C_{\text{Cu}^{2+}}^R} = \left( \frac{C_{\text{H}^+}^L}{C_{\text{H}^+}^R} \right)^2 \]  (8.38)

When the acid concentration in the collection liquid is kept high enough and the condition \( C_{\text{H}^+}^L \ll C_{\text{H}^+}^R \) is present, the concentration of Cu²⁺ ions in the L side is extremely lowered and consequently the recovery efficiency of Cu²⁺ in the R side is raised significantly. Furthermore, its efficiency is raised by adding a metal chelator to the R side.

A series of cross-linked cation-exchange membranes having graded levels of IEC were prepared by irradiation-induced grafting on polyethylene substrates. A kinetic model was proposed for the transport of metal counter-ions across the membrane in Donnan dialysis.

![Figure 8.7 Donnan exchange dialysis.](image-url)
The transport was found to be adequately described by an equation in which the rate is proportional to the metal concentration. Sulfonated-styrene-grafted membranes were more effective than acrylic-acid-grafted membranes in Donnan dialysis separation applications. The metal transport rate increased with increasing the IEC of the membrane. The metal removal rates were essentially the same with sodium sulfate, sodium chloride or sulfuric acid as the strip agent; however, the use of chelating trisodium ethylenediamine-tetraacetate brought about higher rates of metal removal. The rate of metal transport across a membrane of low IEC and gel water content decreased with increasing size and valence of the metal cation. However, a negligible effect was observed concerning the size and valence of a metal cation on the metal’s transport across a membrane of high IEC and gel water content.

Donnan dialysis is an ion-exchange process between two solutions separated by a membrane to achieve a separation. Only cation- or anion-exchange membranes are installed in a stack. The driving force for the transport of ions is their concentration difference in the two solutions. A typical application of Donnan dialysis is the removal of divalent ions such as Ca\(^{2+}\) ions from a feed stream by exchange for monovalent ions such as Na\(^+\) ions, as shown in Figure 8.8, which shows a feed solution containing CaCl\(_2\) in a relatively low concentration and a stripping solution containing NaCl in a relatively high concentration placed into alternating cells of a stack of cation-exchange membranes. Because of the concentration difference in the feed and the stripping solution, Na\(^+\) ions diffuse from the stripping solution through the cation-exchange membrane into the feed solution. Since the Cl\(^-\) ions cannot permeate the negatively charged cation-exchange membrane, an electrical potential is generated between the two solutions which acts as driving force for the transport of Ca\(^{2+}\) ions from the feed to the stripping solution. Because of the required electroneutrality the identical charges are exchanged between the two solutions; that is, for two Na\(^+\) ions diffusing from the stripping into the feed solution one Ca\(^{2+}\) ion is removed from the feed solution if the membrane is completely impermeable for Cl\(^-\) ions. In addition to water softening, there are several other interesting potential applications in wastewater treatment [78].

8.2.2 Membranes and Technology of Donnan Dialysis

Tubular cation- and anion-exchange membranes were used for the Donnan dialysis of acidic wastewater. The membrane material was prepared from polyethylene modified with styrene and DVB copolymers. The experimental wastewater was a model solution. Its composition and concentration were comparable to those of the wastewater discharged from the manufacture of nitrogenous fertilizers or to the effluent from the washing of nitrocellulose. The treatment method proposed enables both reclamation of water and reuse of nitrates in the form of sodium, or ammonium, salts [79].

The conventional devices (e.g. stirred and tubular dializers) employed in Donnan dialysis experiments do not permit precise description of the associated hydrodynamics. Consequently, detailed analysis of the transport mechanism (e.g. decoupling of boundary-layer and membrane diffusion effects) is often difficult. In an effort to alleviate this difficulty, the rotating diffusion cell (RDC) introduced by Albery et al. [80] was adapted to the study of Donnan dialysis. The porous filter used in
the original design was replaced with an ion-exchange membrane (Nafion® 117, DuPont). The membrane, which separates the reservoir and receiving solutions, is mounted on the base of a hollow rotating cylinder which contains a stationary baffle. The rotation of the cylinder causes well-defined fluid motion on both sides of the membrane so that boundary layer and membrane diffusion control can be readily distinguished and studied. Application of the RDC to Donnan dialysis is illustrated with the Nafion membrane/CoSO₄–H₂SO₄ system [81].

The transfer of ions through an ion-exchange membrane during Donnan dialysis was studied theoretically and experimentally by Miyoshi [82]. By applying the Nernst–Planck equation to the flux of ions in the ion-exchange membrane, an equation was derived for Donnan dialysis in which feed ions and driving ions were of equal valence. The theoretically derived equation was fitted to the experimental values by adjusting diffusion coefficients. Thus, the diffusion coefficients of ions in the ion-exchange membrane which satisfied all the experimental data were determined. It was clearly shown that the ratio of the diffusion coefficient in the membrane to that in solution remained constant at 70 for a system of monovalent feed and monovalent driving ions, and remained constant at 175 for a system of bivalent feed and bivalent driving ions. The flux of ions in Donnan dialysis was found to be influenced by the concentrations of both feed ions and driving ions. Monovalent ions showed a larger flux than bivalent ions, suggesting that they were better as driving ions. The flux of ions was scarcely affected by the kinds of co-ions. It was necessary to pretreat the membrane with driving ions. Donnan dialysis with ion-exchange membranes was investigated experimentally. The equation derived theoretically in [82] was then fitted to the results of a Donnan dialytic experiment, and the diffusion coefficients of various kinds of ions and in various kinds of ion-exchange membranes were obtained. The flux of monovalent ions in Donnan dialysis was much larger than that of bivalent ions. Thus, monovalent drive ions are the best kind of drive ions to employ. It was found that the ratio of the diffusion coefficient in the ion-exchange membrane to that in solution remained constant at 70 for monovalent feed and drive ions except for H⁺ ions, and at 175 for bivalent feed and drive ions. It became apparent that the fundamental equation derived from Fick’s equation and no electric current might be used for Donnan dialysis instead of the Nernst–Planck equation [83]. Donnan dialysis with ion-exchange membranes was studied under various kinds of experimental conditions using ions of different valences. The diffusion coefficients $D_d$ of various kinds of ions in the ion-exchange membrane were obtained by curve fitting an equation derived from the mass balance to three kinds of Donnan dialytic experiments. It was found that the value of $D_d/D_s$ using $D_d$ of monovalent ions in Donnan dialysis with a set of monovalent feed ions and bivalent driving ions was 1/175, where $D_s$ represents a diffusion coefficient in solution. $D_s$ was calculated from the Nernst–Einstein equation substituted by the ionic conductance of ions at infinite dilution in water. Using $D_d$ of bivalent ions in Donnan dialysis with the same set led to a $D_d/D_s$ value of 1/438. Moreover, using $D_d$ in Donnan dialysis with the same set, the value of $D_d/D_e$ was kept constant at 0.4 ($D_e$ expresses the diffusion coefficient in the membrane when the valences of the feed and driving ions are equal). On the other hand, both $D_d/D_s$ and $D_d/D_e$ using $D_d$ in Donnan dialysis with a set of bivalent feed ions and monovalent driving ions were not constant [84].

### 8.3 Neutralization Dialysis

#### 8.3.1 Principle of Neutralization Dialysis

Neutralization dialysis was reported by Igawa et al. [85] in 1986. The desalination mechanism by neutralization dialysis is shown in Figure 8.9 [86].
This principle is based on Donnan dialysis. As shown in Figure 8.9, the cation-exchange membrane (C) separates between the salt (ML) solution and the acid solution (HA), and the anion-exchange membrane separates between the ML solution and the base solution (BOH). The cation (M$^+$) and anion (L$^-$) in the desalination compartment (D) are exchanged by the H$^+$ and OH$^-$ ions respectively, and simultaneously continuous desalination moves with the neutralizing reaction. Namely, in this neutralization dialysis, because the neutralizing reaction happens at the same time as Donnan dialysis happens, the concentration differences of the H$^+$ and OH$^-$ ions between both compartments separated by the cation- and anion-exchange membrane respectively are kept high, and the desalination of the D compartment is always higher than in normal diffusion dialysis.

### Figure 8.9
Neutralization dialysis cell and the schematic ion transport. a: anion-exchange membrane; c: cation-exchange membrane; R1 and R2: silicone rubber sheet; S: spacer; F: acrylic resin frame.

8.3.2 Membranes and Technologies of Neutralization Dialysis

Neutralization dialysis is an energy-saving process consisting of the exchange of the ions of the salts from a feed solution which circulates between cation- and anion-exchange membranes for equivalent amounts of H$^+$ and OH$^-$ ions supplied through the respective membranes from acid and alkali solutions. Experiments show the effect of various physico-chemical process parameters on the rate and degree of desalination of model salt solutions and the possibility to efficiently desalinate multicomponent natural mixtures. It should be pointed out that by a 10-fold increase in the concentration of acid and alkali the flow of the mineral ions can be enhanced threefold. It is shown that a high degree of desalination can also be reached at a high salt concentration. The experimental data obtained by modelling the desalination conditions of a real system using a spiral membrane module reveal a similarity between neutralization dialysis and electrodialysis desalination processes [87]. Neutralization dialysis is a deionization method based on a Donnan dialysis. Weak acid and bases, even urea and alcohols, were also removed by this method, and their transport rates increased with the decrease
of their dissociation constants and with the increase of the concentrations of acid and base solutions in the neutralization system. Aqueous silica, which is a typical inorganic weak acid and abundant in surface water, was also effectively removed by this method. Therefore, tap water was effectively deionized to be pure water with a resistivity of 15 MΩ cm and a silica concentration of less than 10 ppb as SiO₂ and the neutralization dialysis was proven to be an effective deionization method [88]. A theoretical model of the kinetics of neutralization dialysis across ideally selective ion exchange membranes is suggested. The model is based on the use of the Nernst–Planck equations describing ion transport through both the membranes and adjacent unstirred layers (ULs) of solution. Special emphasis is made on the kinetics of change in pH of the desalinated solution. The character of this change with time is shown to depend essentially on the solution concentration. At sufficiently high concentration of the solutions in the three compartments, the presence of the ULs can be neglected in the model, and the pH value in the desalination compartment is determined only by the relationship between the intrinsic permeabilities of the membranes. In this case, the model predicts the pH to be in either the acidic or the alkaline range of values during most of the desalination experiment, so that the passage of the pH through neutrality, if it occurs at all, is 'leap-like'. In contrast, in solutions of sufficiently low concentration, the exchange of counter-ions between the compartments is controlled by mass transfer through the ULs. For this limiting case, a rigorous relationship linking the concentrations in the three compartments is derived under which the pH of the desalinated solution assumes the neutral value. Finally, at intermediate concentration of the solutions, the model is found to describe satisfactorily the data of auxiliary experiments with appropriate choice of parameters [89]. In neutralization dialysis, the salt solution is desalinated continuously. The cations in the desalination compartment are exchanged with protons in the acid compartment across a cation-exchange membrane and the anions are exchanged with hydroxide ions in the base compartment across an anion-exchange membrane. A simple index \( C/J \), where \( C \) (mol cm\(^{-3}\)) is the source phase concentration and \( J \) (mol cm\(^{-2}\) min\(^{-1}\)) is the flux, was proposed for the estimation of the desalination properties in neutralization dialysis. The index was based on the concepts of the ion-exchange reaction rate at the membrane interface and was related to the permeation constant in the source-phase boundary layer at the membrane interface \( P_a \) (cm min\(^{-1}\)), as \( C/J = 1/(k_1 C_{ex}) + 1/P_a \), where \( k_1 \) (mol\(^{-1}\) cm\(^{4}\) min\(^{-1}\)) is the rate constant of the ion-exchange reaction and \( C_{ex} \) (mol cm\(^{-3}\)) is the IEC of the membrane. The desalination efficiency increased with the decrease of the desalination compartment thickness and the decrease of the linear velocity, which can be estimated well by using the index. Tap water was desalinated by neutralization dialysis and pure water was obtained at the outlet of the desalination cell [90].

### 8.4 Piezodialysis

#### 8.4.1 Membranes for Piezodialysis

Amphoteric electric charge membranes or mosaic membranes enable piezodialysis [91-93]. The former membranes are prepared by introducing an anion-exchange group into a cation-exchange membrane having an intermediate ion-exchange group or by introducing a cation-exchange group into a similar anion-exchange membrane. As for the latter, a domain having a cation-exchange group and an anion-exchange group is separated by a neutral domain and those domains are arranged into a mosaic form, as shown in Figure 8.10. A typical mosaic membrane could be prepared by
microphase-separating in lamella form each component of a tricomponent pentablock copolymer from styrene, 4-vinylbenzyldimethylamine and isoprene [94].

Piezodialysis is a membrane process for desalination utilizing a mosaic membrane under a pressure gradient [95], and this concept was first predicted in 1932 by Söllner [91]. The mosaic membrane is composed of anion-exchange elements and cation-exchange elements and enhances salt permeability by circuit current [93]. Various membrane preparation methods for piezodialysis have been reported, such as the phase inversion method [96], ionotropic gel templates method [96], masking method [97], latex-polyelectrolytes method [98], dispersion of ion-exchange resins in a polymer membrane [99] and charge-mosaic membrane including cation- and anion-exchange groups in phase-separated layers [94,100,101]. Charge-mosaic membranes were used for dialytic separations of potassium chloride from low molecular weight non-electrolytes and neutral amino acids. The permeability ratio (potassium chloride to uncharged species) ranged from about 6 in the case of methanol to about 86 in that of mannitol. A theoretical model predicts that optimum rates of dialysis should be achieved by dialysing against salt concentrations other than zero; this prediction was confirmed by experiment. These observations suggest potential applications of mosaics in laboratory separations, industrial processing and haemodialysis [102]. The incompatibility of polymers was used in order to prepare films with regular phase separation. The conversion of the separate phases into polyelectrolytes of different charge should lead to the preparation of charge-mosaic membranes for piezodialysis. Copolymers of suitable monomers with 20–45 mol% butadiene content were synthesized that could be cross-linked with sulfur monochloride. The co-monomers were styrene, 2-vinyl pyridine, 4-vinyl pyridine, methacrylic acid, methyl methacrylate and 2-chloroethyl methacrylate. After conversion into the ionic form, cross-linked films of these copolymers showed salt rejections in the range of 26–78 % and water permeabilities of 40–43 mL m$^{-2}$ day$^{-1}$. These films can be used as anion- and cation-exchange membranes for water desalination. Mixtures of poly(2-vinyl pyridine-co-butadiene) and poly(styrene-co-butadiene) yielded films with regular phase separation. After cross-linking and conversion into the ionic form these charge-mosaic membranes were porous and had poor mechanical strength. Despite these unfavourable properties, a salt enrichment of 4.8% was found in one case [103]. A charge-mosaic membrane was prepared from solution-cast film of the polymer blend of chloromethyl polystyrene (CMPS) with poly(acrylonitrile-co-styrene (SAN)). The membrane was prepared as follows: (1) each polymer was dithiocarbonated to introduce a photo-cross-linkable site (a few mole per cent in the polymer); (2) the dithiocarbonated polymers were solution cast to thin films with regularly phase-separated co-continuous structure (modulated structure); (3) this precursor film was cross-linked by ultraviolet radiation; (4) the CMPS phase was quarternized with bis(dimethylamino)hexane; (5) the SAN phase was sulfonated with chlorosulfonic acid. The film thus modified exhibited negative osmosis and selective permeability; that is, permeable to salt but not to nonelectrolyte, as expected for a charge-mosaic membrane. The high salt permeability seems to originate from the
characteristic two-phase structure in the precursor film [104]. Liu et al. [105] prepared a series of novel hybrid charge-mosaic membranes through a coupling reaction and zwitterionic process. This kind of coupling reaction was conducted between phenylaminomethyl trimethoxysilane and Ti(O-nBu)₄ modified by acetylacetone, which was proved by Fourier transform infrared (FTIR) spectra and the conventional properties of the membranes. IEC measurements indicate that both anion- and cation-exchange capacities of the membranes coated one to three times are in the range of $4.62 \times 10^{-4}$ to $1.48 \times 10^{-2}$ meq cm$^{-2}$ and $1.57 \times 10^{-2}$ to $3.2 \times 10^{-2}$ meq cm$^{-2}$ respectively; while these IECs increase with the elevating Ti content. Streaming potentials show that the isoelectric points (IEPs) of the membranes coated one time are in the range of pH 6–7.5 and decrease with increasing Ti content; but for those coated two times, the IEPs are in the range of pH 6–7.0 and increase with increasing Ti content. Water content demonstrates a decline tendency with increasing pH, whether for the membranes coated once or twice. Pure water flux reveals a downward trend with both the increasing coating times and the ingredients of hybrid precursors. The surface morphologies of the membranes coated three times show that the membrane microstructures can be affected by the compositions of coating solutions, while cross-section scanning electron microscope images suggest that the membrane thickness elevates with increasing coating times.

### 8.4.2 Principle and Fundamental Analysis of Piezodialysis

The principle of piezodialysis [106,107] is explained by ion transport of the charge-mosaic membrane as follows.

When cation- and anion-exchange membranes are set in an electrolytic solution and the pressure, $\Delta p$ is added on one side, an electromotive force $\Delta \psi$ in proportion to added pressure between both sides on the membranes occurs.

These states are shown by I and II in Figure 8.11 and $\Delta \psi$ is represented by the following equation:

$$\Delta \psi = -\beta \Delta p$$

(8.39)

![Figure 8.11 Principle of ion transport through mosaic membrane under pressure difference.](image)
where $\Delta \psi$ and $\beta'$ are the streaming potential and electro-osmosis rate respectively. The value of $\beta'$ is respectively positive and negative in the cation- and anion-exchange membranes. Therefore, an electromotive direction occurring in the cation-exchange membrane is reversed in an anion-exchange membrane. However, as shown in III in Figure 8.11, when a cation- and anion-exchange membrane are arranged across the neutral domain a loop-formed circuit is made, and an electric current called the circulation electric current flows. A cation and an anion permeate each ion-exchange domain and, as a result, an electrolyte is transported.

When the fixed electric charge density in the charge-mosaic membrane is sufficiently greater than the salt concentration of the solution, and the distance between the cation- and the anion-exchange domains in III in Figure 8.11 decreases sufficiently, and the resistance of the solution parts in the circuit is decreased, then the volume flow $J_v$ and solute flow $J_s$ are expressed as follows:

$$J_v = L^m_p (\Delta p - \Delta \pi) - \kappa' (\beta_a - \beta_c) \frac{\Delta \mu_s}{F}$$ (8.40)

$$J_s = -\kappa' \frac{\beta_a - \beta_c}{F} (\Delta p - \Delta \pi) + \kappa' \frac{\Delta \mu_s}{F^2}$$ (8.41)

where $L^m_p$ and $\Delta \pi$ are the volume transmissivity and osmotic pressure respectively. $\beta_c$ and $\beta_a$ are the electro-osmosis transmissivity of the cation- and anion-exchange membrane respectively. $\kappa'$ and $\Delta \mu_s$ are the electrical conductivity of the circulating electric current and the chemical potential difference by the dependence of solute concentration respectively.

In piezodialysis, when the high- and low-pressure sides are phase I and phase II and the salt concentrations in each side are $C_I$ and $C_{II}$ respectively, since the membrane surface on the low-pressure side is also wet enough, the relation, $J_s/J_v = C_{II}/C_I$ is established. When $C_{II} > C_I$ is established, the signs of terms 1 and 2 in Equations 8.40 and 8.41 are reversed. If these term 2s are small enough so as to be able to ignore, then $J_v$ is proportional to $\Delta p$ and $C_{II}/C_I$ should become constant without stopping at $\Delta p$ because $\Delta p \gg \Delta \pi$ is usually established in piezodialysis. On the other hand, when the pressure is constant, $L^m_p$ and $\kappa'$ are not dependent upon the concentration. Consequently, it is expected that $J_v$ becomes a big value, so as to be small if an effect of salt concentration is small. Such a result is confirmed by really preparing an amphoteric membrane [108].

8.4.3 Technologies of Piezodialysis

An explicit but highly schematic theory of the effect of the heterogeneity of charge-mosaic membranes on piezodialysis is given. An effect exists because the ions being transported through different parts of the membrane leave the feed bath at different points and also arrive in the filtrate bath at different points. The effect is always to reduce the salt flux through the membrane. The amount of reduction has been calculated for two geometric arrangements of the parts of the mosaic membrane; namely, alternating strips and a chequerboard of squares [109].

Charge-mosaic membranes are currently being considered for a number of practical applications, most notably ‘piezodialysis’ desalination. Weinstein et al. [110], in the first of a series of papers, discussed the properties of a charge-mosaic membrane subjected to a nonequilibrium thermodynamic analysis, with emphasis on the role of the electrical resistance in the solutions bathing the membrane. Four regimes of operation were delineated by their analysis: (i) membrane control, (ii) solution control, (iii) co-ion leakage control and (iv) polarization control.
For a charge-mosaic membrane operating in the regime of membrane control, the ‘complete’ phenomenological coefficients are essentially concentration independent; hence, the flows may be expressed as linear functions of the global forces. If the membrane operates instead in the regime of solution control, the relationships are not linear but the coefficients are still directly calculable [110]. The nonequilibrium thermodynamic analysis developed in [110] was then subjected to experimental test [111]. Experiments were performed to evaluate a set of six independent transport coefficients characterizing the individual anion- and cation-exchange elements. The results were used in conjunction with calculated values of the solution conductances to predict the transport properties of the charge-mosaic membrane as a whole [111]. A nonequilibrium thermodynamic analysis of piezodialysis is presented. The expressions derived in [110] for the flows as linear functions of the global forces are used to predict the fractional recovery and rate of production of potable water in desalination by piezodialysis. An illustrative calculation is performed for a cylindrical tube (or hollow fibre) made from a hypothetical mosaic membrane whose properties have been calculated from those of Zeo-karb 315 cation-exchange membrane. Perfect radial mixing and the absence of concentration polarization are assumed in order to focus attention on the role played by the membrane elements and circulating currents. For a 1 mm thick membrane under an applied pressure difference of 100 atm, the calculation shows an 81% recovery of potable water of 350 ppm from a brackish water feed of 1500 ppm, the rate of production being 23 gpd ft$^{-2}$ (~564 m$^3$ m$^{-2}$ day$^{-1}$). A thinner mosaic with a correspondingly reduced pattern size would give a proportionately higher production rate with no loss in recovery, provided that significant polarization could be prevented. This calculation sets upper limits on the performance of a given membrane by assuming that its properties, rather than the hydrodynamic conditions, are rate controlling. The analysis suggests ways of changing membrane properties to improve performance [112]. A charge-mosaic membrane has high permselectivity for electrolytes. While there are many reports of attempts to prepare such membranes, it is difficult to make charge-mosaic membranes for practical applications. Higa et al. reported the preparation of charge-mosaic membranes from laminated structures of charged-PVA membranes. The membranes were prepared by alternately stacking negatively charged base membranes and positively charged base membranes and by cutting the stack of charged layers. Permeation experiments were performed in a dialysis system consisting of the membrane and mixed solutions of KCl and sucrose. Although the salt flux through the membrane was about 30 times less than that through the charge mosaic membrane Desalton® (Tosoh Co. Ltd), which was prepared using microphase separation, the permselectivity for salt of their membrane was more than 30 times higher than that of Desalton® [113]. A novel composite charge-mosaic membrane (CCMM) was prepared via interfacial polymerization (IP) of poly(epichlorohydrin amine) and trimesoyl chloride on a PES support. FTIR spectroscopy, environmental scanning electron microscopy, AFM and water contact-angle analysis were applied to characterize the resulting CCMM. The FTIR spectrum indicates that trimesoyl chloride reacts sufficiently with the polyamine. Environmental scanning electron microscopy and AFM pictures show that the IP process produces a dense selective layer on the support membrane. The water contact angle of the CCMM is smaller than that of the substrate membrane because of the cross-linked hydrophilic polyamine network. Several factors affecting the IP reaction and the performance of the CCMM, such as monomer concentration, reaction time, pH value of aqueous phase solution and post-treatment, were studied. The pure water flux of the optimized CCMM was 14.73 L m$^{-2}$ h$^{-1}$ MPa$^{-1}$ at the operating pressure of 0.4 MPa. The values of separation factor $a$ for NaCl–PEG 1000–water and MgCl$_2$–PEG 1000–water are 11.89 and 9.96 respectively. These results demonstrate that CCMM is promising for the separation of low molecular weight organics from their salt aqueous solutions [114].
8.5   Electrodialysis

8.5.1 Principle of Electrodialysis

Electrodialysis transfers ions, as shown in Figure 8.12, by using direct current as a driving force. Cation- and anion-exchange membranes are arranged alternately between electrode cells at both ends, and desalination and concentration are carried out utilizing the selectivity that these membranes can provide [115].

The following reactions take place at each electrode in Figure 8.12:

at the cathode

\[ 2e^- + 2H_2O \rightarrow H_2(g) + 2OH^- \]

at the anode

\[ H_2O \rightarrow 2H^+ + \frac{1}{2}O_2(g) + 2e^- \text{ or } 2Cl^- \rightarrow Cl_2(g) + 2e^- \]

Small amounts of hydrogen gas are generated at the cathode and small amounts of either oxygen or chlorine gas (depending on composition of the electrode stream and end ion-exchange membrane arrangement) at the anode. These gases are typically subsequently dissipated, as the electrode stream effluent from each electrode compartment is combined to maintain a neutral pH and discharged or recirculated to a separate electrode tank.

8.5.2 Fundamental Analysis of Electrodialysis

The main mass transfer in a compartment partitioned off with a cation exchange membrane and anion exchange membrane in electrodialysis tank is shown in Figure 8.13.
Of course the most important term is the migration of ions with the electrodialysis $\Delta m_e$ but is movement of the water $\Delta V_e$ by the electro-osmosis, movement of the salt $\Delta m_c$ and water $\Delta V_c$ by the concentration diffusion in others. The quantities for those movements are expressed by the following equations:

$$\Delta m_e = (t_C - t_A - 1) \frac{I}{F}$$

$$\Delta V_e = (\beta_C + \beta_A) \beta I$$

$$\Delta m_e = -\left( \frac{D_{SC}}{d_C} - \frac{D_{SA}}{d_A} \right) \Delta C \equiv -K_s \Delta C$$

$$\Delta V_e = -\left( \frac{D_{WC}}{d_C} + \frac{D_{WA}}{d_A} \right) \Delta C \equiv K_W \Delta C$$

where $t_C$ is the cation transport number, $t_A$ is the anion transport number, $\beta_C$ and $\beta_A$ are the electro-osmosis coefficients of the cation- and anion-exchange membranes, $D_{SC}$ and $D_{SA}$ are the diffusion coefficients of salt for the cation- and anion-exchange membranes, $D_{WC}$ and $D_{WA}$ are the diffusion coefficients of water for the cation- and anion-exchange membranes, $d_C$ and $d_A$ are the membrane thicknesses of the cation- and anion-exchange membranes, $K_s$ and $K_W$ are the generalization salt diffusion coefficient and generalization water diffusion coefficient, $I$ is the electric current, $F$ is the Faraday constant and $\Delta C$ is the difference of salt concentration across the membrane. Suffixes C and A in these symbols mean cation- and anion-exchange membrane.

From Equations 8.42–4.45, Equation 8.46 can be derived, and the best arrival concentration $C_{\text{max}}$ is determined as shown in Equation 8.47:

$$C_{\text{max}}(\Delta V_e + \Delta V_c) = \Delta m_e + \Delta m_c$$

$$C_{\text{max}} = \frac{(t_C - t_A - 1)(I/F) - K_s \Delta C}{\beta I + K_W \Delta C}$$
8.5.3 Membranes of Electrodialysis

The function of electrodialysis is evaluated by important factors like the selectivity, seclusion ability, electrical conductivity and strength and the homogeneity of the structure of the polymer constructing a membrane, stable hydration characteristics, density and dissociation degree of the fixed dissociation group, mechanical strength, heat resistance and chemical resistance.

8.5.3.1 Fundamental Characteristics

Selective Permeability of Ion-Exchange Membrane The property that an ion-exchange membrane distinguishes an ion by the sign is called selective permeability. The selective permeability of an ion-exchange membrane is explained as follows. When an ion-exchange membrane contacts an electrolytic solution a Donnan equilibrium is attained. The Donnan membrane equilibrium consists of the distribution of the ions inside and outside of the membrane; namely, the membrane phase and the outside solution phase.

The condition of the equilibrium is given by Equation 8.48 when cation A, anion X, and water W as component \( i \) constitute the membrane–solution system considered:

\[
\mu_i = \mu_i^\circ
\]  
(8.48)

where \( \mu_i \) is the electrochemical potential of component \( i \) and the overbar represents the membrane phase. The electrochemical potential of component \( \mu_i \) is given by

\[
\mu_i = \mu_i^\circ + RT \ln a_i + PV_i + z_i F \varphi
\]  
(8.49)

where \( T, P, R, F, \varphi, a_i, V_i, z_i \), and \( \mu_i^\circ \) are absolute temperature, pressure, gas constant, Faraday constant, electric potential, activity, molar volume, valence and standard chemical potential.

When \( z_W \) is zero, Equation 8.50 is derived from Equations 8.48 and 8.49:

\[
\pi \equiv \bar{P} - P = \frac{RT}{V_W} \ln \frac{a_W}{\bar{a}_W}
\]  
(8.50)

where \( \pi \) is the difference in pressure inside and outside the membrane and called swelling pressure. From the equilibrium condition of ion \( A^+ \) or ion \( X^- \) we obtain

\[
\varphi_D \equiv \bar{\varphi} - \varphi = \frac{1}{z_i F} \left( RT \ln \frac{a_i}{\bar{a}_i} - \pi V_i \right)
\]  
(8.51)

where \( \varphi_D \) is the potential difference inside and outside the membrane and called the Donnan potential. When an electrolyte of 1 mol dissociates into ion \( A \) of \( \nu_A \) moles and ion \( X \) of \( \nu_X \) moles according to Equation 8.52, when \( \varphi_D \) is substituted from Equation 8.51 for \( A \) and \( X \), and \( \pi \) is substituted using Equation 8.50, we obtain Equation 8.53:

\[
\nu_A z_A + \nu_X z_X = 0
\]  
(8.52)

\[
\ln \left[ \left( \frac{a_A}{\bar{a}_A} \right)^{\nu_A} \left( \frac{a_X}{\bar{a}_X} \right)^{\nu_X} \right] = \frac{V_{AX}}{V_W} \ln \frac{a_W}{\bar{a}_W}
\]  
(8.53)

This is the Donnan membrane equilibrium equation.
When the molar volume and ratio of electrolyte and water are defined as in Equation 8.54, Equation 8.53 becomes Equation 8.55:

\[
\gamma = \frac{V_{AX}}{V_W}
\]  
(8.54)

\[
\frac{a_A^{\mu a}a_X^{\mu X}}{a_W^{\mu W}} = \frac{a_X^{\mu X}}{a_W^{\mu W}}
\]  
(8.55)

Specially, if \(a_W \approx a_W\), the concise relation is given as

\[
a_A^{\mu a}a_X^{\mu X} = a_X^{\mu X}a_X^{\mu X}
\]  
(8.56)

Using the aforementioned relations, the selective permeability of the ion-exchange membrane with a high fixation charge density can be explained.

For example, we will consider about the case that a cation exchange membrane having fixed dissociation group \(X^-\) contacts with outside solution including \(Na^+\) ion and \(Cl^-\) ion.

The Donnan equilibrium condition in Equation 8.56 becomes

\[
\tilde{C}_{Na}C_{Cl} = \tilde{C}_{Na}C_{Cl}
\]  
(8.57)

where the concentration \(C_i\) is used in substitution for activity here. Because there is fixed dissociation group \(X^-\) other than the \(Cl^-\) as the anion in the membrane phase, the following relation is required for the establishment of electroneutrality:

\[
\tilde{C}_{Na} = \tilde{C}_{Cl} + \tilde{C}_{R}
\]  
(8.58)

From Equations 8.56 and 8.57, the \(Na^+\) and \(Cl^-\) concentrations in the membrane phase, which is kept at equilibrium with the outside solution, are found using the following equations:

\[
\tilde{C}_{Na} = \frac{1}{2}\left(\sqrt{\tilde{C}_{R}^2 + 4C_{Na}C_{Cl}} + \tilde{C}_{R}\right)
\]  
(8.59)

\[
\tilde{C}_{Cl} = \frac{1}{2}\left(\sqrt{\tilde{C}_{R}^2 + 4C_{Na}C_{Cl}} - \tilde{C}_{R}\right)
\]  
(8.60)

**Function of Electrodialysis** The function of electrodialysis is significantly dependent upon the fixed charge and is estimated by using

\[
A_W = \frac{A_R(1-W)}{W}
\]  
(8.61)

where \(A_W\), \(A_R\) and \(W\) are the concentration of the fixed dissociation group, IEC and water content respectively.

When a membrane is immersed in an electrolytic solution, the Donnan equilibrium is attained. When this is approximately expressed by an analytical concentration, the ion concentration in a cation membrane in a KCl aqueous solution as an example can be expressed by the following approximate equations:

\[
C_A = \frac{\sqrt{A_W^2 + 4C_S^2} - A_W}{2}
\]  
(8.62)

\[
C_C = A_W + C_A
\]  
(8.63)
where $C_C$, $C_A$ and $C_S$ are respectively the cation concentration in the cation-exchange membrane, the anion concentration in the anion-exchange membrane and the salt concentration in the external solution which is in equilibrium with that in the membrane. Using Equations 8.62 and 8.63, their approximate values are summarized in Table 8.3. As can be seen from Table 8.3, the selectivity increases with an increase in the concentration of the fixed dissociation group.

### 8.6 Technologies of Electrodialysis

The electrodialysis method is applied to the production of table salt by the concentration of sea water, and of fresh water by desalination of brackish water for example. Applied domains of electrodialysis are summarized in Table 8.4.

#### 8.6.1 Salt Production

Although salt has been manufactured successfully for many years at plants in Japan, the Republic of China and the Republic of Korea by electrodialysis utilizing ion-exchange membranes, rising oil prices since 1973 have increased the proportion of energy cost to over 50% of the total salt manufacturing cost at these plants. It has therefore become increasingly important to find ways to reduce the consumption of the electric and the thermal energy used in these plants, and important improvements have been developed and implemented. Kawate et al. describe current and scheduled improvements for energy savings in the ion-exchange membranes, electrodialyser and evaporating crystallizer [116].

### Table 8.3 Effect of concentration of fixed dissociation group on selectivity.

<table>
<thead>
<tr>
<th></th>
<th>$A_W$ (meq/g H$_2$O)</th>
<th>$C_A$ (meq/g H$_2$O)</th>
<th>$C_C$ (meq/g H$_2$O)</th>
<th>$C_A/C_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_W$</td>
<td>3.5</td>
<td>$7 \times 10^{-2}$</td>
<td>3.57</td>
<td>$2 \times 10^{-2}$</td>
</tr>
<tr>
<td>$C_A$</td>
<td></td>
<td>$3.6 \times 10^{-2}$</td>
<td></td>
<td>$5 \times 10^{-3}$</td>
</tr>
<tr>
<td>$C_C$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_A/C_C$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Table 8.4 Application of electrodialysis.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Desalination, purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production of table salt by sea water concentration</td>
<td>Production of drinking and industrial water from sea and brackish water</td>
</tr>
<tr>
<td>Recovery of useful substance from wastewater</td>
<td>Demineralization and purification of enzymes and protein solution</td>
</tr>
<tr>
<td>Recovery of useful substance from plating wastewater</td>
<td>Desalination and purification of sugar solutions</td>
</tr>
<tr>
<td>Concentration of radio isotopes</td>
<td>Demineralization and purification of amino acid solutions in the food industry</td>
</tr>
<tr>
<td>Production of inorganic medicine</td>
<td>Production of low-salt soy sauce</td>
</tr>
<tr>
<td></td>
<td>Desalination and purification of electroplating waste liquor or industrial wastewater</td>
</tr>
<tr>
<td></td>
<td>Desalination and purification of inorganic and organic chemicals</td>
</tr>
</tbody>
</table>
Tanaka [117] developed the theory of ionic transport processes in ion-exchange membrane electrodialysis systems. The fundamentals in this theory are expressed by the overall mass transport equation of ions and a solution across a membrane pair. The equation includes overall transport number $\lambda$, overall diffusion coefficient $\mu$, overall electro-osmotic coefficient $\phi$ and overall osmotic coefficient $\rho$. These parameters indicate the characteristics of an ion-exchange membrane pair placed in an electrolyte solution containing more than two kinds of ions. These parameters were measured by the electrodialysis of seawater. Parameters $\lambda$, $\mu$ and $\phi$ were expressed by empirical functions of $\rho$. These functions facilitate the simulation of the electrodialytic process. Parameter $\rho$ was found to be related to a non-equilibrium parameter: filtration coefficient $L_p$. Formulas were obtained in order to express various aspects, such as the transport of ions and solutions across membranes, electrolyte concentration in both a desalting and concentrating cell, desalting ratio of a desalted solution and current efficiency. Ionic constituents in a concentrated solution were also measured by the seawater electrodialysis. The relationship between current density and the equivalent ratio of ions in a concentrated solution was expressed by empirical formulas. Thereby, the concentrations of Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$ and SO$_4^{2-}$ ions in a concentrated solution were estimated. The voltage applied to a cell pair is known to be related to electrical resistance and membrane potential. The electrical resistance of solutions in a cell pair was determined by the specific resistance measurement of electrolyte solutions. The direct current electrical resistance of membranes in a cell pair was measured by the seawater electrodialysis. The effect of concentration polarization on the voltage applied to a cell pair is seen in the direct current resistance of the membrane. Energy consumption during the process of seawater electrodialysis was evaluated using the function of the voltage applied to a cell pair. The energy consumption, the limiting current density and the saturation current density were discussed on the basis that the current density and solution velocity (electrolyte concentration) in desalting cells are distributed in an electrodialyser.

Operating parameters of an ion-exchange membrane electrodialytic salt manufacturing plant (NaCl production capacity: 200 000 t per year) using brine discharged from a reverse osmosis seawater desalination plant are discussed. The results were compared with the data obtained from a salt manufacturing plant using seawater. The specifications of the electrodialyser are as follows: the thickness of the desalting cell, 0.05 cm; the flow-pass length in a desalting cell, 2 m; effective membrane area, 2 m$^2$; overall osmotic coefficient of a membrane pair, 30 cm$^4$ eq$^{-1}$ h$^{-1}$; and solution velocity at the inlets of desalting cells, 5 cm s$^{-1}$. The electrolyte concentration at the inlets of desalting cells was set at 1.5 eq dm$^{-3}$, which is consistent with the electrolyte concentration of brine discharged from a reverse osmosis seawater desalination plant. The energy consumed in the salt manufacturing process was assumed to be supplied by a simultaneous heat-generating electric power unit using a back-pressure turbine. The number of evaporators (evaporation pans) was selected to minimize the electric power shortfall of the salt manufacturing process but to be larger than zero. The electric power shortage was assumed to be made up by purchased electric power, which was generated by a condensing turbine. The energy consumption in a salt manufacturing process was obtained by adding the generation energy in the back-pressure turbine, the evaporation energy in the no. 1 evaporator in multiple-effect evaporators, the condensing energy in the heater in the no. 1 evaporator and the purchased energy. The energy consumption in a salt manufacturing process using the brine discharged from a reverse osmosis seawater desalinating plant was 80% of the energy consumption in the process using seawater. The optimum current density at which the energy consumption is minimized was 3 A dm$^{-2}$ for both electrodialyses of brine discharged from the reverse osmosis desalination plant and of seawater [118].
Electrodialysis is applied in Japan for seawater concentrating to total dissolved solids (TDS) of approximately 200 mg L\(^{-1}\) followed by thermal concentration and salt crystallization. A partially desalinated water (electrodialysis diluate) is obtained at the same time. Its further desalination for potable water production may be considered to decrease the costs of electrodialysis by obtaining two valuable products instead of mere salt. Univalent-ion permeable ion-exchange membranes, however, are applied in the electrodialysis process and as a result the contents of calcium, magnesium and sulfate ions in the diluate are relatively high (in relation to chloride), which makes any further processing difficult. Electrodialysis reversal may overcome these shortcomings. The salinity of partially desalinated water is as high as TDS 22.9 mg L\(^{-1}\). If dual-purpose desalination–salt production electrodialysis concern is high degree of desalination, which is however necessary, this implicates many problems in the electrodialysis process that are the result of major differences in electrodialysis concentrate and diluate concentrations and the small conductivity of the potable-water-grade diluate. Electrodialysis of seawater was investigated in a two-step stand with an electrodialysis–multistage flash distillation–crystallization system being the first stage. Univalent ion-permeable Tokuyama Co. ACS and CMS membranes were applied in the first step and normal-grade CMV, AMV Asahi Glass membranes in the second step (for the first step diluate treatment). The electrodialysis stack developed by the author and equipped with a 0.19 mm spacer was applied. A single-pass low residence time mode of operation was applied to avoid gypsum crystallization in the second step electrodialysis concentrate. The first-step diluate containing 0.38 g L\(^{-1}\) Ca\(^{2+}\), 1.26 g L\(^{-1}\) Mg\(^{2+}\), 4.08 g L\(^{-1}\) Cl\(^-\) and 2.78 g L\(^{-1}\) SO\(_4^{2-}\) was treated by electrodialysis reversal, yielding 90% recovery. Potable-water-grade electrodialysis reversal diluate was obtained. No gypsum crystallization in the electrodialysis reversal concentrate was observed despite its 360% saturation. The total water recovery of the electrodialysis–multistage flash distillation–crystallization system is equal to 90%. As there are two valuable products in the process described, the cost of each of them is obviously related to their selling price. If $30 per ton of salt is assumed, the potable water cost is estimated to be only $0.44 m\(^{-3}\) [119].

Mother liquid discharged from a salt-manufacturing plant was electrodialysed at 25 and 40 °C in a continuous process integrated with SO\(_4^{2-}\) ion low-permeable anion-exchange membranes to remove Na\(_2\)SO\(_4\) and recover NaCl in the mother liquid. Performance of electrodialysis was evaluated by measuring ion concentration in a concentrated solution, permselectivity coefficient of SO\(_4^{2-}\) ions against Cl\(^-\) ions, current efficiency, cell voltage, energy consumption to obtain one ton of NaCl and membrane pair characteristics. The permselectivity coefficient of SO\(_4^{2-}\) ions against Cl\(^-\) ions was low enough particularly at 40 °C and SO\(_4^{2-}\) transport across anion-exchange membranes was prevented successfully. Applying the overall mass transport equation, Cl\(^-\) and SO\(_4^{2-}\) ion transport across anion-exchange membranes was evaluated. SO\(_4^{2-}\) ion transport number decreased due to the decrease of electro-migration of SO\(_4^{2-}\) ions across the anion-exchange membranes. SO\(_4^{2-}\) ion concentration in desalting cells became higher than that in concentration cells, and SO\(_4^{2-}\) ion diffusion was accelerated across the anion-exchange membranes from desalting cells toward concentrating cells [120].

Seawater reverse osmosis brines have been identified as an alternative to common NaCl sources for the chlor-alkali industry. Electrodialysis was evaluated as a preliminary step of NaCl concentration for these brines. Experimental results showed that electrodialysis was an effective concentration technology, where NaCl values up to 252 g L\(^{-1}\) were reached at 0.3–0.4 kA m\(^{-2}\) with a power consumption of approximately 0.20–0.30 kW h kg\(^{-1}\) NaCl. As the membranes used (Neosepta CIMS and ACS) were mainly selective for univalent ions, polyvalent ions were partially removed from the brine, benefiting its reuse. NaCl concentrated solutions are to be used as feed brine in the chlor-alkali industry after a purification step [121].
8.6.2 Recovery

An aliphatic organic acid fraction is separated from the kraft black liquor by subjecting the liquor to ultrafiltration, treating the resulting permeate by electrodialysis, acidifying the resultant deionate to about pH 4–5, separating the lignin solids which precipitate following this acidification, raising the pH of the separated solution to about 7–8 and finally subjecting the neutralized solution to electrodialytic water-splitting [122].

Caustic soda leaching liquor of tungsten ore always contains a certain amount of free alkali. The general method of removing free alkali in the liquor is to neutralize it by inorganic acid. A new method—that is, applying electrolysis with ion-exchange membrane to recover free alkali from caustic soda leaching liquor of tungsten ore—was proposed by Zhang and Zhang [123]. In the electrolysis cell the effective membrane area is 100 mm × 100 mm, the anode was β-PbO₂ plated on screen of titanium net, the cathode was active nickel plated on screen of stainless steel net, and the membrane was a kind of perfluorosulfonic acid membrane. Some factors that affect the electrolysis process—including the NaOH concentration in the anolyte and catholyte, the distance between the electrodes, the temperature and the current density—were investigated. The results showed that by choosing the proper operating condition the specific energy consumption could be controlled within 2 kW h kg⁻¹ NaOH. Electrolysis with ion exchange membrane not only can recover free alkali from caustic soda leaching liquor and reduce the consumption of inorganic acid, but also utilize the hydrogen gas produced in the process to produce tungsten powder [123].

Stimulated by the depletion of phosphate resources, phosphate recovery systems have been studied in recent years. The use of struvite reactors has proven to be an effective phosphate recovery process. However, the struvite reactor effluent still consists of an excessive amount of phosphate that cannot be recovered or directly discharged. In the study by Zhang et al., selectrodialysis (SED) was used to improve the efficiency of phosphate recovery from a struvite reactor. SED was implemented in such a way that phosphate from the effluent of an upflow anaerobic sludge blanket reactor was transferred to the recycled effluent of a struvite reactor. Prior to the experiments, synthetic water with chloride and phosphate were used to characterize the efficiency of SED for phosphate separation. Results indicate that SED was successful in concentrating phosphate from the feed stream. The initial current efficiency reached 72%, with a satisfying (9 mmol L⁻¹) phosphate concentration. In the experiments with the anaerobic effluent as the phosphate source for enrichment of the effluent of the struvite reactor, the phosphate flux was 16 mmol m⁻² h⁻¹. A cost evaluation shows that 1 kWh electricity can produce 60 g of phosphate by using a full-scale stack, with a desalination rate of 95% on the feed wastewater. Finally, a struvite precipitation experiment showed that 93% of phosphate could be recovered. Thus, an integrated SED–struvite reactor process can be used to improve phosphate recovery from wastewater [124].

Güvenç and Karabacako-lu [125] investigated the feasibility of the removal of Ag⁺ ions in a model solution, and a sample of rinse water provided from an industrial plating plant was investigated in a batch electrodialysis system. The experiments were carried out using two different types of ion-exchange membranes. The effects of applied potential, pH value and initial silver concentration on the duration of electrodialysis and energy consumption were examined. Full removal of Ag⁺ ions was achieved from model solutions and the sample of rinse water. The most convenient applied voltage and energy consumption values to remove Ag⁺ ions were reported. These results will be useful for designing and operating different capacities of electrodialysis plants for recovering Ag⁺ ions.

To remove the excess nitrogen and phosphorus in swine wastewater, an electrodialysis technique was applied to an advanced treatment method. The laboratory-scale swine wastewater treatment system constructed for the study by Fumoto and Haga consisted of an activated sludge process, as the
main treatment unit, and electrodialysis, as an advanced treatment unit. This system was operated for 200 days and the processing performance was evaluated. By electrodialysis, approximately 99% of NO$_3^-$ and PO$_4^{3-}$ in the activated sludge-treated water (AT solution) was removed during operation. Furthermore, electrodialysis decreased the colour density of the AT solution at a rate of 58%. The advanced treatment of swine wastewater by electrodialysis proved to be an efficient technique to remove excess nitrogen and phosphorus, and decrease colour density [126].

Galvanic processes are one of the main activities that contribute to metal discharges into the environment. The wastewater generated contains a high load of salts and metals that must be treated for recovery chemicals and water, thus saving resources. In a study by Benvenuti et al., the treatment of effluents from a bright nickel electroplating process by electrodialysis was investigated in order to concentrate and extract nickel and its salts and recover water for reuse, saving industrial and environmental resources. The study was started as a case requested by a European company, a manufacturer of electrodialysis plants, due to the operation of equipment used in the treatment of nickel plating wastewater at a Brazilian enterprise. After many tests using real and synthetic nickel plating effluent and determination of limiting current values in previous studies, one bench-scale electrodialysis system was evaluated, containing five compartments separated by four 16 cm$^2$ membranes. A synthetic effluent was used based on industrial bath compositions, including salts and organic additives. Nickel extraction, pH and conductivity were evaluated for all compartments. After electrodialysis, the treated effluent was evaluated by chemical analysis to verify its quality. It was found that electrodialysis treatment generates, as product, a very low conductivity solution, allowing the reuse as rinse water, and a concentrated solution able to fortify the bath and recover volumes lost by evaporation and drag during the nickel electroplating process [127].

### 8.6.3 Water Desalination

Electrodialysis was one of the first commercially available large-scale water desalination processes based on membranes and is still widely used all over the world. However, in spite of long-term reliable operation experience and clear technical advantages of electrodialysis in brackish water desalination and wastewater treatment, the process is being increasingly replaced by reverse osmosis and nanofiltration in recent years. The main reason for the decreasing use of electrodialysis in the production of potable water is the overall process costs. Strathmann presented a brief description of the fundamentals of electrodialysis and analysed the various parameters determining the process costs. As a result, it was shown that, in addition to the investment-related costs, energy consumption is the dominating factor determining the economics of the process. In electrodialysis, both investment and the energy costs depend strongly on the feed water salt concentration. By comparing the costs of various desalination processes the range of feed and product water concentration – in which electrodialysis has a clear advantage over the competing processes in terms of the overall costs, including pre- and post-treatment procedures – was identified. The assessment indicated that electrodialysis can be most effectively used for the production of potable water from feed waters with concentrations between 1000 and 10 000 ppm total dissolved salts. For seawater desalination, electrodialysis cannot presently compete in terms of overall process costs with reverse osmosis [128].

Solar energy is a clean source of energy that is available in all regions of the world. Bahrain, where the research by AlMadani was conducted, is rich in solar energy expressed as hours of sunshine, which ranges between 13 h per day in the summer months to 10 h per day in the winter months. Water desalination by solar energy can be effectively achieved by using an electrodialysis process operated with photovoltaic cells. This method is attractive because electrodialysis requires a DC power supply as the driving force for removing the salt ions. This experimental work involved a small-scale
commercial-type electrodialysis stack powered by photovoltaic cells. The stack consisted of 24 cell pairs, arranged in four hydraulic stages and two electrical stages. The feed water was fed from two sources, the first being sodium chloride solutions prepared in the laboratory and the second was groundwater of medium salinity. The experiments were done at temperatures ranging from 10 to 40 °C and product flow rates ranging from 50 to 300 gallons/day. Increasing the flow rate resulted in lower product quality, in terms of percentage salt removal. Increasing the temperature generally resulted in better product quality [129].

The shortage of drinking water is a major problem in southeast Spain. In these areas, it is essential to make use of water from underground reservoirs, most of which are overexploited and suffer from saline contamination given their proximity to the sea. The desalination of brackish water is a means of obtaining low-cost drinking water. Electrodialysis is a technique based on the transport of ions through selective membranes under the influence of an electrical field. This technique has proved its feasibility and high performance in the desalination of brackish water, the desalting of amino acids and other organic solutions, effluent treatment and/or recycling of industrial process streams and salt production. In the study by Ortiz et al., a mathematical model for the desalination of brackish water through controlled potential electrodialysis was developed. The application of this model allows: (i) to predict the behaviour of the system, (ii) to calculate the electrical energy consumption and (iii) to calculate the necessary time for successful desalination. The model was applied with satisfactory results to the desalination of an NaCl solution in different experimental conditions. The model developed could be applied to commercial electrodialysers (pilot/industrial plant) working in batches with recirculation and controlled potential, which is the usual mode of operation of such equipment when the requirements for treated water are moderated [130].

Most widely applied and commercially proven desalination technologies fall into two categories of thermal- (evaporative) and membrane-based methods. Membrane methods are less energy intensive than thermal methods, and since energy consumption directly affects the cost-effectiveness and feasibility of using desalination technologies membrane methods such as reverse osmosis and electrodialysis they have attracted great attention. In the paper by Sadrzadeh and Mohammadi, water desalination using a laboratory electrodialysis set-up was described and evaluated. The Taguchi method was initially used to plan a minimum number of experiments. An L9 orthogonal array (four factors in three levels) was employed to evaluate effects of temperature (at 25, 40 and 55 °C), voltage (at 5, 7 and 9 V), flow rate (at 0.07, 0.13 and 0.25 mL s⁻¹) and feed concentration (at 10 000, 20 000 and 40 000 ppm) on separation percentage of salt ions. Maximum percentage of desalination was obtained at the lowest feed concentration and flow rate levels (10 000 ppm and 0.07 mL s⁻¹ respectively) and the highest voltage and temperature levels (9 V and 55 °C respectively). Analysis of variance was applied to calculate the sum of square, variance, ratio of factor variance to error variance and contribution percentage of each factor on response. The results showed that all factors had a significant effect on the response. It was found that feed concentration is the most influential factor on electrodialysis performance (its contribution percentage was 82.4%). It was finally found that, contrary to the case of wastewater treatment (concentrations of lower than 1000 ppm), in which flow rate is the influential factor, in desalination of seawater (concentrations of upper than 10 000 ppm) it is feed concentration that is the key parameter [131].

The composition of feed water used in electrodialysis desalination causes the risk of CaCO₃ scale crystallization in electrodialysis equipment, which leads to a decrease in process efficiency. To control scaling in water systems, several scaling indices and tests, permitting prediction of scaling occurrence, have been devised. Ben Salah Sayadi et al. [132] proposed an accelerated scaling test allowing the following of CaCO₃ formation in a water desalination plant using the electrodialysis process. Tests were performed using a pilot unit as a conventional electrodialysis in batch recirculation mode. By simple in
situ measurements of pH and flow rate of the concentrate, the crystallization onset and growth of CaCO₃ were followed during the pilot operation. This led to a precise determination of the number of concentrate recirculation times, and therefore to the highest recovery rate without scaling risk, as a function of the inlet water quality and the antiscale pretreatment.

8.6.4 Production of Organic Acid

A process for producing, recovering and purifying lactate from a fermentation broth so that it can be efficiently and economically converted to lactic acid is disclosed in the patent of Datta. The process comprises growing a high lactate-producing microorganism on an inexpensive substrate until a whole broth containing about 75–90 g of lactate salt is obtained. The whole broth including the viable cells is then electrodialysed in a unit having anionic-permeable and cationic-permeable membranes to cause the lactate salt to concentrate in an aqueous liquid which can be treated to convert the lactate salt to lactic acid [133].

Organic acids are increasingly used for various industrial applications. Their production is mainly achieved by fermentation. Precipitation or extraction stages, which generate large amounts of effluent, are then traditionally used to get the acid in a suitable form. To lower the impact on the environment, the implementation of cleaner operations are investigated. In this context, a complete process targeted around membrane operations for clarification, concentration and conversion was studied by Bailly et al. Their paper is devoted to the study of the concentration step, carried out by conventional electrodialysis. A model, based on the description of the solute and solution fluxes through the membranes was developed. Dedicated procedures were proposed to determine the different contributions (i.e. electromigration and diffusion) to these fluxes so as to feed the model. This approach was then applied to the concentration of sodium lactate solutions. The preponderance of electromigration was thus demonstrated, as well as the existence of a maximum achievable concentration, the predicted value of which was confirmed experimentally. Comparison between conventional electrodialysis of sodium and ammonium lactate solutions showed that the counter-ion had a negligible influence on the transport of lactate. The influence of the membrane characteristics was also drawn from a comparison with previously published results. Finally, the predictions of the model were compared with the experimental results concerning the concentration of a fermentation broth and a good agreement was stated. The approach proposed by Bailly et al. can also be used to design electrodialysis concentration of organic acid salts other than lactate [134].

Electrodialysis was used for lactic acid recovery from fermentation broth. In the first step, lactate was recovered and concentrated by desalting electrodialysis, and the second step was electroconversion of lactate to lactic acid by water-splitting electrodialysis. A final lactic acid concentration of 151 g L⁻¹ was obtained. The total energy required in both electrodialysis processes was about 1.5 kW h per 1 kg of lactic acid obtained. The fermentation broth had to be pretreated prior to the electrodialysis experiments. The pretreatment consisted of ultrafiltration, decolorisation, and the removal of multivalent metal ions [135].

The production of organic acids needs innovations to keep up with the development of modern chemical and biochemical industries. Electrodialysis may be the key innovation. Accordingly, based on a summary on the related literature, Huang et al. compiled an introduction to the production of organic acids by using electrodialysis, which includes conventional electrodialysis, electrometathesis, electro-ion substitution, electroelectrodialysis, electrolydrolysis with bipolar membranes, electrodeionization and two-phase electrodialysis. The hope expressed is that, apart from the separation and conversion of organic acids or organic salts, electrodialysis can promote the comprehensive utilization of renewable resources and contribute to the sustainable development of humankind [136].
Water provision for developing countries is a critical issue as a vast number of lives are lost annually due to lack of access to safe drinking water. The presence and fate of inorganic trace contaminants is of particular concern. Trace inorganic contaminants have been found in elevated concentrations in drinking waters supplied directly from brackish groundwaters in developing countries. Desalination and the removal of trace inorganic contaminants from bore water sources from a remote community in Australia using electrodialysis were investigated by Banasiak and Schäfer. The influence of applied voltage on the removal of the trace contaminants was evaluated. While the results from the study demonstrated that electrodialysis is an effectual method for the removal of TDS and a number of trace inorganic contaminants from brackish groundwaters to below drinking water guideline levels, the deposition of trace contaminants on the membranes (fouling) influenced the electrodialysis process in relation to ionic flux and the effectiveness of trace contaminant removal [137].

Whey protein materials (such as from cheese-making processes), whey protein concentrates and whey protein isolates are deflavoured by adjusting the pH of an aqueous composition of such whey protein materials to about 8.0 to about 12 using membrane electrodialysis to solubilize the whey proteins and to release the flavouring compounds. Thereafter, the pH-adjusted composition is passed to an ultrafiltration membrane having a molecular weight cut-off up to about 50 000 Da under conditions in which the flavouring compounds pass through the membrane, leaving the retained whey protein material with improved flavour [138].

Eliseeva et al. [139] studied transport of basic amino acids during the electrodialysis and suggested procedures for their recovery from various mixtures. Peculiarities of basic amino acids transfer through the ion-exchange membranes are closely connected with their amphoteric nature and high values of IEPs in comparison with neutral amino acids. Dimensionless concentrations for the components of systems of basic amino acid–tartaric acid were calculated and the values of amino acid recovery were measured. The possibility of basic amino acids solution demineralization using the method of electrodeionization was shown.

The high salt concentration of soybean oligosaccharides extract from sweet slurry, a by-product of soybean sheet production, limits its full utilization in the food industry. Conventional electrodialysis demineralization of the extract was performed to reduce the ion content. The effects of operation parameters on efficiency of desalination and oligosaccharides retention in the sweet slurry extract were investigated. The experimental results showed that high desalination efficiency and oligosaccharides retention could be achieved under optimal conditions of 20 V working voltage with 60 L h\(^{-1}\) flow rate, which resulted in a reduction of the total ion concentration from 5.022 mg mL\(^{-1}\) to about 0.26 mg mL\(^{-1}\) (94% reduction), and more than 80% of oligosaccharides retention in the dilute compartment. The result showed that ion-exchange-membrane-mediated electrodialysis was feasible for desalination of oligosaccharides extract from the sweet slurry [140].

### 8.7 Electrodialysis with Bipolar Membranes

#### 8.7.1 Principle and Fundamental of Bipolar Membrane Electrodialysis

See http://www.fumatech.com/EN/Membrane-technology/Membrane-processes/Bipolar-membranes.

The essential characteristic of electrodialysis with bipolar membranes is the combination of conventional electrodialysis for salt separation with electrodialysis water splitting for the conversion of a salt...
into its corresponding acid and base. Bipolar membranes induce the splitting of water into protons and hydroxide ions:

$$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$$ (8.64)

The process can be considered a rival to the electrolytic production of acids and bases. As a result of the compulsory co-production of hydrogen and oxygen, the energy theoretically needed for electrolytic water splitting is more than twice as high:

$$\frac{5}{2}\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{4}\text{O}_2$$ (8.65)

The potential difference needed for the electrodialytic production of 1 M solutions is 0.83 V, which is equivalent to an energy consumption of 22 W h. In contrast, the electrolytic production of a theoretical drop in potential is equivalent to an energy consumption of 55 W h. Further advantages of bipolar membrane technology include the comparatively simple apparatus configuration, the option of a stack-like set-up and the low investment costs. As shown in Figure 8.14, bipolar membranes consist of a cation-exchange membrane, an anion-exchange membrane and a catalytic intermediate layer to accelerate the splitting of the water into protons and hydroxide ions.

The main requirements for a bipolar membrane are as follows. The simplest design for bipolar membrane processes is the so-called three-chamber stack. In this case, the recurring membrane unit in the stack is composed of one bipolar membrane, one cation-exchange membrane and one anion exchange membrane. In the electric field, the $X^-$ ions migrate through the anion-exchange membrane to the anode, are then retained on the cation-selective side of the bipolar membrane and finally form...

**Figure 8.14** Scheme of electrodialysis stack for ionic liquid synthesis. ChoCl: choline chloride ((HOCH$_2$CH$_2$N(CH$_3$)$_3$)$^+$Cl$^-$); ERS: electrode rinse solution.
acid \((H^+X^-)\) together with the \(H^+\) ions produced in the bipolar membrane. Similarly, base \((M^+OH^-)\)
solution is formed on the anion-selective side of the bipolar membrane, while a diluate is produced in
the central chamber for the raw solution.

A large number of different applications for bipolar membrane technology have been tested and
developed. The first industrial process was developed by Aqualytics for the recovery of hydrofluoric
acid and nitric acid from pickling baths in the steel industry. Nowadays, much interest is paid to the
separation and treatment of organic acids such as lactic acid and citric acid from fermentation solu-
tions. The first plants for producing amino acids were developed not only in the field of biotechnology
but also in the chemical and pharmaceutical industries. A bipolar membrane process, suitable for
standardization, can result from the production of ultrapure water via continuous deionization using
bipolar membranes. Considering the bipolar membrane electrodialysis unit as a black box, it allows
the production of an acid and a base from a neutral salt feed stream. Bipolar membrane electrodialysis
can become interesting if either the acid or the base is the desired product [141]. Further, it has certain
applications in process integration. Examples are the pH control of fruit juices or fermentation reac-
tors. Reviews of the possible use of bipolar membrane electrodialysis have become available recently
[142-144]. From salt solution and water, base, acid and diluted salt can be produced using bipolar
membrane electrodialysis. Promising applications have been investigated in acid and base production,
in the acidification of product streams or for special separations, such as the separation of amino acids
on the basis of their IEPs. The economically most interesting applications are those in the overlap of
the areas. Then Davis et al. could reduce side products or achieve process schemes not possible before.
As an example, sodium lactate from a fermentation step can be converted into lactic acid by bipolar
membrane electrodialysis [145]. The side product, sodium hydroxide, can be used to control the fer-
mentation reaction. Designing bipolar membrane electrodialysis in the areas of overlap provides
increasing prospects for its economic feasibility; however, it also increases the complexity and chal-
lenges that have to be met. Possible areas of application for bipolar membrane electrodialysis are in
organic (e.g. lactic, ascorbic, salicylic, amino) and inorganic (e.g. HF, H₂SO₄, HCl) acid production,
base production (e.g. sodium hydroxide, potassium hydroxide, sodium methoxide) and process inte-
gration (e.g. recycling – such as of pickling acid – purification, pH stabilization, fermentation).

8.7.2 Technologies of Bipolar Membrane Electrodialysis

Electrodialysis is an electrochemical process mainly used in industry for solution demineralization.
A new type of membrane, the bipolar membrane, allows the electro-dissociation of water. The first
industrial application of bipolar membrane electrodialysis was oriented toward the recovery of acids
and bases from salt streams. Recently, bipolar membrane electrodialysis has been used to inhibit pol-
yphenol oxidase in apple juice, the enzyme responsible for the enzymatic browning of cloudy juice,
and to separate soybean proteins from other components without denaturing them, in order to pro-
duce protein isolates. Bipolar membrane electrodialysis technology is an environmentally friendly
technology with a wide-ranging application potential [146].

Wilhelm et al. [147] investigated the influence of asymmetric bipolar membranes on the salt impu-
rities in the acid and base product. The thickness of either or both of the ion-permeable layers of a
bipolar membrane is increased. With increased layer thickness, the current–voltage curves of the elec-
trodialysis repeat unit recorded in a pilot-scale module show a reduced limiting current density, and
thus they indicate an overall higher selectivity of these arrangements. Furthermore, these curves indi-
cate water transport limitations for some membrane arrangements. Electrodialysis experiments with
the same module at a high current density confirm the overall salt ion flux reduction. Moreover, these
acid–base electrodialysis experiments directly reveal an increased asymmetry of the salt ion fluxes
which can be utilized to design custom-made bipolar membranes with very high purity of either the
produced acid or the base while keeping the bipolar membrane functioning without water transport
limitations. The experiments presented also show that the bipolar membrane behaviour can be char-
acterized in situ; that is, as a part of an electrodialysis repeat unit mounted in a pilot-scale electrodial-
ysis module.

Xu and Wang [148] investigated the production of citric acid from sodium citrate by electrodialysis,
using bipolar membranes prepared from poly(phenylene oxide). The process feasibility was tested
using a laboratory electrodialysis cell with an effective area 20 cm². Based on the configuration of bipo-
lar membranes—cation membranes, the performances of various sodium sulfate and sodium citrate
concentrations were compared and discussed in terms of ionic transport and ion exchange. It is sug-
gested that, in such an operation, the optimum concentration range is 0.5–1.0 M for sodium citrate and
0.25–1.5 M for sodium sulfate from the viewpoint of energy consumption, current efficiency and acid
concentration.

Igliński et al. [149] carried out investigations on sodium citrate conversion to citric acid by the pure
electrodialysis process with a bipolar membrane. The current efficiencies based on the number of
moles of acid produced and on the concentration changes were determined. Both the mean and
the instantaneous efficiencies were calculated. It was found that the mean efficiencies of acid and base
are higher at the lowest current densities (52 mA cm⁻²), with the maximum being observed at 78 mA
cm⁻² for the highest initial salt concentration (1.4 mol dm⁻³). Higher initial sodium citrate concen-
tration in the salt circuit increases the process efficiency. In the case of low initial salt concentrations, as
the process progresses, the acid instantaneous efficiency (CEa) decreases with time. For a salt concen-
tration of 1 mol dm⁻³ CEa is practically constant, and for higher salt concentrations CEa can even
grow. In the case of the highest current density investigated (104 mA cm⁻²), the opposite situation
was observed; that is, CEa decreased with time for the higher salt concentration of 1.3 mol dm⁻³.

Wang et al. developed a mathematical model of a typical three-compartment electrodialysis with
bipolar membranes process to calculate the energy consumption and total cost of the process. In par-
ticular, gluconic acid was chosen as a model product; the energy consumption was calculated on the
basis of the Nernst–Planck equation, Donnan equilibrium and electroneutrality assumption. The con-
centration profiles and resistance distributions across the respective layers were also displayed. Results
indicated that the resistances of the solutions, diffusion layers and Donnan interfaces were highly
dependent on the applied current. The resistances in the diffusion layers were the dominant resis-
tances, while the resistances due to Donnan interfaces and resistances of the membranes could be
neglected. The energy consumption of the electrodialysis with bipolar membranes process increased
with an increase in current. The energy consumption in the validation experiment was in good agree-
ment with the prediction, suggesting the reliability of the model [150].

Caustic solvents such as sodium or potassium hydroxides, converted via CO₂ capture to aqueous
carbonates or bicarbonates, are a likely candidate for atmospheric CO₂ separation. Eisaman et al.
[151] performed a comprehensive experimental investigation of CO₂ gas regeneration from aqueous
potassium carbonate and bicarbonate solutions using bipolar membrane electrodialysis (see
Figure 8.15). This system allows the regeneration of pure CO₂ gas, suitable for subsequent sequestra-
tion or reaction to synthetic hydrocarbons and their products, from aqueous carbonate/bicarbonate
solutions. Their results indicate that the energy consumption required to regenerate CO₂ gas from
aqueous bicarbonate (carbonate) solutions using this method can be as low as 100 kJ (200 kJ) per mole
of CO₂ in the small-current-density limit.

Venugopal and Dharmalingam [152] fabricated bipolar ion-exchange membranes using polystyrene
ethylene butylene polystyrene (PSEBS) with polyvinyl alcohol as the intermediate and evaluated their
potential to remove secondary salts from laboratory-prepared salt solutions. Experiments were carried
out in batch recirculation mode. The mechanical properties and microscopic images of the membranes were analysed before, during and after the electrodialysis process. The performance of the membranes in the stack was evaluated in terms of energy consumption and current efficiency, and found to be 1.07 W h mol\(^{-1}\) and 0.67 respectively. Commercially produced membranes were used as a comparison with the PSEBS-based membranes. In the case of a commercial polystyrene–DVB membrane, the values for these parameters were 2.59 W h mol\(^{-1}\) and 0.63 respectively. In addition, other parameters, such as transport number of ions and acid–alkali production, were evaluated for both PSEBS-based and commercially produced membranes. The results indicated that PSEBS-based membranes exhibited better performance than the commercial membranes.

Bipolar membrane electrodialysis to produce morpholine was first reported by Jiang et al. Current density, feed concentration and configuration all have an effect on final product yield. The lowest total process cost was $1.2 per kilogram of morpholine. It was feasible and creditable to produce morpholine using bipolar membrane electrodialysis. To produce morpholine in an environmental friendly manner, bipolar membrane electrodialysis was used to convert morpholine sulfate into morpholine with 0.3 mol L\(^{-1}\) Na\(_2\)SO\(_4\) as electrode supporting solution. The results indicated that a high current efficiency and low energy consumption can be obtained when morpholine sulfate solution concentration is in the range 0.15–0.22 mol L\(^{-1}\), current density in the range 20–30 mA cm\(^{-2}\) with bipolar membrane (BP)–anion-selective membrane (A)–cation-selective membrane (C)–BP cell configuration. Product yield rate was increased with increasing current density and feed concentration. At the same time, BP–A–BP and BP–C–BP cell configurations were also examined. A lowest process cost of $1.20 per kilogram and energy consumption of 4.27 kW h kg\(^{-1}\) were obtained through a BP–A–BP configuration, compared with the other types. This process was not only cost-effective, but also environmentally benign [153].
The removal of salts from industrial effluents by sustainable techniques is of great interest to many companies. An industrial saline water, mainly composed of NaCl and KCl, was treated with conventional electrodialysis and bipolar membrane electrodialysis on laboratory scale by Ghyselbrecht et al. [154]. The saline water also contained significant amounts of sulfate and calcium, which may give rise to various types of scaling. A partial desalination (target was a removal of 50% of the chlorides) was easily achieved with both electrodialysis and bipolar membrane electrodialysis. By using electrodialysis, a concentrate containing approximately 2 M of chlorides was obtained. The formation of scaling was avoided by using monovalent selective anion- and cation-exchange membranes, which was particularly necessary to avoid CaSO4 scaling. A further improvement was obtained by applying bipolar membrane electrodialysis, which yielded an acid and a base stream with a concentration of around 2 M, with a relatively good purity. From the initial laboratory-scale study it was concluded that both electrodialysis and bipolar membrane electrodialysis are technologically feasible to desalinate saline water. In a second phase, the electrodialysis scenario was scaled up in a pilot-scale study, which demonstrated that the electrodialysis pilot plant was operated in a stable way during a long-term experiment.

The salt in Trona brine seriously affects soda ash recycling in the production process of soda ash, which not only results in low quality of soda ash recycling but also wastes resources. Consequently, the Trona brine should be desalted. The treatment of Trona brine using bipolar membrane electrodialysis can reduce the concentration of NaCl effectively. Desalination with a two-compartment bipolar membrane electrodialysis composed of anion-exchange membrane and bipolar membrane was investigated in a study by Zhou et al. Parameters such as the membrane stack voltage, material flux, temperature and concentration were adjusted. The effect of the parameters on desalination rate, current efficiency and electricity consumption was researched. The optimum process conditions were obtained through a single-factor experiment and orthogonal experiment when the membrane stack voltage is 24 V, material flux is 5 L h⁻¹, the temperature is 20 °C and the concentration is 2.0 mol L⁻¹. The desalination rate reached 97.0%, while the current efficiency was 84.3%. The process not only has low current consumption but also has a better treatment effect [155].

Some techno-economic analyses and environmental impact evaluations have proved that bipolar membrane electrodialysis is feasible for the reclamation of industrial saline water. However, to date, the technology cannot be put into practice due to some unsolved application-oriented problems, such as the requirements of bipolar membrane electrodialysis for feed solution, the availability of the acid and base produced, the relatively high salt concentration of the effluent, and the relatively low desalinating efficiency and capacity. In the study of Wang et al., a novel hybrid process that coupled conventional electrodialysis installed with monovalent selective cation-exchange membranes with bipolar membrane electrodialysis running in a constant-voltage mode was designed to reclaim brine generated from surface water desalination by the ion-exchange process. Subsequently, the response surface methodology was employed to establish the empirical models for understanding the influences of some initial operating conditions on bipolar membrane electrodialysis performance. Finally, the bipolar membrane electrodialysis-based reclamation scheme was confirmed again by a continuous bipolar membrane electrodialysis experiment on a real solution. In particular, the effects of product concentration on current efficiency and energy consumption were investigated. In this case, an acceptable current efficiency and energy consumption were obtained on the basis of the conventional membranes and spacers when the product concentration was set as 0.9 M, which is adequate for the regeneration of ion-exchange resins [156].

Wasserscheid and co-workers [157] reported a new environmentally benign process for the production of aqueous solutions of [EMIM]OH (EMIM: 1-ethyl-3-methylimidazolium). Electrodialysis with bipolar membranes using the system shown in Figure 8.16 was implemented for the first time to produce this hydroxide-based precursor in 5% concentration in water from the non-toxic bulk ionic liquid
Figure 8.16 Precursor production by electrodialysis with bipolar membrane (IL: ionic liquid).

Figure 8.17 CO₂ extraction from seawater using bipolar membrane electrodialysis.
[EMIM][EtOSO₃] at the kilogram scale. The results were discussed with regard to ease of operation, productivity and product quality obtained. Moreover, several structurally new ionic liquids were synthesized by reaction of the aqueous precursor solution with different acids, such as H₂SiF₆ or hexafluoroacetylacetone. But the synthesis of well-established ionic liquids, such as [EMIM][BF₄], has also been carried out using the hydroxide intermediate and the full procedure is compared with well-established ion metathesis protocols.

An efficient method for extracting the dissolved CO₂ in the oceans would effectively enable the separation of CO₂ from the atmosphere without the need to process large volumes of air, and could provide a key step in the synthesis of renewable, carbon-neutral liquid fuels. While the extraction of CO₂ from seawater has been previously demonstrated, many challenges remain, including slow extraction rates and poor CO₂ selectivity, among others. Eisaman et al. [158] describe a novel solution to these challenges: efficient CO₂ extraction from seawater using bipolar membrane electrodialysis, as shown in Figure 8.17. They characterized the performance of a custom-designed and built CO₂-from-seawater prototype, demonstrating the ability to extract 59% of the total dissolved inorganic carbon from seawater as CO₂ gas with an electrochemical energy consumption of 242 kJ per mole of CO₂.

References

involve the use of auxiliary electrodes. II. A quantitative test of the theory in model systems which do

13 Carr, C.W., Sollner, K. (1964) Electroosmotic effects arising from the interaction of the selectively


copolymers. I. Fabrication of a charge-mosaic membrane and preliminary tests of dialysis and


18 Graham, T. (1861) Liquid diffusion applied analysis. *Philosophical Transactions of the Royal Society of


(accessed 9 August 2016).

Transplant Association*, vol. V. Excerpta Medica, Amsterdam, p. 78.


39–45.

on positively and negatively charged cellulose dialysar membranes. *Journal of Materials Science:


hemodialysis bioincompatibility: absence of an acute benefit on expression of leukocyte surface


9

Reverse Osmosis

The principle of reverse osmosis was proposed as a new method for the desalination of seawater by Professor Reid, University of Florida, in 1953 [1]. Reid and Breton found that cellulose acetate membranes could reject 96% salt in seawater by reverse osmosis [2]. However, the permeation flux of water was extremely low. Then, Professor Loeb and Sourirajan developed excellent semipermeable cellulose acetate membranes using their original membrane preparation method [3] and their membranes went into practical use [4].

The invention of reverse osmosis (RO) by Professor Reid and co-workers and the development of the asymmetric cellulose membrane by Professor Loeb and Sourirajan seem to be extremely natural as we hear the story related now, but this is a fine example of the birth of new science and technology by looking into the underlying phenomena slowly and carefully.

9.1 Principle of Reverse Osmosis

Osmosis, which is a natural phenomenon, is the spontaneous passage of water through a semipermeable membrane; it occurs when pure water flows from a dilute aqueous solution through a semipermeable membrane into a higher concentrated aqueous solution. Semipermeable means that the membrane is permeable to some species but not to others. The phenomenon of osmosis is shown as Figure 9.1a.

Osmotic pressure varies according to temperature and concentration of the aqueous solution; however, as fresh water passes through the semipermeable membrane, the levels of the two aqueous solutions become unequal. The resulting difference in pressure eventually brings the migration to a stop, as shown in Figure 9.1b. This phenomenon is osmotic equilibrium, and its pressure difference is called the osmotic pressure of the aqueous solution.

Reverse osmosis is the process of forcing the water from the higher concentration side through a semipermeable membrane to the lower concentration side by applying excess pressure, thus ‘reversing’ the natural tendency of water flow, as shown in Figure 9.1c. This is RO.

9.2 Fundamental Analysis of Reverse Osmosis

Membrane permeation models of the RO method have been proposed by some researchers. The main permeation models are (1) the nonequilibrium thermodynamics model, (2) the friction model, (3) the solution-diffusion model, (4) the micropore model and (5) the preferential sorption-capillary flow model.
Figure 9.1 Principle of RO.
9.2.1 Nonequilibrium Thermodynamics Model

The phenomenological equation of the membrane transport is expressed as follows generally.

\[ J_i = L_{ii}X_i + L_{ij}X_j \]  
\[ J_j = L_{jj}X_j + L_{ji}X_i \]  

where \( J_i \) and \( J_j \) are the fluxes of the \( i \) and \( j \) components respectively, \( X_i \) and \( X_j \) are the respective conjugate powers, and \( L_{ii}, L_{jj}, L_{ij}, L_{ji} \) are phenomenological coefficients. Powers \( X_i \) and \( X_j \) correspond to the slopes of the physicochemical potential \( \mu_i \) and \( \mu_j \) in nonequilibrium thermodynamics:

\[ X_i = -\text{grad} \mu_i \]  
\[ X_j = -\text{grad} \mu_j \]  

On the other hand, phenomenological coefficients are the reciprocity of Onsager as follows:

\[ L_{ij} = L_{ji} \]  

Kedem and Katchalsky [5] developed the membrane transport phenomenon for these relations and derived the following equations:

\[ J_v = L_P \Delta p + L_{PD} \Delta \pi \]  
\[ J_D = L_{DP} \Delta p + L_D \Delta \pi \]  

where \( J_v \) is the volume flux of solution, \( J_D \) is the diffusion flux of solute, and \( \Delta p \) and \( \Delta \pi \) are respectively the pressure and osmotic pressure difference between both sides of membrane.

The reflection coefficient \( \sigma \) is given by dividing the coefficient \( L_{PD} \) by the filtration coefficient \( L_f \):

\[ \sigma = \frac{L_{DP}}{L_f} = \frac{-L_{PD}}{L_P} \]  

where \( L_f \) is a volume flow per pressure defined by

\[ L_f = -L_P = -\left( \frac{J_v}{\Delta p} \right)_{\Delta \pi = 0} \]  

where \( L_P \) is the permeation coefficient of pure water. Consequently, Equation 9.6 is derived as

\[ J_v = L_P (\Delta p - \sigma \Delta \pi) \]  

The reflection coefficient \( \sigma \) represents the semipermeability of the membrane; when \( \sigma = 1 \) the solute is completely rejected and the volume flow is proportional to \( \Delta p - \Delta \pi \). On the other hand, when \( \sigma = 0 \) the solute permeates freely through the membrane; the volume flow is not affected by the osmotic pressure and is proportional to difference in pressure.

The permeation flux of the solute \( J_w \) is expressed with Equation 9.12 when the permeation coefficient of the solute \( w \) is defined with Equation 9.11:

\[ w = -\left( \frac{J_v}{\Delta \pi} \right)_{J_v = 0} = -C_S (L_D + \sigma^2 L_f) \]
\[ J_s = (1 - \sigma) \bar{C}_S J_v - w \Delta \pi \]  
\hspace{1cm} (9.12)

where \( \bar{C}_S \) is the average concentration of solute in the both sides of membrane.

Spiegler and Kedem [6] applied Equations 9.10 and 9.12 to a microsection of membrane thickness direction and integrated it about a film thickness, which led to the following equations:

\[ J_v = L_p (\Delta p - \sigma \Delta \pi) \]  
\hspace{1cm} (9.13)

\[ R = 1 - \frac{C_p}{C_m} = \frac{(1 - F) \sigma}{1 - \sigma F} \]  
\hspace{1cm} (9.14)

where \( F \) is given by

\[ F = \exp \left[ -J_v \frac{(1 - \sigma)}{P} \right] \]  
\hspace{1cm} (9.15)

and \( C_m \) and \( C_p \) are the feed and permeate concentration respectively, \( P \) is the permeation coefficient of solute based on the concentration and \( R \) is the rejection percentage of solute.

Transport equations in the membrane permeation of Equations 9.13–9.15 are characterized by three transportation coefficients of the permeation coefficient of pure water \( L_p \), the reflection coefficient of solute \( \sigma \) and the permeation coefficient of the solute \( P \).

### 9.2.2 Friction Model

This model connected the transportation of the material through the membrane with friction and was unfolded by Spiegler [7] and Kedem and Katchalsky [8].

The power to act on a solute in an aqueous solution \( X_s \) is proportional to the sum of the relative velocity of the movement of solute and water \( X_{sw} \) and the relative velocity of the movement of solute and membrane \( X_{sm} \):

\[ X_s = X_{sw} + X_{sm} \]  
\hspace{1cm} (9.16)

where \( X_{sw} \) and \( X_{sm} \) are defined by Equations 9.17 and 9.18 respectively:

\[ X_{sw} = f_{sw}(v_s - v_m) \]  
\hspace{1cm} (9.17)

\[ X_{sm} = f_{sm}(v_s - v_m) \]  
\hspace{1cm} (9.18)

\( X, v \) and \( f \) are frictional force, velocity and frictional coefficient respectively. Subscripts s, w and m are the solute, water and membrane respectively.

Spiegler [7] and Kedem and Katchalsky [8] derived the following relations by combining the three transport coefficients in Equations 9.13, 9.14 and 9.15 in the nonequilibrium thermodynamics model and the frictional coefficient \( f_{ij} \) between the components \( i \) and \( j \) in the friction model:

\[ L_p = \phi_v \frac{\nabla w}{\delta f_{wm}} \]  
\hspace{1cm} (9.19)

\[ \sigma = 1 - \frac{K}{\phi_v} \frac{f_{sw} + f_{sm}(\nabla s / \nabla w)}{f_{sw} + f_{sm}} \]  
\hspace{1cm} (9.20)

\[ P = K \frac{RT}{\delta (f_{sw} + f_{sm})} \]  
\hspace{1cm} (9.21)
where $\phi_v$, $K$, $V_s$, $V_w$, $\delta$, $T$ and $R$ are the water content, partition coefficient to the membrane of the solute, partial molar volume of solute, partial molar volume of water, membrane thickness, absolute temperature and gas constant respectively. The three transport coefficients are all expressed in the product with the ‘exclusion term’ depending on the distributed coefficient of the water and solute and the ‘kinetic term’ depending on their friction coefficient.

### 9.2.3 Solution-Diffusion Model

Lonsdale et al. [9] proposed a model in which initially both the solvent and solute dissolve into a non-porous membrane; afterwards, under the driving force of the difference of chemical potential the solvent and the solute diffuse independently in the membrane and consequently the movement of solvent and solute occurs. In this model, the solubility coefficient (partition coefficient) of a material into the membrane and the diffusion coefficient of a material in the membrane are important factors.

The volume flow of water $J_w$ and the flux of a solute $J_s$ in an aqueous solution are expressed by Equation 9.22 and 9.23 respectively:

$$J_w = A(\Delta p - \Delta \pi) \tag{9.22}$$

$$J_s = \frac{D_{AM}K}{\delta} \Delta C = B\Delta C \tag{9.23}$$

where $A$, $B$, $D_{AM}$, $K$ and $\Delta C$ are the permeation coefficient of pure water, permeation coefficient of solute, diffusion coefficient in a membrane, solubility coefficient and concentration difference between both solutions separated by the membrane respectively.

On the other hand, the rejection $R$ is given as Equation 9.24 using the volume flux $J_v$:

$$R = \frac{J_v}{J_v + B} \tag{9.24}$$

In Equations 9.14 and 9.15, driven in the nonequilibrium thermodynamics model, when $\sigma \approx 1$ the following equation is given:

$$R = \frac{J_v}{J_v + (P/\sigma)} \tag{9.25}$$

In other words, when $\sigma \approx 1$, the permeation coefficient $P$ and the membrane permeation coefficient $B$ ($=D_{AM}K/\delta$) are equal. This suggests that for the system indicating a high rejection the nonequilibrium thermodynamics model and the solution-diffusion model are usable for data reduction.

### 9.2.4 Micropore Model

In the solution-diffusion model, the membrane is considered to be a perfect nonporous membrane without pores. However, this does not explain sufficiently the transport phenomenon of the membrane, and so Jonsson and Boeson [10] proposed a micropore model considering the existence of pores. In this model, when the viscous flow of a solvent and the solute flow through the pore average together, the volume flux $J_v$ obeys Hagen–Poiseuille flow and the flux of solute $J_s$ is due to the viscous flow and diffusion. In addition, the following equations hold:

$$J_v = \frac{\varepsilon r_p^2 \Delta p}{8\mu \tau \delta} \tag{9.26}$$
\[ J_s = -D_{AM} \frac{dC_S}{dx} + \frac{C_S}{b} J_v \]  

(9.27)

where

\[ b = \frac{D_0}{D_{AM} s} \]  

(9.28)

and \( \varepsilon, \eta_p, \mu, \tau, C_S \) and \( D_0 \) are the porosity of the membrane surface, the pore radius, the viscosity of the solvent (water), the tortuosity, the solute concentration in the membrane and the diffusion coefficient of solute in the solution respectively.

When a curve fitting of \( 1/(1 - R) \) versus \( J_v \) is performed by transforming Equations 9.26–9.28, the membrane permeation coefficients \( \varepsilon b/K, \tau \delta / \varepsilon \) and \( \varepsilon \eta_p^2 / \delta \) are determined. In these membrane permeation coefficients, elements of the distribution of solute, frictional coefficient between the membrane and the solute and average pore size are included, and the permeation mechanism of the membrane from the data of the RO experiment to some extent can be understood.

### 9.2.5 Preferential Sorption-Capillary Flow Model

Sourirajan [11] proposed a preferential sorption-capillary flow model, as shown in Figure 9.2. When an aqueous solution contacts with a membrane with pores, the chemical characteristics of the membrane repel the solute and adsorb water; the concentration of the solute in the vicinity of the membrane becomes remarkably dilute and consequently a pure water layer exists at the solution–membrane interface. This pure water layer flows through the pores of the membrane under pressure and is separated from the aqueous solution. As can be seen from Figure 9.2, when the pore diameter \( 2t \) is double the thickness of the pure water layer \( t \), a maximum flow rate of pure water can be obtained. Therefore, a membrane with a pore size of \( 2t \) is the best. The equations derived from this are

\[ J_w = A(\Delta p - \Delta \pi) \]  

(9.29)

\[ J_s = \frac{D_{AM}}{K \delta} (C_m - C_p) \]  

(9.30)

where \( C_m \) and \( C_p \) are the solute concentration on the membrane surface and in the permeate respectively. In a dilute solution, because all molar concentrations are almost equal with the molar concentration of water, the following equation is obtained:

\[ J_s = \frac{D_{AM}}{K \delta} C (X_f - X_p) \]  

(9.31)

where \( X_f \) and \( X_p \) are the mole fractions of solute in the feed solution and the permeate respectively. Also, in a dilute solution the following equation is given:

\[ X_p = \frac{J_s}{J_v} \]  

(9.32)

When the rejection of solute \( R \) is defined as follows, Equation 9.34 is obtained:

\[ R = \frac{X_f - X_p}{X_f} \]  

(9.33)
Equation 9.34 suggests that the permeation coefficient of the solute $D_{AM}/K\delta$ affects the rejection.

The permeation coefficient of pure water $L_P$, the reflection coefficient $\sigma$ and the permeation coefficient of solute $P$ in Section 9.2.1 can be determined as follows. The $L_P$ value is easily obtained from the flux of pure water. The $\sigma$ and $P$ values are determined by the curve fitting method using Equations 9.14 and 9.15 in a plot with the true rejection $R$ measured by changing only pressure and the reciprocal of the volume flux $1/J_v$ [12].

The transport coefficients $L_P$, $\sigma$ and $P$ in the friction model of reverse osmosis in Section 9.2.2 are determined by the above curve fitting method. By using these values and Equations 9.19–9.21, the friction coefficients $f_{sw}, f_{wm}$ and $f_{sm}$ are determined. Also, when the curve fitting of the relationship of $1/(1-R)$ and $J_v$ is carried out by using Equations 9.26–9.28, the membrane permeation coefficients $eb/K$, $\tau_{b}/e$ and $e/\rho_{p}^{2}/\delta$ are obtained. Since the distribution of solute, the friction between the solute and
the membrane, and the element of average pore size in these membrane permeation coefficients are involved, the behaviour of permeation and separation can be understood from the experimental data of RO.

In this preferential sorption-capillary flow model, when the difference between the activation energy of the diffusion coefficient in the membrane $D_{AM}$ and the free energy of the distribution coefficient is considered, the sum of this difference between the activation energy and the free energy is $E$, the following equation is given:

$$\frac{D_{AM}}{K\delta} = Be^{-E/RT} \quad (9.35)$$

By substituting Equation 9.35 for Equation 9.34, the rejection $R$ is represented by the following equation:

$$R = \frac{1}{1 + \frac{B}{J/C} e^{-E/RT}} \quad (9.36)$$

Figure 9.3 shows the relationship of $R$ and $E$.

Matsuura [13] described the energies for the solute permeation as being due to the following three steps: (1) the energy required for moving a solute from an aqueous solution to the solution–membrane interface, (2) the energy required for putting a solute in the pore of the membrane, and (3) the energy required for moving a solute in a pore. The energies of (1) and (2) are related to the distribution of the solute; the energies of (2) and (3) are dependent on the micropore size of the membrane. Therefore, the membrane permeation coefficient $D_{AM}/K\delta$ is related to all of energy term of the membrane permeation of the solute.

### 9.3 Materials and Structures of Reverse Osmosis Membranes

Loeb, Sourirajan and others developed the manufacturing process of the asymmetric cellulose diacetate membrane which has an anisotropic structure (see Figure 2.2b) and succeeded in practical use in 1962. Thereafter, many membranes from various natural and artificial polymers have been prepared:

1. Cellulosic derivative membranes (cellulose triacetate, cellulose butyrate, blend of cellulose ester).
2. Polyamide derivative membranes (aliphatic 6,6-Nylon, copolymers grafted acrylic acid and ethylene oxide on 6,6-Nylon).
3. Polyethylene imine derivative membranes (derivatives substituting part of the imine group with an aromatic ring, derivatives reacted with dimethyl piperazine or isophthaloyl chloride, polyethylene oxide derivatives (derivative substituted with ethylene diamine chloride groups in polyepichlorohydrin, derivative cross-linked with tolylenediisocyanate polyeopichlorohydrin, derivative reacted with isophthalic acid derivative substituted with piperazine chloride groups in polyepichlorohydrin).
4. Membranes from heat-resistant resin having an aromatic ring (polybenzimidazole from terephthalic acid and tetraamino benzene derivative, Nylon from pyromellitic acid anhydride and...
diaminobenzene derivative, polybenzimidazolone from diaminophenyl ether and substituted diphenychloro phenylsulfone, polyimide from pyromellitic anhydride and methoxy-\(m\)-phenylene diamine).

5) Charge membranes (cross-linking of thin membranes from polyelectrolyte with sulfonic acid and carboxylic acid group – excellent in physicochemical durability).

6) Organic–inorganic hybrid membranes (aromatic polyamide thin films underneath titanium dioxide nanosized particles [14], preparation of organic–inorganic hybrid membranes in interfacial polymerization of trimesol chloride (TMC)–\(m\)-phenylenediamine (MPD)-derived polyamide [15].


There are two forms of RO membrane: asymmetric (see Figure 2.2b) and composite (see Figure 2.2c). The overall thickness of the asymmetric membranes is about 100–150 \(\mu\)m and consist of a dense active layer with a thickness of less than 1 \(\mu\)m and a spongiform support layer with a lot of micropores of around several micrometres. The material of these two layers is the same. Since the effective active layer for the desalination is 1000 \(\mu\)m or less in thickness in total, the resistance for the permeation of water is very low and consequently the membrane permeation flux of water is high. Also, the existence of the support layer facilitates the handling of the membrane. The general preparation method of the asymmetric membranes is shown in Figure 3.1, and the membrane performances are significantly influenced by the conditions of the preparation of casting solution, the membrane casting, the gelation of membrane and the post-treatment of membrane, as summarized in Table 2.1.

The composite membrane is constructed of an ultrathin dense layer (corresponding to the surface dense layer of the asymmetric membrane) and the support layer (corresponding to the porous layer of the asymmetric membrane), as illustrated in Figure 2.3. These layers are comprised of different kinds of materials. Since the composite membrane is formed from different materials, the flexibility in the design to optimize each layer is remarkably higher than for an asymmetric membrane.

A typical preparation method of the composite membrane for RO is shown in Figure 9.4. Thin-film composite (TFC) membranes are semipermeable membranes manufactured principally for use in water purification or water desalination systems. A TFC membrane can be considered as a molecular sieve constructed in the form of a film from two or more layered materials. Membranes used in RO are typically made out of polyamide deposited on top of a polyethersulfone or polysulfone porous layer on top of a non-woven fabric support sheet. The three-layer configuration gives the desired properties of high rejection of undesired materials (like salts), high filtration rate and good mechanical strength. The polyamide top layer is responsible for the high rejection and is chosen primarily for its permeability to water and relative impermeability to various dissolved impurities, including salt ions and other small, unfilterable molecules. There are both the coating of the polymer solution and the polymerization of the monomer (interfacial and acid catalysis polymerization) on a porous support membrane (polysulfone ultrafiltration membrane is usually used) in the formation of a skin layer that exercises an RO performance, as shown in Table 3.1. Either way, there is a great deal of material forming a thin membrane layer on a support film, but there is not so much material forming a thin membranous layer, indicating the RO performance. Typical materials forming the skin layer of the composite membrane are shown in Table 9.1.

In the asymmetric membranes of the cellulose acetate and polyamide system, there are faults such as (1) the RO performance (balance of salt rejection and water permeability) is low, (2) the durability is not good, (3) scope of application (such as use pH range, temperature and pressure) is small, and (4) it is weak to microbes. On the other hand, composite membranes have characteristics such as (1) the
ultrathin dense layer and the porous support layer can be separately optimized, (2) an ultrathin technology can be used, (3) ultra thinning on the support surface is possible, (4) high performance and durability can be expected and (5) it can be used as a dry membrane. On the other hand, there are some difficulties, such as (1) unevenness on coating a uniform ultrathin membrane, (2) adhesive property with a support and the ultrathin membrane, (3) limitation of the membrane formation condition by the support material and (4) complexity of the membrane formation process.

In the RO membranes, the following needs are required: (1) ease of the preprocessing, (2) contamination resistance, (3) high chlorine and acid resistance, (4) high heat resistance, (5) high separation characteristics for aqueous low molecular weight organics, (6) use in a nonaqueous solvent system, (7) high pressure resistance, (8) high concentration by the high pressure driving, (9) separation of organic and inorganic in low molecular weight region and (10) functionality of true molecular sieve membrane.

To directly determine the gap between the polyamide molecules which construct the dense active layer for separation in a composite polyamide membrane for RO, positron annihilation lifetime spectroscopy (PALS) is applied [16]. A trial to estimate the free volume of polymer using PALS was performed, and the correlation between the free volume of polymer membrane and the material permeability was clarified [17]. Chen et al. [18] investigated the free-volume depth profile of asymmetric polymeric membrane systems prepared by interfacial polymerization using positron annihilation spectroscopy coupled with a variable monoenergy slow positron beam. Significant variations of $S$, $W$ and $R$ parameters from the Doppler broadened energy spectra versus positron incident energy up to 30 keV, and orthopositronium lifetime and intensity were observed at different doping times of triethylenetetraamine reacting with TMC in an interfacial polymerization on modified porous polyacrylonitrile (PAN) asymmetric membrane. The positron annihilation data were analysed in terms of free-volume parameters as a function of depth from the surface to nano- and micrometre regions of

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**Figure 9.4** Typical preparation method of composite membrane for RO.
Table 9.1 Structure of skin layer of typical composite membranes.

<table>
<thead>
<tr>
<th>Material of skin layer</th>
<th>Structure of skin layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_2 \text{CH}_2 \text{CH}_2 \text{NH}_2 )</td>
<td>( \text{CHCH}_2 \text{O}_n ) ( \text{NCO} + \text{ClO}_2 \text{C} \text{Cl} )</td>
</tr>
<tr>
<td>( \text{OHCO-} \text{CHCH}_2 \text{O} \text{CH}_2 \text{NH}_2 \text{NH}_2 \text{CH}_2 \text{NH}_2 \text{NH}_2 \text{Cl} )</td>
<td>( \text{CHCH}_2 \text{O}_n ) ( \text{NHCH}_2 \text{CH}_2 \text{NHCO-} )</td>
</tr>
<tr>
<td>( \text{CH}<em>2 \text{CH}</em>{2} \text{NH}_2 \text{NH}_2 \text{CH}_2 \text{NH}_2 \text{NH}_2 \text{Cl} )</td>
<td>( \text{CHCH}_2 \text{O}_n ) ( \text{NHCH}_2 \text{CH}_2 \text{NHCO-} )</td>
</tr>
<tr>
<td>( \text{H}_2 \text{SO}_4 )</td>
<td>( \text{CHCH}_2 \text{O}_n ) ( \text{SO}_3 \text{H} )</td>
</tr>
<tr>
<td>( \text{CH}<em>2 \text{CH}</em>{2} \text{OH} )</td>
<td>( \text{CHCH}_2 \text{O}_n ) ( \text{SO}_3 \text{H} )</td>
</tr>
<tr>
<td>( \text{CH}<em>2 \text{CH}</em>{2} \text{COOH} )</td>
<td>( \text{CHCH}_2 \text{O}_n ) ( \text{SO}_3 \text{H} )</td>
</tr>
<tr>
<td>( \text{CH}<em>2 \text{CH}</em>{2} \text{COOH} )</td>
<td>( \text{CHCH}_2 \text{O}_n ) ( \text{SO}_3 \text{H} )</td>
</tr>
</tbody>
</table>
asymmetric membranes. A multilayer structure was obtained in polymerized polyamide on modified PAN (m-PAN) membranes: a nanometre-scale skin polyamide layer, a nanometre- to micrometre-scale transition layer from dense to porous m-PAN, and the porous m-PAN support. The results of the free-volume parameters and layer thicknesses obtained were compared with the flux (permeability) and water concentration in permeate (selectivity) through the pervaporation separation of 70 wt% 2-propanol aqueous solution. It was found that the water concentration in the permeate is mainly controlled by the free-volume properties of skin polyamide and weakly related to the transition layer from the skin to the porous m-PAN. The layer structures of the asymmetric polymeric membranes obtained are supported by the data obtained by atomic force microscopy, scanning electron microscopy (SEM) and attenuated total reflection Fourier transform infrared spectroscopy.

Shintani et al. [19] synthesized three kinds of polyamides from three diamines – MPD, \(N\)-methyl-\(m\)-phenylenediamine, and \(N, N'\)-dimethyl-\(m\)-phenylenediamine – and TMC. The average free-volume sizes of the polyamides were measured by PALS, and the free-volume fractions were evaluated by molecular dynamics simulations. The methyl substitution on amino groups of diamines brought about an increase in interstitial space of molecular chains of the polyamides. In addition, RO membranes were prepared by interfacial polymerization from the three diamines and TMC. The increase in the degree of methyl-substitution of diamines led to increased chlorine resistance and decreased salt rejections of the polyamide RO membranes. Thus, the methyl-substitution of diamines significantly influenced membrane performance. The vacancy sizes and fractional volumes in polyamides evaluated by PALS measurement and molecular dynamics simulation were well correlated with salt rejection of polyamide RO membranes.

Henmi et al. [20] made good use of PALS measurement to develop a new separation membrane material. A membrane with ordered three-dimensional ionic nanochannels constructed by in-situ photopolymerization of a thermotropic liquid-crystalline monomer shows high filtration performance and ion selectivity. The nanostructured membrane exhibits water-treatment performance superior to that of an amorphous membrane prepared from the isotropic melt of the monomer. Self-organized nanostructured membranes have great potential for supplying high-quality water.

9.4 Concentration Polarization and Fouling

9.4.1 Concentration Polarization

The effect of feed water flow rate on the concentration polarization of magnesium sulfate, sodium chloride and sodium selenate in RO spiral-wound elements was investigated and modelled by Mariñas et al. [21]. Experiments were performed with 40” long and 2.5” diameter spiral-wound elements tested with feed solutions of the single electrolyte magnesium sulfate, and a mixture of sodium chloride and sodium selenate as major and trace components respectively. The feed flow rates investigated ranged from 1.12 to 13.5 L min\(^{-1}\), corresponding to Reynolds numbers \(Re\) from 25 to 300. The element was modelled by dividing it into \(n\) identical sub-elements, each separated into two compartments, feed channel and product water carrier, by the RO membrane. The feed channel compartment of each sub-element was assumed to be an ideal continuous-flow stirred tank reactor. Model predictions generally correlated well with experimental observations. Predicted product water flow rates and solute concentrations were within 12% and 24% respectively of the corresponding experimental values.

A comprehensive finite-difference model was developed and presented by Madireddi et al. to predict the concentration polarization in commercial spiral-wound membranes [22]. The model was
developed by solving the non-conservative mass balance equation in the feed channel employing fluid flow profiles based on feed spacer mixing. Both ideal membranes with complete solute rejection characteristics and non-ideal membranes were considered. The model predicts the concentration polarization for low, moderate and high solvent recovery up to 90%. The model was tested for numerical stability and convergence, and subsequently applied to generate the concentration polarization and permeate flow loss information for a range of feed and operating conditions. The model results were verified experimentally on a $1.89 \times 10^{-4} \text{ m}^3 \text{s}^{-1}$ pilot-scale spiral-wound RO unit. Since flow loss in membranes is a dynamic phenomenon, it is anticipated that the model will be an appropriate choice for further work on predicting long-term permeate flow loss from membrane fouling.

The application of a simple technique for determining the mass transfer coefficient and the concentration polarization level in an RO system was described by Sutzkover et al. [24]. The technique is based on evaluation of the permeate flux decline induced by the addition of a salt solution to an initially salt-free water feed. Since the net pressure driving force is influenced by the level of the osmotic pressure prevailing on the membrane surface, the magnitude of flux decline enables the evaluation of membrane surface concentration, and hence the determination of the mass transfer coefficient $k$. The mass transfer coefficient is given by

$$k = \frac{I_v \text{salt}}{I_n \left\{ \frac{\Delta P}{\pi_b - \pi_p} \left[ 1 - \frac{(I_v)_{\text{salt}}}{(I_v)_{\text{H}_2\text{O}}} \right] \right\}}$$

Hence, the value of $k$ can be simply determined from the osmotic pressures $\pi_b$ and $\pi_p$ of the saline feed and of the permeate respectively and by measuring $(I_v)_{\text{H}_2\text{O}}$, the permeate flux of the salt-free water, and $(I_v)_{\text{salt}}$, the permeate flux of the saline solution. The proposed technique was verified by experiments performed in a tabular RO system under turbulent flow conditions. Experiments covering the $Re$ range of 2600–10 000 yielded the following mass transfer correlation:

$$Sh = \frac{kd}{D} = 0.020Re^{0.91}Sc^{0.25}$$

This expression is practically identical to the theoretically anticipated Deissler correlation, thus lending strong support to the proposed mass transfer measurement technique.

A dimensionless governing equation was formulated by Song and Yu for a crossflow RO process in which the local variation of concentration polarization was rigorously considered. It was shown in this formulation that the crossflow RO process could be fully characterized with a single dimensionless parameter. The coupling between permeate flux and concentration polarization was properly solved and a closed-form analytical solution was obtained. This analytical solution enabled them to conveniently investigate concentration polarization in the RO process. The significance of local variation of concentration polarization was demonstrated, and the operations of RO under various conditions were simulated and investigated with the newly developed model [24].

Accurate prediction of concentration polarization phenomena is critical for properly designing reverse osmosis (RO) processes because it enhances transmembrane osmotic pressure and solute passage, as well as surface fouling and scaling phenomena. The objective of the study by Kim and Hoek was to compare available analytical concentration polarization models with a more rigorous numerical concentration polarization model and experimental concentration polarization data. A numerical concentration polarization model was developed to enable local description of permeate flux and solute rejection in crossflow reverse osmosis separations. Predictions of channel-averaged water flux and salt rejection by the developed numerical model, the classical film theory model and a recently
proposed analytical model were compared with well-controlled laboratory-scale experimental data. In operating conditions relevant to practical RO applications, film theory and the numerical model accurately predicted channel-averaged experimental permeate flux and salt rejection data, while the more recent analytical model did not. Predictions of local concentration polarization, permeate flux and solute rejection by film theory and the numerical model also agreed well for realistic ranges of RO process operating conditions [25].

Concentration polarization in narrow RO channels with parabolic crossflow was numerically simulated with finite-difference equations related to permeate velocity, crossflow velocity, average salt concentration and wall salt concentration by Liu et al. [26]. A significant new theoretical development was the determination of two correction functions, F2 and F3, in the governing equation for average salt concentration. Simulations of concentration polarization under various conditions were then presented to describe the features of the new model, and there were discussions about the differences of concentration polarizations of the more realistic parabolic flow with those when plug flow or shear flow was assumed. The situations in which the simpler models based on shear or plug flow can be used were indicated. Concentration polarization was also simulated for various conditions to show the applicability of the model and general features of concentration polarization in a narrow, long RO channel.

As a typical membrane technology by which the solute substances are separated from a solution, a haemodiafilter and RO module were studied, in particular regarding solute transport through the membrane. The solute transport equation, as a key point of this paper by Sekino, was derived from the modified Kedem–Katchalsky equation combined with the film theory model. As the next key point for the numerical analysis, the solute transport equation was inserted into the previous module model, and the differential equations comprising this module model were converted to the difference equations calculated with a nonlinear secant method. It was clear that the occurrence of concentration polarization in the boundary layer is dependent on values of the membrane parameters, including solute permeability $P_m$ and reflection coefficient, the ultrafiltration flux and the mass transfer coefficient [27].

**9.4.2 Fouling of Reverse Osmosis**

An experimental study of ultrafiltration and RO membrane fouling by colloidal particles was presented by Yiantsios and Karabelas [28]. Membrane flux and rejection were monitored on a laboratory-scale, crossflow, narrow-channel unit employing flat-sheet membranes, which are challenged by suspensions of monodisperse colloidal particles. Apart from the influence of basic parameters, such as particle size, concentration, crossflow velocity and transmembrane pressure, the effect of colloid stability was systematically investigated by regulating the suspension ionic strength. In parallel, colloid stability was assessed by Brownian aggregation measurements employing light-scattering techniques. Finally, the fouling tendency of the model suspensions was assessed by performing standard batch filtration tests for fouling index determination. It was found that stable colloidal suspensions cause relatively less fouling, whereas, when colloid stability is decreased, significant deposits form on the membranes. Furthermore, it appears that the commonly used fouling indices may give opposite trends from those observed in crossflow filtration tests. Finally, the experimental results were compared with existing colloidal fouling models and it was demonstrated that these models are not adequate to predict membrane performance.

Hoek et al. [29] designed a laboratory-scale crossflow membrane filtration apparatus to investigate the relative influence of filter geometry and shear rate on colloidal fouling of RO and nanofiltration (NF) membranes. An expression that allows clarification of the mechanisms of flux decline due to
colloidal fouling in RO and NF separations was derived by combining the solution-diffusion model, film theory and a modified cake filtration model. With this new fouling model, the interplay between the salt concentration polarization layer and a growing colloid deposit layer may be quantified. The hydraulic pressure drop across a colloid deposit layer was shown to be negligible compared with cake-enhanced osmotic pressure. The difference in flux decline observed in filters with different channel heights resulted from different cake layer thickness, and thus different cake-enhanced osmotic pressure. A moderate reduction in the initial concentration polarization and cake-enhanced osmotic pressure was obtained by operating at a higher shear rate within a given filter. However, thicker cakes were produced in the filter with greater channel height regardless of crossflow hydrodynamics, which resulted in greater loss of flux. In all modes of operation for either channel height, salt rejection decreased in proportion to the extent of flux decline. By decreasing channel height, both flux and salt rejection were enhanced by reducing all fouling mechanisms – salt concentration polarization, cake layer resistance, and the cake-enhanced osmotic pressure.

RO membranes have been applied for the separation of water from its dissolved constituents. The presence of silica and other dissolved solids in water and industrial water systems is prevalent. Consequently, silica fouling causes adverse effects on RO process, which includes flux decline, shorter membrane lifetime and also an increase in energy consumption. Dynamics tests using an Osmonics Sepa CF flat sheet RO unit were conducted by Sahachaiyunta et al. to investigate the effect of silica fouling of RO membranes in the presence of minute amounts of various inorganic cations – such as iron, manganese, nickel and barium – that are present in industrial and mineral processing wastewaters. Experimental results showed that the presence of iron greatly affected the scale structure on membrane surface compared with manganese, nickel and barium [30].

A bench-scale RO process simulator was operated in a batch concentration mode by Jawor and Hoek to determine the effects of product water recovery and feed water temperature on flux, rejection and inorganic fouling by gypsum scale formation for simulated brackish water. As feed water temperature increased, salt rejection and concentration polarization decreased (reducing scale formation potential at a given recovery). However, gypsum crystal nucleation and growth rates increased with temperature. Specifically, at 15 and 25 °C, gypsum scale formation resulted in slow, steady flux decline at recoveries as low as 10–20%. At these temperatures, many small crystals formed over the entire membrane surface. In contrast, at 35 °C, flux decline was due to the increasing feed solution osmotic pressure – up to a recovery of about 70%. At this recovery, Jawor and Hoek observed a sudden, rapid loss of flux and a concomitant spike in feed water turbidity. Relatively few (in number) large crystals formed on the membrane toward the brine outlet of the RO simulator, but the entire membrane surface was covered with ‘needle-like’ crystal fragments. The crystal fragments broke off from growing gypsum rosettes and redeposited uniformly across the membrane, forming a ‘cake layer’ that caused the massive flux decline. These results suggest that high-temperature operation of brackish water RO processes could enable higher recovery and lower energy consumption, but operating near the limiting recovery (at elevated temperature) creates an increased risk of a catastrophic fouling event [31].

Lu et al. [32] synthesized aluminium-doped ZSM-5 zeolite membranes by seeding and secondary growth. The membrane has Na+ rejection of 97.3% and water flux of 4.72 kg m⁻² h⁻¹ for 0.1 M NaCl at 2.76 MPa operating pressure. Toluene solution was selected as a foulant to investigate organic fouling and its influence on membrane performance. The fouling resulted in a 34.8% loss in water flux. The Na+ and organic separation efficiencies did not change after the membrane was fouled. Oxidative regeneration by using 15% H₂O₂ solution was employed for cleaning the toluene-fouled zeolite membrane at room temperature. Results showed H₂O₂ solution was an effective way to fully recover the membrane flux.
9.5 Technologies and Applications of Reverse Osmosis

9.5.1 Polymer Membranes

The semipermeable membrane for RO applications consists of a thin skin layer of 0.1–0.2 μm thickness of polymeric material and a fabric support. Commercial-grade membranes require high water permeability and semipermeability. It is requested that the membranes are also stable over a wide range of pH and temperature, and have high mechanical completeness. The stability of these properties in field conditions is needed for 3–5 years. RO membranes that satisfy in practical applications are produced from cellulose acetate and composite polyamide. Membrane fabrication differs significantly in those polymeric materials. There are significant differences in operating conditions and membrane performance.

9.5.1.1 Cellulose Acetate Membranes

The original cellulose acetate membrane, developed in the late 1950s by Loeb and Sourirajan, was made from cellulose diacetate. Current cellulose acetate membrane is usually made from a blend of cellulose diacetate and triacetate. The membrane is formed by casting acetone-based solution of cellulose acetate with swelling additives onto a non-woven polyester fabric. Then the membrane with the support is immersed in a cold bath to remove the remaining acetone and other leachable compounds and annealed in a hot water bath at a temperature of 60–90 °C to improve the semipermeability of the membrane with a decrease of water transport and a significant decrease of salt passage (see Figure 3.1). After processing, the cellulose acetate membrane has an asymmetric structure with a dense surface layer of about 0.1–0.2 μm which is responsible for the salt rejection property (see Figure 2.2b). The rest of the membrane film is spongy and porous and has high water permeability. Salt rejection and water flux of a cellulose acetate membrane can be controlled by changing the temperature and time in the annealing step.

9.5.1.2 Composite Polyamide Membranes

Composite polyamide membranes are manufactured in two distinct steps. First, a porous polysulfone support layer is formed by casting a polysulfone solution onto a non-woven polyester fabric. The polysulfone layer is not semipermeable. In the next stage, a semipermeable thin skin layer is formed on the porous polysulfone substrate by the interfacial polymerization of monomers containing multivalent amine and multivalent carboxylic acid chloride. This membrane manufacturing procedure enables independent optimization of the distinct properties of the support layer and skin layer for salt rejection. The water flux and salt rejection of the resulting composite membranes are higher than those of cellulose acetate membranes. Polyamide composite membranes are stable over a wider pH range than cellulose acetate membranes. However, polyamide membranes are susceptible to oxidative degradation by free chlorine, while cellulose acetate membranes can tolerate limited levels of exposure to free chlorine. Compared with a polyamide membrane, the surface of cellulose acetate membrane is smooth and has little surface charge. Because of the neutral surface and tolerance to free chlorine, cellulose acetate membranes will usually have a more stable performance than polyamide membranes in applications where the feed water has a high fouling potential, such as with municipal effluent and surface water supplies (see Table 9.2).

As shown in Table 9.2, cellulose acetate and polyamide membranes both have advantages and disadvantages. Cellulose acetate membrane has a higher flux, and a smaller area of membrane is therefore required. It is also resistant to small concentrations of free chlorine and may therefore be kept free of
bacteria and also produce a product with residual chlorine in it to prevent subsequent regrowth. The polyamide membrane can be used at a higher temperature (35 °C) than cellulose acetate membrane (30 °C); it cannot tolerate chlorine, but it is not attacked by bacteria, whereas some bacteria which can occur in surface water in woodlands actually destroy cellulose acetate. Also, the polyamide membrane can be used over a much wider pH range (2–12) than the cellulose acetate membrane (4–7).

A series of experiments was conducted by Vos et al. to investigate the influence of feed water pH on the long-term performance of cellulose acetate RO membranes [33]. The decline in salt rejection observed for these membranes after extended exposure to feed solution was attributed to hydrolysis of cellulose acetate and was found to be strongly pH dependent. The rate of change of the membrane parameters was correlated with the previous measurements of hydrolysis rate of cellulose acetate, and the dependence of membrane parameters on the acetyl content of the ester.

Wet–dry reversible membranes were prepared by a two-step coagulation procedure by Vasarhelyi et al. A cast film containing a blend of cellulose triacetate as polymers, dioxane and acetone as solvents and maleic acid and methanol as additives was immersed consecutively in two aqueous coagulation baths, the first bath being kept at 0 °C and the second at 60 °C. The effects of casting solution composition and coagulation conditions on reverse osmosis performance and membrane morphology were examined. Light transmission measurements and demixing experiments were carried out to investigate the phase separation phenomena in this six-component system. These experiments proved to be very helpful in explaining the RO results. High-performance membranes were obtained with salt rejections of more than 99% and permeation rates in the range of 10–12 L m⁻¹ s⁻² h⁻¹. These desalination properties, combined with a good wet–dry reversibility, made their membranes superior to RO membranes that had been produced hitherto [34].

Membranes based on cellulose acetate for RO can possibly be applied to the so-called salinity process of energy generation and water desalinization. The requirements for membranes for these two different applications are a relatively high water flux and low salt permeability. Duarte et al. [35] presented the optimization of the composition of such membranes. They started by producing membranes with a patented casting solution with the following composition: 45.77 wt% dioxane, 17.61 wt% acetone and 8.45 wt% acetic acid (solvents); 14.09 wt% methanol (nonsolvent); and 7.04 wt% cellulose diacetate and 7.04 wt% cellulose triacetate. The membranes produced with this solution were

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Polyamide membrane</th>
<th>Cellulose acetate membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt rejection (%)</td>
<td>&gt;99</td>
<td>98</td>
</tr>
<tr>
<td>total dissolved solids</td>
<td>&gt;99</td>
<td>&lt;95</td>
</tr>
<tr>
<td>SiO₂</td>
<td>&gt;99</td>
<td>&lt;95</td>
</tr>
<tr>
<td>Salt rejection change (%)</td>
<td>99 → 98.7</td>
<td>98 → 96</td>
</tr>
<tr>
<td>Maximum operating temperature (°C)</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>Operating pH</td>
<td>2–12</td>
<td>4–7</td>
</tr>
<tr>
<td>Operating pressure (kg cm⁻²)</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Chlorine tolerance (ppm)</td>
<td>&lt;0.1</td>
<td>1</td>
</tr>
<tr>
<td>Membrane fouling</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>

Table 9.2 Characterization of polyamide and cellulose acetate membrane in the operation of RO desalination.
analysed comparatively, with the membranes obtained by the introduction of modifications to the following parameters: the solvent mix, the nonsolvent mix, the proportion of cellulose diacetate and cellulose triacetate in the casting solution, and the addition of reinforcing cellulose fibres. The results led them to conclude that the best membrane formulation had the following composition: 45.77 wt% dioxane, 17.61 wt% acetone, and 8.45 wt % acetic acid (solvents); 4.22 wt% cellulose triacetate and 9.86 wt% cellulose diacetate (polymers); 14.09 wt% methanol (nonsolvent); and 0.5 wt% cellulose fibres (with respect to the total polymer content).

A mixture of equal parts of cellulose diacetate and cellulose triacetate was dissolved in dipropylene glycol and exposed to shear stresses of varying intensity on a three-roll calender. Asymmetric RO membranes were prepared from these materials by the phase-inversion method. RO tests in a dead-end module provided membrane performance data. A structure analysis was performed by SEM and the microstructure of the membranes was investigated by differential scanning calorimetry and X-ray diffraction. It was observed that increasing shear times as well as shear rates reduced the salt rejection, while the permeate flux was escalating. The size-exclusion chromatography analysis showed a strong decrease of $M_w$ and $M_z$ at a constant $M_n$, indicating the degradation of the higher molar mass macromolecules. Since the physical structure of the membranes was not affected and a change in polymorphism could not be related to the variations in the RO performance, the reduced salt rejection should be caused by this degradation process, supposedly through affecting the material’s diffusion properties by changing the fractional free volume [36].

Recently, La et al. [37] reported new polyamide TFC membranes. They were prepared by interfacial polymerization of hexafluoroalcohol (HFA)-containing aromatic diamine and TMC on a porous polysulfone support. The surface properties of the resulting membranes were characterized by water contact angle, X-ray photoelectron spectroscopy (XPS) and SEM. Additionally, the desalination separation performance was evaluated by the crossflow filtration of 2000 ppm NaCl solution. Water contact angle and XPS analyses indicated that the HFA-containing polyamide membrane is relatively hydrophobic at neutral conditions but becomes hydrophilic at basic conditions due to ionization of the HFA groups, so they referred to this group as an ‘ionizable hydrophobe’ or ‘i-phobe’. The membrane showed strongly pH-dependent RO behaviour with enhanced performance (high water flux and high salt rejection) at high pH (~10). Both the electron-withdrawing nature and the steric bulkiness of the HFA functionality are also advantageous in protecting the polyamide membrane from chlorine attack. Based upon nuclear magnetic resonance studies of model polymers (linear polyamides with and without the HFA functionality) and the membrane performance measured before and after chlorine exposure, the HFA-containing polyamide had improved chlorine stability compared with the reference polyamide made from MPD and TMC.

Pendergast et al. prepared composite RO membranes formed by interfacial polymerization of polyamide thin films over pure polysulfone and nanocomposite-polysulfone support membranes [38]. Nanocomposite support membranes were formed from amorphous nonporous silica and crystalline microporous zeolite nanoparticles. For each hand-cast membrane, water flux and NaCl rejection were monitored over time at two different applied pressures. Nanocomposite-polysulfone-supported RO membranes generally had higher initial permeability and experienced less flux decline due to compaction than pure polysulfone-supported membranes. In addition, observed salt rejection tended to increase as flux declined from compaction. Cross-sectional SEM images verified significant reduction in thickness of pure polysulfone supports, whereas nanocomposites better resisted compaction due to enhanced mechanical stability imparted by the nanoparticles. A conceptual model was proposed to explain the mechanistic relationship between support membrane compaction and observed changes in water flux and salt rejection. As the support membrane compacts, skin layer pore constriction increased the effective path length for diffusion through the composite membranes, which reduced
both water and salt permeability identically. However, experimental salt permeability tended to
decline to a greater extent than water permeability; hence, the observed changes in flux and rejection
might also be related to structural changes in the polyamide thin film.

A novel TFC RO membrane was developed by the interfacial polymerization of TMC and MPD on
the hollow-fibre ultrafiltration polysulphone membrane by Li et al. The performance of the TFC mem-
brane was optimized by studying the preparation parameters, which included monomer TMC con-
centration, monomer MPD concentration and alcohol additive in aqueous solution. The RO
performance of the resulting membrane was evaluated through a permeation experiment with
1000 ppm NaCl at 0.7 MPa. The results showed that the optimum concentration of MPD and
TMC were 0.5 wt% and 3 g L\(^{-1}\) respectively. To improve flux, alcohol was added to the aqueous phase;
when a certain concentration of alcohol was added to the aqueous solution the flux of the prepared
membrane increased from 5.0 to 9.1 L m\(^{-2}\) h\(^{-1}\) without loss of salt rejection. The properties and struc-
tures of the skin layer of RO composite membranes were characterized by atomic force microscopy. It
was found that the interfacial polymerization had occurred and the separation layer was formed, and
the novel RO membrane appeared to comprise a thicker, smoother and less cross-linked film struc-
ture. Additionally, the TFC membrane exhibited good long-term stability [39].

Liu et al. [40] investigated the surface modification and the improved acid stability and chlorine
resistance of commercial TFC polyamide RO membranes coated with a hydrophilic surface layer
of copolymer poly(N-isopropylacrylamide-co-acrylamide) (P(NIPAM-co-Am)). The virgin flat-sheet
polyamide membranes were modified in situ with dilute P(NIPAM-co-Am) aqueous solution, and
the modified membranes were then tested for their acid stability and chlorine resistance through
long-term crossflow permeation tests with aqueous solution containing 0.5 mol L\(^{-1}\) HCl and 2000
ppm NaCl and through chlorine exposure experiments with hypochlorite aqueous solutions of differ-
ent concentrations respectively. The membrane properties were characterized in terms of RO perfor-
mance and surface chemical structure. The membrane modification was found to improve the
chlorine tolerance and acid stability significantly. The P(NIPAM-co-Am) surface coating layer
impeded the hydrolysis and the replacement of hydrogen with chlorine on the amide groups of the
aromatic polyamide thin-film through enhancing intermolecular hydrogen bonding, and prevented
the attack of acid and chlorine on the underlying polyamide film as a protective and sacrificial layer.
The P(NIPAM-co-Am)-coated membrane could potentially be used as a new type of TFC polyamide
membrane with improved acid stability and chlorine resistance.

Xu et al. [41] developed a novel process to modify TFC polyamide membrane involving surface
treatment of the polyamide membrane by chlorine, followed by supramolecular assembly of chit-
osan on the membrane surface. While the original polyamide membrane was negatively charged,
the surface modification led to a charge reversal due to skin layer of chitosanium in the resulting
polyamide–chitosan (PA–CS) composite membrane. The PA–CS composite membrane was shown
to perform better than the original polyamide membrane. The parameters involved in the chlori-
nation of polyamide (e.g. chlorination time and chlorine concentration) and supramolecular assem-
bly of chitosan (e.g. concentration and deposition time) on the membrane surface were investigated.
The following conditions for membrane modification were found to be appropriate: NaClO concentra-
tion 200 mg L\(^{-1}\), chlorination time 2–5 min, and chitosan concentration 1000 mg L\(^{-1}\); the PA–CS
membrane so formed exhibited a permeation flux of 57.7 L m\(^{-2}\) h\(^{-1}\) and a salt rejection of 95.4% for a
feed NaCl concentration of 1500 mg L\(^{-1}\) at 0.8 MPa. The PA–CS composite membrane also exhib-
ited good performance for rejection of divalent salts (99.8% for MgCl\(_2\) and 98.5% for Na\(_2\)SO\(_4\)) at the
same concentration. This modification technique is simple and practical because dilute solutions
are used for surface treatment and commercial membrane units can be modified in their original
modules.
The influence of synthesis conditions (e.g. monomer concentration and membrane preparation protocol) on transport properties of polyamide TFC membranes prepared using MPD and TMC via interfacial polymerization was reported by Freeman and co-workers [42]. For example, at 25 °C, NaCl rejection and permeate flux combinations of 99.6 ± 0.1% and 42 ± 3 L m\(^{-2}\) h\(^{-1}\) respectively were achieved in crossflow filtration using a 2000 ppm aqueous solution of NaCl and a transmembrane pressure difference of 225 psi (15.5 bar). Additionally, a sulfone diamine, disulfonated bis[4-(3-amino-phenoxy)phenyl]sulfone, was used in place of MPD to prepare TFC membranes. The resulting membranes had low NaCl rejection but somewhat higher permeate flux than MPD/TMC membranes. These membranes had reduced chlorine tolerance compared with those prepared using MPD as the diamine.

Polyamide TFC membranes are becoming increasingly widely used for water desalination both in industrial and experimental plants owing to their superior properties. However, the trade-off between the permeability and the salt rejections, fouling and chlorination are seriously restricting their better operational functions. Therefore, various strategies have been explored to tackle these problems, among which surface modifications (e.g. surface coating) and nanoparticles incorporations have been identified to be the most effective ones. Thus, in their review, Xu et al. focused on and summarized the state-of-the-art developments and breakthroughs in surface-modified and nanoparticles-incorporated polyamide TFC RO membranes and their prospects. Their review provides comprehensive information and gives an outlook on the surface modifications and nanoparticles incorporations, which might supply some clues to explore more advanced and innovative strategies for improving the performance of the polyamide TFC RO membranes [43].

Four different types of nanocomposite RO membranes were formed by interfacial polymerization of either polyamide or zeolite A–polyamide nanocomposite thin films over either pure polysulfone or zeolite A–polysulfone nanocomposite support membranes cast by wet phase inversion [44]. All three nanocomposite membranes exhibited superior separation performance and interfacial properties relative to hand-cast TFC analogues, including (1) smoother, more hydrophilic surfaces, (2) higher water permeability and salt rejection and (3) improved resistance to physical compaction. Less compaction occurred for membranes with nanoparticles embedded in interfacially polymerized coating films, which adds further proof that flux decline associated with physical compaction is influenced by coating film properties in addition to support membrane properties. The new classes of nanocomposite membrane materials continue to offer promise of further improved RO membranes for use in desalination and advanced water purification.

### 9.5.2 Inorganic Membranes

Inorganic membranes are versatile. They can operate at elevated temperatures, with metal membranes stable at temperatures ranging from 500 to 800 °C and with many ceramic membranes usable at over 1000 °C. They are also much more resistant to chemical attack. Because of the wide variety of materials that may be used in the fabrication of inorganic membranes, resistance to corrosive liquids and gases, even at elevated temperatures, can be realized. Inorganic membranes compete with organic membranes for commercial use. In many of the harsh operational environments listed earlier, organic membranes will not perform well, or will not survive at all. For these environments, only inorganic membranes offer the solutions needed.

Inorganic RO membranes can be applied to the desalination of the brackish water, seawater and brine water. Their membranes have a very long lifetime and are resistant to chemicals, such as chlorine and other disinfectants, and heat.
Inorganic membranes are mainly produced from aluminium oxide (Al₂O₃), silicon oxide (Si₃O₂), titanium oxide (Ti₂O₃) and zirconium oxide (ZrO₂). Also stainless steel (SUS) and glass (Sirasu Porous Glass, SPG) are being investigated as membrane materials. The supply security of fresh drinking water is decreasing and raising a critical situation for communities worldwide. Inorganic membranes such as alumina and molecular sieve silica have in the past been shown to be highly effective at separating gases and could offer promise as liquid separators owing to their high flux and stability. Duke et al. developed a range of inorganic membranes with pore size ranging from 0.3 to 500 nm and relate this to separation and transport performance. Best separation results were achieved for the silica membrane pressurized to only 7 bar, exhibiting a flux of around 1.8 kg m⁻² h⁻¹ and NaCl rejection of 98% with 3.5 wt% (seawater-like) feed. Potable water from seawater-like feed was achieved from the membrane in a single stage after regeneration. Conditions such as pressure and temperature were also modified, showing performance characteristics and diffusion mechanisms. The non-osmotic setup for inorganic membranes is therefore a viable technology for desalination [45].

RO is currently the most important desalination technology and it is experiencing significant growth. Lee et al. [46] review the historical and current development of RO membrane materials which are the key determinants of separation performance and water productivity, and hence to define performance targets for those who are developing new RO membrane materials. The chemistry, synthesis mechanism(s) and desalination performance of various RO membranes are discussed from the point of view of membrane materials science. The review starts with the first generation of asymmetric polymeric membranes and finishes with current proposals for nanostructured membrane materials. The paper provides an overview of RO performance in relation to membrane materials and methods of synthesis. To date, polymeric membranes have dominated the RO desalination industry. From the late 1950s to the 1980s the research effort focused on the search for optimum polymeric membrane materials. In subsequent decades the performance of RO membranes has been optimized via control of membrane formation reactions, and the use of polycondensation catalysts and additives. The performance of state-of-the-art RO membranes has been highlighted. Nevertheless, the advances in membrane permselectivity in the past decade has been relatively slow, and membrane fouling remains a severe problem. The emergence of nanotechnology in membrane materials science could offer an attractive alternative to polymeric materials. Hence, nanostructured membranes are discussed in this Lee et al. review, including zeolite membranes, thin film nanocomposite membranes, carbon nanotube (CNT) membranes and biomimetic membranes. It is proposed that these novel materials represent the most likely opportunities for enhanced RO desalination performance in the future, but that a number of challenges remain with regard to their practical implementation.

Produced water, generated from underlying formations during the recovery of hydrocarbons, constitutes the largest waste stream associated with oil and gas production. In 2009, Li and Lee reported that over 90% of produced water is reinjected into the formation, either in support of enhanced oil recovery or for disposal. In arid areas, reclamation of produced water for beneficial uses such as irrigation or tower cooling may be an attractive alternative if the produced water can be purified to an adequate quality, specifically through the removal of dissolved components, including inorganic compounds (salts, heavy metals and radiochemicals) and organic compounds (fatty acids, aliphatics and aromatics). Membrane technologies show advantages in both energy efficiency and high water quality. Owing to the presence of dissolved organics, RO with organic membranes is highly limited. Research efforts focus on developing new materials that are less prone to fouling and are easy to regenerate. Novel ceramic membranes are relatively new classes of material that show promising application in produced water purification due to their extreme stability in harsh environments and optional choices for regeneration. The Li and Lee paper details the results of investigations of produced water purification by microporous ceramic membranes, including metal oxide membranes, clay membranes.
and zeolite membranes. Techniques for membrane fabrication, process design and economic aspects are also discussed [47].

Humplik et al. [48] note that desalination of seawater and brackish water is becoming an increasingly important means to address the scarcity of fresh water resources in the world. Decreasing the energy requirements and infrastructure costs of existing desalination technologies remains a challenge. By enabling the manipulation of matter and control of transport at nanometre length scales, the emergence of nanotechnology offers new opportunities to advance water desalination technologies. The focus of their paper is on nanostructured materials that are directly involved in the separation of water from salt as opposed to mitigating issues such as fouling. They discuss separation mechanisms and novel transport phenomena in zeolites, CNTs and graphene with potential applications to RO, capacitive deionization and multistage flash, among others. Such nanostructured materials can potentially enable the development of next-generation desalination systems with increased efficiency and capacity.

Duke et al. [49] note that seawater desalination is now commonly performed using membrane technology, but new materials research is needed to address issues such as membrane fouling. Ceramic materials such as zeolites are capable of providing the required desalination properties while being potentially tolerant to waters which readily foul polymer membranes and/or can withstand more cost-effective cleaning methods. In their paper they developed Silicalite and ZSM-5 zeolite membranes and tested desalination using the thermally based pervaporation and more common RO operation modes. Zeolite membranes were synthesized by the template-free secondary growth technique with varying Si/Al ratios. X-ray diffraction spectra of all membranes showed a randomly oriented MFI-type structure. For intact membrane films, gas permeation was not measurable at room temperature until the membrane was first heated to at least 125 °C under dry helium, implying minimal defects and zeolite pore plugging by water. In pervaporation with 3.8 wt% seawater feed, zeolites containing alumina actively rejected ions, displaying equivalent rejections exceeding 99%. Flux typically decreased after introduction of seawater, but the membrane with Si/Al ratio of 100 uniquely showed a 30% increase in flux which could only be explained by an ion exchange/interaction mechanism that opened the zeolite structure to permeation. Optimal temperature for pervaporation was found to be 80 °C, where high rejections persisted, and flux increased to 0.72 kg m⁻² h⁻¹. In RO, the Silicalite membrane achieved the highest rejections, but had not reached steady state after 25 h of operation. Negative rejections were initially observed, but eventually crossed into positive values over time. Despite the complexity of water and multiple ion diffusion through molecular-dimensioned zeolites with complex charged surfaces, MFI zeolite membranes with tailored Si/Al ratios are regarded as ideal candidates for desalination [49].

Li et al. reported on the separation of ions from aqueous solutions performed by RO on an α-alumina-supported MFI-type zeolite membrane synthesized by in-situ crystallization. For the 0.1 M chloride single-salt solutions, the separation efficiency in terms of ion rejection was found to increase with the ion valence in the order $r_{\text{Al}^{3+}} > r_{\text{Mg}^{2+}} > r_{\text{Na}^{+}}$, while the ion and water fluxes changed in the reverse order. The charge density, size and apparent dynamic hydration number of the ion as well as the mobility of the hydrated ion were found to have critical influences on ion diffusion and water permeation through the polycrystalline zeolite membrane [50].

Lin and Murad [51] developed a molecular simulation scheme for studying solutions undergoing osmosis and RO to study the separation of aqueous solutions using thin zeolite membranes. This method allowed for the preservation of the atomic roughness of the membranes, while the molecules that constitute the membranes were also allowed to vibrate. In the simulations, two thin membranes cut from a cubic cell of ZK-4 zeolite were used as the semipermeable membranes to separate water from aqueous NaCl solutions. Both osmosis and RO phenomena were observed. They showed that
ZK-4 zeolite membranes show promise for use in membrane-based separation of aqueous electrolyte solutions, as well as other similar systems.

Li et al. [52] noted that desalination of brines produced from oil and gas fields is a potential resource for potable water in the southwestern USA and other semi-arid areas. Oilfield brines typically contain high concentrations of Na\(^+\) and Cl\(^-\), as well as other multivalent cations and anions that can reduce efficacy of RO. RO separation of NaCl solutions in the presence of other co-ions or at increased ion concentration and operating pressure was experimentally tested on a pure Silicalite zeolite membrane. Water fluxes increased linearly with increase of net driving force (\(\Delta P - \Sigma \tau_i R T C_{c,i}\)). Ion flux was essentially independent of the operating pressure but increased exponentially by a power factor of 1.13 as feed concentration increases from 0.001 to 0.3 M. Inorganic cations (K\(^+\), Ca\(^{2+}\), and Al\(^{3+}\)) and anions (Br\(^-\) and SO\(_4^{2-}\)), when present in a 0.01 M NaCl solution, play an important role in the separation performance of the NaCl solutions. A notable variation of water flux and ion rejection in the presence of counter-cations was observed, while the permeation behaviour of 0.01 M NaCl solution was hardly affected by counter-anions. This study was part of a broader project seeking to make desalination of oilfield-produced waters economically viable [52].

Liu et al. [53] investigated separation of an organics–water mixture by RO using an \(\alpha\)-alumina-supported MFI-type zeolite membrane. The organic rejection performance was strongly dependent on the ionic species and dynamic size of dissolved organics. The membrane showed high rejection efficiency for electrolytes such as pentanoic acid. An organic rejection of 96.5\% with a water flux of 0.33 kg m\(^{-2}\) h\(^{-1}\) was obtained for 100 ppm pentanoic acid solution at an operation pressure of 2.76 MPa. For nonelectrolyte organics, separation efficiency was governed by the molecular dynamic size: the organics with larger molecular dynamic size show higher separation efficiency. The zeolite membrane gave an organic rejection of 99.5\% and 17\% for 100 ppm toluene and 100 ppm ethanol respectively, with a water flux of 0.03 kg m\(^{-2}\) h\(^{-1}\) and 0.31 kg m\(^{-2}\) h\(^{-1}\) respectively at an operation pressure of 2.76 MPa. It was observed that organic rejection and water flux were affected by the organic concentration. As pentanoic acid concentration increased from 100 to 500 ppm, both organic rejection and water flux decreased slightly.

Molecular sieve zeolite membranes were shown by Li et al. to be potentially useful for treating saline wastewater by RO. In their paper [55], RO of 0.1 m solutions of alkali metal chlorides, including LiCl, NaCl, KCl, RbCl and CsCl, were investigated on MFI-type zeolite membranes synthesized from an aluminium-free precursor. The MFI zeolite membrane exhibited high rejection rates (\(r_i > 95\%\)) for all alkali metal ions at an applied pressure of 2.75 MPa. The rejection rates of Li\(^+\) and Na\(^+\) declined slightly while the ion flux increased more dramatically than did the water flux with moderately raising the temperature. Increasing the hydraulic pressure difference across the membrane resulted in significant enhancements in both the water flux and the ion rejection rates, but with much less influence on the ion flux. The ion flux increased monotonically with the crystallographic ion size from Li\(^+\) to Cs\(^+\), while the dependence of the corresponding water flux on ion size exhibited a maximum for the 0.1 M KCl solution. The ion separation by RO on the MFI zeolite membranes was found to rely on the restricted access of hydrated ions to the zeolitic pores and the competitive diffusion of water and ions in the zeolite channels [54].

### 9.5.3 Mixed Matrix Membranes

Mixed matrix membrane, also known as composite membrane, produced by dispersing fillers in a polymeric matrix, has shown advantages in the development of advanced membranes with improved properties for numerous separation processes [55]. The main objective of mixed matrix membrane is to combine the benefits offered by each material; that is, the high packing density, good
permselectivity, and long operational know-how of polymeric membranes, coupled with the superior chemical, biological and thermal stability of inorganic membranes [46].

9.5.3.1 Composite Membranes of Nanoparticle–Polymer
Zeolite–polyamide thin-film nanocomposite membranes were coated onto polysulfone ultrafiltration membranes by interfacial polymerization of amine and acid chloride monomers in the presence of Linde type A zeolite nanocrystals by Lind et al. A matrix of three different interfacial polymerization chemistries and three different-sized zeolite crystals produced nanocomposite thin films with widely varying structure, morphology, charge, hydrophilicity and separation performance (evaluated as reverse osmosis membranes). Pure polyamide film properties were tuned by changing polymerization chemistry, but addition of zeolite nanoparticles produced even greater changes in separation performance, surface chemistry and film morphology. For fixed polymer chemistry, addition of zeolite nanoparticles formed more permeable, negatively charged and thicker polyamide films. Smaller zeolites produced greater permeability enhancements, but larger zeolites produced more favourable surface properties; hence, nanoparticle size may be considered an additional ‘degree of freedom’ in designing thin-film nanocomposite RO membranes. The data presented offer additional support for the hypothesis that zeolite crystals alter polyamide thin-film structure when they are present during the interfacial polymerization reaction [56].

Jeong et al. [57] reported on a new concept for formation of mixed matrix RO membranes by interfacial polymerization of nanocomposite thin films in situ on porous polysulfone supports. Nanocomposite films created for this study comprised NaA zeolite nanoparticles dispersed within 50–200 nm thick polyamide films. Hand-cast pure polyamide membranes exhibited surface morphologies characteristic of commercial polyamide RO membranes, whereas nanocomposite membranes had measurably smoother and more hydrophilic, negatively charged surfaces. At the highest nanoparticle loadings tested, hand-cast nanocomposite film morphology was visibly different, and pure water permeability was nearly double that of hand-cast polyamide membranes with equivalent solute rejections. Comparison of membranes formed using pore-filled and pore-opened zeolites suggest nanoparticle pores play an active role in water permeation and solute rejection. The best-performing nanocomposite membranes exhibited permeability and rejection characteristics comparable to commercial RO membranes. As a concept, thin-film nanocomposite membrane technology may offer new degrees of freedom in tailoring RO membrane separation performance and material properties.

Microbial biofouling is one of the major obstacles for reaching the ultimate goal to realize high permeability over a prolonged period of reverse osmosis operation. In the study of Kim et al., a hybrid TFC membrane consisting of a self-assembly of TiO₂ nanoparticles with a photocatalytic destructive capability on microorganisms was devised as a novel means to reduce membrane biofouling. Then, the antifouling and fouling mitigation on the actual commercialized TFC was verified. TiO₂ nanoparticles of a quantum size (~10 nm or less) in anatase crystal structure were prepared from the controlled hydrolysis of titanium tetraisopropoxide and characterized by X-ray diffraction analysis and transmission electron microscopy. Hybrid TFC membrane was prepared by self-assembly of the TiO₂ nanoparticles through coordination and H-bonding interaction with the COOH functional group of the aromatic polyamide thin-film layer, which was ascertained by XPS. The hybrid membrane was shown to possess a dramatic photobactericidal effect on Escherichia coli under ultraviolet (UV) light illumination. Finally, the introduction of TiO₂ nanoparticles on an actual commercial TFC membrane and application of an RO field test after exposure to microbial cells verified a substantial prevention against microbial fouling by showing less loss of RO permeability, offering a strong potential for possible use as a new type of anti-biofouling TFC membrane [58].
9.5.3.2 Composite Membranes of Carbon Nanotube–Polymer

Majumder et al. [59] reported that liquid flow through a membrane composed of an array of aligned CNTs is four to five orders of magnitude faster than would be predicted from conventional fluid-flow theory. Based on an idea of this report, some CNT-based membranes were prepared and their membrane performances investigated. Figure 9.5 shows the typical structure of a composite membrane of CNT–polymer [60].

Membranes based on CNTs have been highlighted as an emerging technology for water purification system applications. With their ultrahigh water flux and low biofouling potential, CNT membranes are believed to lack various problems encountered when using the conventional membrane separation process that requires a large amount of energy and meticulous maintenance. Although diverse types of CNT membranes have been reported, no commercialized products are available. Kukovitsky et al. reviewed the proper manufacturing methods for CNT membranes and speculated on their performances. Future applications of integrated CNT membrane systems were also outlined [61].

Hinds et al. incorporated an array of aligned CNTs across a polymer film to form a well-ordered nanoporous membrane structure [64]. The membrane structure was confirmed by electron microscopy, anisotropic electrical conductivity, gas flow and ionic transport studies. The measured nitrogen permeance was consistent with the flux calculated by Knudsen diffusion through nanometre-scale tubes of the observed microstructure. Data on Ru(NH$_3$)$_6$$_{3+}$ transport across the membrane in aqueous solution also indicated transport through aligned CNT cores of the observed microstructure. The lengths of the nanotubes within the polymer film were reduced by selective electrochemical oxidation, allowing for tunable pore lengths. Oxidative trimming processes resulted in carboxylate end groups that were readily functionalized at the entrance to each CNT inner core. Membranes with CNT tips that were functionalized with biotin showed a reduction in Ru(NH$_3$)$_6$$_{3+}$ flux by a factor of 15 when bound with streptavidin, thereby demonstrating the ability to gate molecular transport through CNT cores for potential applications in chemical separations and sensing.

Multi-walled CNTs (MWNTs)–polysulfone blend membranes were prepared by Choi et al. by a phase inversion process, using N-methyl-2-pyrrolidinone as a solvent and water as a coagulant [65]. Before making the blend membranes, MWNTs were first treated with strong acid to make them well dispersed in organic solvents such as N-methyl-2-pyrrolidinone for the preparation of homogeneous MWNTs–polysulfone blend solutions. The prepared MWNTs–polysulfone blend membranes were then characterized using several analytical methods, such as a Fourier transform infrared spectroscopy, a contact-angle goniometer, scanning electron microscopy and permeation tests. Because of the hydrophilic MWNTs, the surface of the MWNTs–polysulfone blend membranes appeared to be

![Figure 9.5 Schematic cross-section of CNT embedded TFC membrane.](image-url)
more hydrophilic than just a polysulfone membrane. The carboxylic acid functional groups developed by the treatment with acid on the surface of MWNTs seemed to act to increase hydrophilicity of the blend membranes. The morphology and permeation properties of the blend membranes were also found to be dependent on the amounts of MWNTs used. The pore size of the blend membranes increased along with the contents of MWNTs up to 1.5%, then decreased, and at 4.0% of MWNTs it became even smaller than polysulfone membrane. The polysulfone membrane with 4.0% of MWNTs showed higher flux and rejection than the polysulfone membrane without MWNTs.

A patent by Ratto et al. describes the formation of membranes for filtration by size exclusion from open-ended nanotubes embedded in a polymeric matrix. The matrix forms a layer whose thickness is substantially less than the average length of the nanotubes, allowing the nanotubes to be randomly oriented throughout the matrix while providing channels extending through the layer for the selective passage of molecular species or particles based on size [64].

### 9.5.4 Organic–Inorganic Hybrid Membranes

Kwak et al. fabricated hybrid organic–inorganic RO membranes composed of aromatic polyamide thin films underneath TiO$_2$ nanosized particles by a self-assembly process, aiming at a breakthrough in biofouling problems. First, positively charged particles of the colloidal TiO$_2$ were synthesized by a sol–gel process, and the diameter of the resulting particles in acidic aqueous solution was estimated to be approximately 2 nm by analysing the UV–visible absorption characteristics with a quantum mechanical model developed by Brus. Transmission electron microscopy further confirmed the formation of the quantum-sized TiO$_2$ particles (approximately 10 nm or less). The TiO$_2$ particles appeared to exist in the crystallographic form of anatase as observed with the X-ray diffraction pattern in comparison with those of commercial 100% rutile and a commercial 70:30% anatase-to-rutile mixture. The hybrid TFC aromatic polyamide membranes were prepared by self-assembly of the TiO$_2$ nanoparticles on the polymer chains with COOH groups along the surface. They showed improved RO performance in which the water flux even increased, though slightly. Field-emission scanning electron microscopy showed the TiO$_2$ nanoparticles were well adsorbed onto the surface. XPS demonstrated quantitatively that a considerable amount of the adsorbed particles were tightly self-assembled at the expense of the initial loss of those that were loosely bound, and became stabilized even after exposure to the various washing and harsh RO operating conditions. The antibacterial fouling potential of the TiO$_2$ hybrid membrane was examined and verified by measuring the viable numbers and determining the survival ratios of the *E. coli* as a model bacterium, both with and without UV light illumination. The photocatalytic bactericidal efficiency was remarkably higher for the TiO$_2$ hybrid membrane under UV illumination, compared with that of the same membrane in darkness, as well as those for the neat membranes under either light condition [65].

A hybrid membrane inter-stage design (HID) combines membranes of different nominal flux and salt rejection (i.e. different models) in the same pressure vessel of seawater RO racks. The HID experiences reported in the literature show there are no quantitative analyses published and very few seawater RO plants have used it to date. The main objective of the paper by Peñate and García-Rodríguez was to present the results of a thorough computer assessment of this innovative design for conventional seawater RO installations. Two types of analysis were conducted for all representative models of membranes. First, membrane replacement with a view to reduce the energy consumption due to lower working pressures while the plant capacity remains unchanged. Second, to increase plant capacity by reducing the specific energy consumption while maintaining the power consumption of the plant. A general HID design criterion was defined for the three main membrane manufacturers: that is,
Filmtec, Hydranautics and Toray. Moreover, the quantitative results are useful for retrofitting plants thanks to membrane replacement [66].

With the rapidly increasing demands on water resources, fresh water shortage has become an important issue affecting the economic and social development in many countries. As one of the main technologies for producing fresh water from saline water and other wastewater sources, RO has been widely used so far. However, a major challenge facing widespread application of RO technology is membrane fouling, which results in reduced production capacity and increased operation costs. Therefore, many researches have been focused on enhancing the RO membrane resistance to fouling. The paper by Kang and Cao presents a review of developing antifouling RO membranes in recent years, including the selection of new starting monomers, improvement of the interfacial polymerization process, surface modification of conventional RO membranes by physical and chemical methods, as well as the hybrid organic–inorganic RO membranes. The review of research progress in this article may provide an insight for the development of antifouling RO membranes and extend the applications of RO technology in water treatment in the future [67].

9.5.5 Boron Separation in Reverse Osmosis

Boron (boric acid, 5 mg L\(^{-1}\)) contained in seawater is an essential element in plants, but growth inhibition and genotoxic hazard are a concern. The World Health Organization quality of water guidelines specifies less than 0.5 mg L\(^{-1}\).

Boron is known to cause damping-off of citrus fruits and also infertility, and there is a need for technology that can efficiently remove the substance during seawater desalination and wastewater treatment. There are some reports on the removal of boron by RO.

Seawater desalination systems using RO membranes have been constructed to settle the lack of drinking water. RO desalination membranes have high rejection for most solutes in seawater. Japanese drinking water standards for water quality of the permeate can be achieved except for boron. Therefore, boron rejection needs to be considered in the design of the RO process and during the operation of the plant. Luckily, there is a simple and easy method to estimate boron concentration. Taniguchi et al. [68] report measured boron permeabilities and their relation to salt permeabilities using cross-linked polyamide membranes. Chemical degradation of the membranes affected these permeabilities to different degrees. Boron concentrations in the permeate were then calculated using a computer program that was based on the boron permeabilities calculated from the measured salt permeabilities. The results obtained were compared with actual data taken at an RO plant of Toray Industries, Inc., Ehime. The model data fitted the experimental result well. It was also found that a relationship existed in the permeate between salt and boron concentrations and that the boron concentration can be obtained from measurement of the salt concentration.

A numerical analysis tool for the estimation of boron reduction, in RO desalination plants, was developed by Sagiv and Semiat [69]. The derived model enables proper variations of some controllable parameters for significant permeate boron reduction. These parameters are temperature, applied pressure, permeate splitting along the membranes module and pH changes of the feed. Upon verification of the model with existing data, parametric reduction of the permeate boron concentration was calculated. It was found that lowering the RO desalination temperature, increasing the applied pressure and/or increasing pH result in reduction of the permeate boron concentration. The optimal permeate splitting was found to be around half of the module length. The effects of the controllable parameters on membrane functions, in regard to other permeate variables, were also analysed and discussed. It was shown that combining contributions of several parameters may yield significant permeate boron reduction to an extent of possibly saving a second desalination stage or ion exchange.
The model presented provides a basis for cost analysis of the required change of the parameters to gain a significant reduction of the permeate boron concentration.

Boron is a vital element for organism growth, but excessive exposure can cause detrimental effects to plants, animals and possibly humans. However, it has been challenging for many of the existing seawater RO membrane plants to remove boron and meet the current World Health Organization guidelines for drinking water quality. The objective of the study by Hyung and Kim was to evaluate the effect of key operating parameters such as pH and temperature on boron rejection and develop a corresponding mechanistic predictive model. Bench-scale crossflow filtration experiments were performed to estimate the rejection of boron by six commercial seawater RO membranes. The rejection of boron appeared to follow a mechanism that is different from those of other ionic solutes and could not be readily correlated with their rejections. An irreversible thermodynamic model coupled with film theory was applied to quantitatively analyse the experimental observations. The model accurately predicted the boron rejection performances of the seawater RO membranes under different operating conditions. The model was further modified to account for the boric acid speciation by pH and temperature dependence of the model parameters. The model developed therein will be fundamental for performance prediction and design of seawater RO processes [70].

The removal of boron from water was investigated by Cengeloglu et al. using the RO technique with SWHR, BW-30 (Filmtec) and AG (GE Osmonics) membranes, not considered previously. The effect of pH and concentration of the feed water and operating pressure on the boron rejection was investigated. The experimental results indicated that boron rejection mostly depends on membrane type, pH of the feed water and operating pressure. The results also showed that boron can be effectively removed only at a feed water pH of 11. The lowest permeate boron concentration (the highest rejection, close to 99%) was obtained when SWHR membrane was used. The rejection efficiency of the membranes was found to be in the order of SWHR > BW-30 > AG. For all membranes, boron rejection increased with increasing operating pressure. Finally, two different natural (ground) water samples containing 24.8 and 9.4 mg L\(^{-1}\) of boron were treated by using RO with SWHR membrane and obtained results showed that RO could be efficiently used (with >95% rejection) for removal of boron from groundwaters [71].

As noted previously, excess of boron in water poses a problem due to adverse effects on crop production as well as human health and aquatic life. Huertas et al. [72] examined the influence of biofouling of NF and RO membranes on the performance of the membranes in removing boron from a synthetic wastewater effluent. Accelerated laboratory-scale biofouling experiments were carried out with commercial TFC NF and RO membranes under controlled conditions. Permeate flux decline, down to less than 25% of its initial value, and substantial decrease in boron rejection were attributed to extensive biofilm growth on the membranes. For the RO membrane, boron rejections declined by 45% and 34% of the initial values for influent boron concentrations of 5.5 mg L\(^{-1}\) and 1.1 mg L\(^{-1}\) respectively, whereas the corresponding declines in boron rejection for the NF membrane were 44% and 13% of the initial values. These adverse effects of biofilm growth on permeate water flux and boron rejection were attributed to both an increase in hydraulic resistance to permeate flow due to bacterial extracellular polymeric substances and a biofilm-enhanced concentration polarization near the membrane surface.

Permeability, one of the key transport parameters, is being used as an intrinsic characteristic of membranes for RO process prediction. The RO process in terms of boron rejection in two steps was predicted by Hung et al. [73]. First, the permeability of boron existing as boric acid, B(OH)\(_3\), and as metaborate ion, B(OH)\(_4\)^{−}, through seawater RO membranes was estimated in three types of feed matrix: deionized water, NaCl and artificial seawater. The second step was to develop a computer program using boric and borate permeabilities as inputs to predict the boron rejection under different
operating conditions. The governing equations were derived from the solution-diffusion model. The effect of temperature was quantitatively determined employing a representative constant and incorporated with the program. The prediction showed good agreement with experimental data obtained from a laboratory-scale plate-frame-type RO system.

The seawater RO membrane desalination process is a relevant and reliable technology for desalination of seawater. However, some serious limitations were discovered during field practice, among which the boron problem seems to be critical. According to the World Health Organization regulations, the boron concentration should be reduced to less than 0.5 mg L$^{-1}$ for drinking water. It was also reported that this limit is rarely reached for conventional RO desalination plants equipped with commercially available membranes. Kabay et al. [74] reviewed the extensive published literature on separation methods of boron removal from seawater.

A mechanistic predictive model was developed to simulate the rejection of boron by a spiral-wound RO membrane element under varying water quality and operating conditions. This model was verified with pilot-scale experiments performed at different pH values and pressures. The model was further applied to simulate boron rejection in pilot- and full-scale RO processes. Simulation results suggest that boron rejection decreases as pH and operating pressure decrease and as temperature increases. A full-scale simulation suggests that boron rejection is also greatly affected by the overall process recovery. The modelling approach presented by Mane et al. can be useful for process design and optimization. For example, it can be used to predict boron removal performance of existing facilities under modified pH conditions or to evaluate different membrane configurations under varying operating conditions [75].

Steady-state performance predictions and optimization of the RO-based desalination process utilizing a given spiral-wound-type membrane modules were investigated by Sassi and Mujtaba [76]. A set of implicit mathematical equations were generated by combining the solution-diffusion model with the film theory approach to model the RO process which is used for simulation and optimization. The simulation results for a three-stage RO process were compared with the results from literature and were found to be in good agreement, having relative errors of 0.71% and 1.02% in terms of water recovery and salt rejection respectively. The sensitivity of different operating parameters (feed concentration and feed pressure) and design parameters (number of elements, spacer thickness, length of spacer filament) on the plant performance were also investigated. Finally, for the same type of spiral-wound membrane, two optimization problems were formulated and solved. In the first one, a nonlinear optimization problem was formulated for the same three-stage RO process (fixed configuration) to minimize the specific energy consumption at fixed product flow rate and quality while optimizing the operating and design parameters. The results showed a 20% saving in specific energy consumption compared with the base case. In the second one, a mixed-integer nonlinear programming (MINLP) problem based on a superstructure was formulated for fixed freshwater demand and quality to minimize the total annualized cost while optimizing the design and operation of the RO network. A variable fouling profile along the membrane stages was introduced to see how the network design and operation of the RO system were to be adjusted to minimize the total annualized cost. An outer-approximation algorithm was used to solve the MINLP problem. The results showed that the fouling distribution between stages affects significantly the optimal design and operation of the RO process.

As has already been stated, boron is a vital element for growth of creations, but excessive exposure can cause detrimental effects to plants, animals and possibly humans, and the RO technique is widely used for seawater desalination and for wastewater treatment. With this in mind, the aim of a study by Patroklou et al. was to identify how different operating parameters such as pH, temperature and pressure can affect boron concentrations at the end of the RO processes. For this purpose, a mathematical model for boron rejection was developed based on the solution-diffusion model, which can describe
the solvent and solute transport mechanism through the membranes. After a wide and thorough research, empirical correlations developed in the past are filtered, adopted and calibrated in order to faction with reliability as part of the solution-diffusion model of this work. The model was validated against a number of experimental results from the literature and was used in further simulations to get a deeper insight of the RO process. The general findings of the boron rejection model support the case that with increasing pH and operating pressure of the feed water the boron rejection increases and with increasing feed water temperature the boron rejection decreases [77].

9.5.6 Removal of Radioactive Materials by Reverse Osmosis Membrane

RO membrane is among the most powerful tools for solving the global water crisis, and Toray has developed high-performance RO membranes for seawater desalination, brackish water desalination and wastewater reclamation by molecular design in the preparation of cross-linked aromatic polyamide membrane, which produces more appropriate water quality and quantity compared with conventional membranes. Existing literature had provided the removal performances of radioactive substances by RO membranes, but accurate data had not been reported concerning the use of advanced RO membranes. Consequently, there was a desire to demonstrate caesium (Cs) and strontium (Sr) removal performance in radioactive water using RO membranes because of the considerable concern over water quality control for nuclear power stations. So Sasaki et al. studied the removal performance of Cs, Sr and iodine using model compounds adding nonradioactive chemicals to seawater and analysing by inductively coupled plasma mass spectrometry for ultra-trace detection. Consequently, Toray advanced seawater RO membrane UTC-80R has high removal performance to reduce the concentration of Cs, Sr and iodine to less than 0.01 in high-salinity water [78].

Contamination of drinking groundwater sources by naturally occurring radioactive materials is a rather common problem in several regions in the Middle East and the Arabian Gulf. This contamination, which represents public health risks and a threat to the environment, complicates the processes of water treatment and increases costs. The study by Khedr [79] summarizes the results of treatment of contaminated groundwater for rejection of radioisotopes. The removal of radium ($^{226,228}$Ra$^{2+}$), uranium (as uranyl cation UO$_2$ $^{2+}$, or carbonate complexes UO$_2$(CO$_3$)$_2^{2-}$ and UO$_2$(CO$_3$)$_3^{4-}$) and radon ($^{222}$Rn) was investigated by RO and NF in comparison with the most common conventional methods of ion-exchange resins (IERs), chemical precipitation/softening, coagulation and adsorption on surface-active media. IERs and chemical softening realized radionuclide rejection from 32 to 95%, but with loss of process efficiency, which attained 24% due to undesired parallel removal of similar ions. Removal by IERs was too dependent on resin form and water pH and required periodic shutdown for regeneration of the resin, which was slow and seldom complete. Softening required chemical dosing stoichiometric to isotope removal, disposal of contaminated sludge and subsequent water filtration. Coagulation failed to remove Ra. Its removal of U ranged from zero to 93% depending on pH due to formation of different U complexes. Only RO, parallel to water desalination, showed steady, high rejection of all isotopes which attained 99% without interference of similar ions, regeneration or subsequent filtration. NF showed similar behaviour, but with lower water desalination [79].

Zakrzewska-Trznadel [80] reviewed membrane methods introduced into the nuclear technology industry against the background of the other, commonly applied separation techniques, with indications of the possibilities and prospects for their further developments. Particular attention was paid to the pressure-driven processes (e.g. ultrafiltration and RO), which were studied at laboratory and pilot scales at the Institute of Nuclear Chemistry and Technology, Warsaw. Verification
of the potential application of RO on an industrial scale for the treatment of liquid low- and inter-
mediate-level radioactive wastes was accomplished with the installation designed and constructed
for the Radioactive Waste Management Plant at Świerk, Warsaw. Great attention was given to
prospective membrane processes for the treatment of high-level liquid waste and partitioning
of actinides, such as liquid membranes and membrane solvent extraction, as well as to membrane
contactors that are the modern apparatus approach for unit operations involving application of
membranes.

9.6 Membrane Module of Reverse Osmosis

See http://www.membranes.com/docs/trc/commerc.pdf#search='Membrane+Module+of+Reverse
Osmosis'.

The two major membrane module configurations used for RO applications are hollow fibre and
spiral wound. Two other configurations, tubular and plate-and-frame, have found good acceptance
in the food and dairy industry and in some special applications, but modules of this configuration have
been less frequently used in RO applications.

9.6.1 Spiral-Wound Membrane Module

In a spiral-wound configuration two flat sheets of membrane are separated with a permeate collector
channel material to form a leaf. This assembly is sealed on three sides with the fourth side left open for
permeate to exit. A feed/brine spacer material sheet is added to the leaf assembly. A number of these
assemblies or leaves are wound around a central plastic permeate tube. This tube is perforated to col-
lect the permeate from the multiple leaf assemblies. The typical industrial spiral-wound membrane
element is approximately 100 or 150 cm (40 or 60") long and 10 or 20 cm (4 or 8") in diameter.
The feed/brine flow through the element is a straight axial path from the feed end to the opposite
brine end, running parallel to the membrane surface. The feed channel spacer induces turbulence
and reduces concentration polarization. Manufacturers specify brine flow requirements to control
concentration polarization by limiting recovery (or conversion) per element to 10–20%. Therefore,
recovery (or conversion) is a function of the feed-brine path length. In order to operate at acceptable
recoveries, spiral systems are usually staged with three to six membrane elements connected in series
in a pressure tube. The brine stream from the first element becomes the feed to the following element,
and so on for each element within the pressure tube. The brine stream from the last element exits the
pressure tube to waste. The permeate from each element enters the permeate collector tube and exits
the vessel as a common permeate stream. A single pressure vessel with four to six membrane elements
connected in series can be operated at up to 50% recovery under normal design conditions. The brine
seal on the element feed end seal carrier prevents the feed/brine stream from bypassing the following
element. Spiral-wound elements are most commonly manufactured with flat-sheet membrane of
either a cellulose diacetate and triacetate (CA) blend or a TFC. A TFC membrane consists of a thin
active layer of one polymer cast on a thicker supporting layer of a different polymer. The composite
membranes usually exhibit higher rejection at lower operating pressures than the cellulose acetate
blends. The composite membrane materials may be polyamide, polysulfone, polyurea or other
polymers.
9.6.2 Hollow-Fibre Membrane Module

This configuration uses membrane in the form of hollow fibres which have been extruded from cellulosic or non-cellulosic material. The fibre is asymmetric in structure and is as fine as a human hair, about 42 μm (0.0016″) inside diameter and 85 μm (0.0033″) outside diameter. Millions of these fibres are formed into a bundle and folded in half to a length of approximately 120 cm (4 ft). A perforated plastic tube, serving as a feed water distributor, is inserted in the centre and extends the full length of the bundle. The bundle is wrapped and both ends are epoxy sealed to form a sheet-like permeate tube end and a terminal end which prevents the feed stream from bypassing to the brine outlet. The hollow-fibre membrane bundle, 10–205 cm (4–8″) in diameter, is contained in a cylindrical housing or shell approximately 137 cm (54″) long and 15–30 cm (6–12″) in diameter. The assembly is called a permeator. The pressurized feed water enters the permeator feed end through the centre distributor tube, passes through the tube wall and flows radially around the fibre bundle toward the outer permeator pressure shell. Water permeates through the outside wall of the fibres into the hollow core or fibre bore, through the bore to the tube sheet or product end of the fibre bundle, and exits through the product connection on the feed end of the permeator. In a hollow-fibre module, the permeate water flow per unit area of membrane is low, and therefore the concentration polarization is not high at the membrane surface. The net result is that hollow-fibre units operate in a non-turbulent or laminar flow regime. The hollow-fibre membrane must operate above a minimum reject flow to minimize concentration polarization and maintain even flow distribution through the fibre bundle. Typically, a single hollow-fibre permeator can be operated at up to 50% recovery and meet the minimum reject flow required. The hollow-fibre unit allows a large membrane area per unit volume of permeator, which results in compact systems. Hollow-fibre perimeters are available for brackish and seawater applications. Membrane materials are cellulose acetate blends and aramid (a proprietary polyamide-type material in an anisotropic form). Because of very close packed fibres and tortuous feed flow inside the module, hollow-fibre modules require feed water of better quality (lower concentration of suspended solids) than the spiral-wound module configuration.

Figure 9.6 summarizes the materials and modules for ROs membrane in the main companies. Toray, Nitto and Dow Chemical are applying the flat polyamide membrane in the spiral module to RO desalination. Only Toyobo is using the hollow-fibre cellulose acetate membrane for the desalination by RO.
9.7 Membrane Cleaning

Common foulants are as follows: calcium carbonate scale, sulfate scale as calcium sulfate, barium sulfate, strontium sulfate, metal oxides as iron oxide, manganese oxide, copper oxide, nickel oxide, aluminium oxide, zinc oxide, polymerized silica scale, inorganic colloidal deposits as iron, aluminium, sulfur, mixed inorganic/organic colloidal deposits, natural organic matter material, manmade materials as antiscalant/dispersants, cationic polyelectrolytes, microbiological deposits as bacterial biofouling, algae, mould and fungi.

Cleaning techniques to remove those foulants adhered on the membrane during RO operation are very important and significantly influence the fortune of RO technology.

Generally, cleaning is done once or twice a year, but more often if the feed water is problematic. The specific cleaning procedure is a function of the feed water chemistry, the type of membrane used and the type of fouling encountered. A typical cleaning regimen consists of flushing the membrane modules by recirculating the cleaning solution at high speed through the module, followed by a soaking period, and a second flush, and so on. The chemical cleaning agents commonly used are acids, alkalis, chelatants, detergents, formulated products and sterilizers.

Acid cleaning agents such as hydrochloric, phosphoric or citric acids, effectively remove common scaling compounds. With cellulose acetate membranes, the pH of the solution should not go below 2.0, or else hydrolysis of the membrane will occur. Oxalic acid is particularly effective for removing iron deposits. Citric acid is not very effective with calcium, magnesium or barium sulfate; in this case a chelant such as ethylenediaminetetraacetic acid may be used.

To remove bacteria, silt or precipitates from the membrane, alkalis combined with surfactant cleaners are often used. Detergents containing enzyme additives are useful for removing biofoulants and some organic foulants. Sterilization of a membrane system is also required to control bacterial growth. For cellulose acetate membranes, chlorination of the feed water is sufficient to control bacteria. Polyamide and interfacial composite membranes do not normally require sterilization, as they are usually fairly resistant to biological attack. Periodic shock disinfection using formaldehyde or peroxide is usually enough to prevent biofouling. Repeated cleaning gradually degrades reverse osmosis membranes. As membranes approach the end of their useful life, the water flux will normally have dropped by at least 20% and the salt rejection will have begun to fall (http://www.separationprocesses.com/Membrane/MT_ChpRO-8.htm).

Polyamide TFC RO membranes are prone to biofouling due to their inherent physicochemical surface properties. In order to address the biofouling problem, Rahaman et al. [81] have developed novel surface coatings functionalized with biocidal silver nanoparticles and antifouling polymer brushes via polyelectrolyte layer-by-layer (LBL) self-assembly. The novel surface coating was prepared with polyelectrolyte LBL films containing poly(acrylic acid) (PAA) and poly(ethylene imine) (PEI), with the latter being either pure PEI or silver nanoparticles coated with PEI (Ag–PEI). The coatings were further functionalized by grafting of polymer brushes, using either hydrophilic poly(sulfobetaine) or low surface energy poly(dimethylsiloxane) (PDMS). The presence of both LBL films and sulfobetaine polymer brushes at the interface significantly increased the hydrophilicity of the membrane surface, while PDMS brushes lowered the membrane surface energy. Overall, all surface modifications resulted in significant reduction of irreversible bacterial cell adhesion. In microbial adhesion tests with E. coli bacteria, a normalized cell adhesion in the range of only 4–16% on the modified membrane surfaces was observed. Modified surfaces containing silver nanoparticles also exhibited strong antimicrobial activity. Membranes coated with LBL films of PAA/Ag–PEI achieved over 95% inactivation of bacteria attached to the surface within 1 h of contact time. Both the antifouling and antimicrobial results suggest the potential of using these novel surface coatings in controlling the fouling of RO membranes.
References


10

Nanofiltration

Nanofiltration (NF) is a membrane filtration technique that has prospered and was reported by Eriksson [1] and Conlon and McClellan [2]. This technique is mainly applied in drinking water purification process steps, such as water softening by reducing hardness. Like reverse osmosis (RO), NF is a pressure-driven separation process with a semipermeable membrane and the principles of crossflow filtration. Membrane softening by NF membranes is an option when high-level salt rejection is not necessary or even desirable, and where removal of disinfection by-product precursors such as natural and organic synthetic organic matter is required [3,4]. NF is also becoming more widely used in food-processing applications such as dairy (production of lactose from cheese whey), for simultaneous concentration and partial demineralization of monovalent ions.

The relationship between the NF membrane and the separation species is shown in Figure 10.1.

10.1 Principle of Nanofiltration

The principle of NF is very similar to that of RO but there are a just slight difference between RO and NF process. As described in the principle of RO in Chapter 8, the RO membrane rejects monovalent ion as Na\(^+\) and Cl\(^-\) ion and easily permeates water. But NF membrane does not almost reject monovalent ion, rejects multivalent ions such as Ca\(^{2+}\) and Mg\(^{2+}\) and permeate water. Therefore, a higher driving force in the pressure driven separation process is required for RO system but not for NF system. Consequently, the membrane strength required for practical applications makes a great difference.

10.2 Fundamental Analysis of Nanofiltration

See the Van der Bruggen and Geens chapter on NF in *Advanced Membrane Technology and Applications* [5].

10.2.1 Permeation Characteristics of Nanofiltration

There are crucial three parameters: solvent permeability or flux through the membrane, rejection of solutes and yield or recovery for the operation of an NF unit. The flux \(J\) or the permeability (flux per unit of applied pressure) of a membrane is, similar to other pressure-driven membrane processes, a
crucial parameter. Most NF membranes are hydrophilic, except some used for solvent applications. If
the Hagen–Poiseuille equation, which is only valid for porous membranes, can be assumed in NF
membranes, the other parameters influencing the permeability are obvious:

\[ J = \frac{4r^2 \Delta P}{8\eta \tau \Delta x} \]

A large membrane surface porosity \( \varepsilon \), large pore radii \( r \), and a low tortuosity \( \tau \) together with a low
membrane thickness \( \Delta x \) are advantageous. The influence of the viscosity \( \eta \) is important when the tem-
perature is varied: a lower viscosity is obtained at higher temperatures, which results in higher fluxes.
An increase of the temperature by 1 °C corresponds to a flux increase of 2–2.5%. For concentrated
solutions or solutions with high salinity, the osmotic pressure \( \Delta \pi \) should be subtracted from the
applied pressure \( \Delta P \). The flux equation then becomes

\[ J = L_p (\Delta P - \sigma \Delta \pi) \]

where \( L_p \) is the solvent permeability and \( \sigma \) is the (maximal) rejection of the solute. The osmotic pres-
sure can be calculated by using the Van’t Hoff equation [6] or, with more precision, by using the Pitzer
model [7].

A similar transport equation can be written for the solute:

\[ J_s = L_p \Delta x \frac{dc}{dx} + (1 - \sigma)Jc \]

where \( c \) is the concentration of the solute and \( P_s \) is the permeability of the solute. Transport by dif-
fusion is represented by the first term in this equation; the second term stands for the contribution of
convection to the transport of (uncharged) molecules.

The rejection of component \( i \) is defined as

\[ R_i(\%) = \left( 1 - \frac{c_{p,i}}{c_{f,i}} \right) \times 100 \]

where \( c_{p,i} \) is the permeate concentration and \( c_{f,i} \) is the feed concentration of component \( i \); \( R \) is a dimen-
sionless parameter and its value normally varies between 100% (complete rejection of the solute) and
0% (solute and solvent pass freely through the membrane). Negative rejections can sometimes be
observed when the solute passes favourably through the membrane; for example, in salt mixtures.

Figure 10.1 Relationship between NF membrane and separation species.
The rejection of a given molecule can be calculated from the aforementioned equations as

$$R = \frac{\sigma(1-F)}{1 - \sigma F}$$

$$F = \exp \left( -\frac{1 - \sigma}{P_s} J \right)$$

The rejection in NF is mainly determined by molecular size, hydrophobicity and charge [8–11], but effects of, for example, molecular shape and dipole moment might play a role as well. The pore/void dimensions are statistically distributed and can be described by a log-normal distribution [10]. This explains the smooth transition from no rejection to complete rejection in a typical S-shaped curve when molecular size is varied. The molecular weight cut-off (MWCO) value is often used to indicate the lower limit of molecules that are (almost completely) retained, similar to ultrafiltration (UF) membranes. For NF membranes, with MWCO values between 150 and 1000 (but often in the range 150–300), this concept should be used with care: hydrophobic molecules larger than the MWCO, for example, often have a low rejection; the pH of the solution might change the membrane’s surface charge as well as the charge of the solute, so that the rejection of this solute can be higher or lower than expected. The third important parameter is the recovery or yield. This is a parameter for the design of an industrial application rather than a membrane characteristic. The recovery is the ratio of the permeate stream to the feed stream; its value ranges from 40 to 90%.

10.2.2 Concentration Characteristics of Nanofiltration

See Van der Bruggen and Geens [5].

One of the main problems still to be solved for NF, and for pressure-driven membrane filtration in general, is the further treatment of the concentrate fraction. The relative volume of the concentrate may range from 40 to 90% of the feed volume; its composition is similar to the feed, but the concentration factor (CF) of rejected compounds is higher by a factor CF calculated as

$$\text{CF} = \frac{c_{r,i}}{c_{f,i}} = \frac{Q_f}{Q_r} \left[ 1 - \text{REC} \left( \frac{c_{p,i}}{c_{f,i}} \right) \right]$$

(10.7)

where $Q$ (L h$^{-1}$) is the volumetric flow and $c$ (mg L$^{-1}$) is the concentration; the subscripts $r$, $f$, $p$ and $i$ refer to the retentate, the feed, the permeate and the component used respectively; and REC is the relative fraction of the permeate compared with the feed. For components that are completely rejected, this equation simplifies to

$$\text{CF} = \frac{1}{1 - \text{REC}}$$

(10.8)

As a consequence of this large variation, the further environmental fate of the concentrate is unpredictable; a large variation in possibilities for reuse, further treatment or discharge exists. Cost factors and legal aspects also play an important role. Generally, all methods for concentrate processing can be classified into one of the following categories: (1) reuse, (2) further treatment by removal of contaminants, (3) incineration, (4) direct or indirect discharge in surface water, (5) direct or indirect discharge in groundwater and (6) landfilling. Reuse is the most attractive option but is only applicable in a few cases where the concentrated fraction is actually the desired product, such as in the food industry. (e.g. dairy: products, starch processing). The permeate is then a side product, which can be reused as a rinsing water or discharged. If reuse of the concentrate is not possible, further treatment may be
necessary before discharge. Two options for further treatment can be distinguished: (a) water removal from the concentrate and (b) removal of specific components by a proper choice of a selective treatment method. The first option leads to a sludge or solid waste that is subsequently reused (if possible), landfilled (if necessary after solidification/stabilization or a similar pretreatment to avoid leaching of contaminants) or incinerated in a rotating kiln furnace (hazardous waste) or a grate furnace (nonhazardous waste). The second option leads to a (treated) wastewater, which has been reused (if possible) or discharged in surface water or in groundwater.

10.3 Membranes and Modules for Nanofiltration

10.3.1 Membranes for Nanofiltration

NF is a membrane filtration based method that uses nanometre-sized cylindrical through-pores that pass through the membrane at 90°. NF membranes have pore sizes from 1 to 10 Å, smaller than that used in microfiltration and UF, but just larger than that in RO. Membranes used are predominantly created from thin polymer and porous inorganic membranes. Materials that are commonly used include polyethylene terephthalate or metal oxides such as alumina [12,13], titania, zirconia and silica–zirconia [4]. Pore dimensions are controlled by pH, temperature and time during development, with pore densities ranging from 1 to 106 pores per square centimetre. Membranes made from polyethylene terephthalate and other similar materials are referred to as ‘track-etch’ membranes, named after the way the pores on the membranes are made [14]. ‘Tracking’ involves bombarding the polymer thin film with high-energy particles. These result in making tracks that are chemically developed into the membrane, or ‘etched’ into the membrane, which are the pores. Membranes created from metal oxide, such as alumina membranes, are made by electrochemically growing a thin layer of aluminium oxide from aluminium metal in an acidic medium.

The traditional materials used for NF membranes are organic polymers. NF membranes are made by phase inversion or by interfacial polymerization [15]. Phase-inversion membranes are homogeneous and asymmetric and often made of cellulose acetate or poly (ether sulfone) (PES). Membranes made by interfacial polymerization are heterogeneous: they consist of a thin-film composite (TFC) layer on top of a substrate UF layer. Typical polymers are (aromatic) polyamides, polysulfone (PS)/PES/sulfonated PS, polyimide and poly(piperazine amide); other polymers or blends can be used as well. Recent trends are the use of highly cross-linked polymers in order to obtain enhanced membrane stability at low or high pH, at high temperature or in organic solvents. NF membranes contain functional groups that can be charged, depending on the pH of the solution in contact with the membrane. Typically, NF membranes are negatively charged at neutral pH, with the isoelectric point around pH 3–4.

The production of ceramic NF membranes is also possible, but to date the pore size of most ceramic NF membranes is still relatively high. The MWCO, the molecular weight of a component retained by 90%, is usually above 500 [16–19], MWCO values of 200 and below were recently reported for Al2O3–TiO2 membranes [20]. These membranes were obtained by a careful preparation of each sublayer. The macroporous substrate consisted of α-Al2O3; the intermediate layers were prepared from TiO2, α-Al2O3, γ-Al2O3 or mixtures of these components; the top layer is a fine-textured polymeric TiO2 top layer.

Most NF membranes are packed into spiral-wound elements; however, tubular, hollow-fibre and flat-sheet or plate-and-frame modules are also available [21]. Tubular membranes with diameter around 1 mm, denoted as capillary membranes, are interesting in view of fouling control [22].
10.3.1.1 Surface Modification

Polyacrylonitrile (PAN) membranes display some unusual features for UF. The meso-macropores of PAN UF membranes can be easily reduced into the range of micro-mesopores by taking advantage of surface tension forces within the capillary pores during heat treatment in the presence of ZnCl₂. Asymmetric PAN NF membranes with controlled highly dense pore surface functional groups were prepared by hydrolysis of the nitrile groups with NaOH. The combined effects of heat treatment and the presence of ZnCl₂ on the formation of NF membranes were investigated. In addition, membrane post-treatment with NaOH was studied. The effect of counter-ion species on the membrane performance was also investigated. A simple new method, which utilized univalent alkaline ions as probes, was developed to derive the average pore size of cationic NF PAN membranes from pure water permeability coefficients [23].

Poly(N-isopropylacrylamide) and poly(N-isopropylacrylamide-block-ethylene glycol methacrylate) were grafted from commercial polyamide TFC NF membranes using surface-initiated atom transfer radical polymerization. The results from Fourier-transform infrared (FTIR) spectroscopy confirmed the successful grafting of both polymers from the membrane surfaces. Contact-angle measurements were done to illustrate the temperature-responsive wettability of the modified membrane surfaces. Modified membranes were used in flux measurements of wastewater produced during coal bed methane gas exploration. The degree of fouling of the original and the modified membranes was examined by pure water flux recovery measurements after produced water filtration and a temperature-controlled water rinse [24].

Fouling of NF membranes remains a major concern that often limits process viability. One method to minimize fouling is to modify the filtration surface and perhaps the pores of the membrane in order to minimize adsorption of dissolved solutes. Himstedt et al. modified NF membranes by growing acrylic acid nanobrushes from the surface of the membrane. If the pH of the feed was above the pKₐ of the grafted nanobrushes, the carboxylic groups were deprotonated and swelled. Dead-end filtration experiments confirmed that polyacrylic acid nanobrushes may be grafted from the surface of high-flux NF membranes without significantly impacting the filtrate flux. Furthermore, swelling of the grafted nanobrushes at pH values above their pKₐ leads to a decrease in filtrate flux. Rejection of glucose was also investigated. For the base membrane, glucose rejection was not affected by feed pH over the range 3–7. However, for modified membranes a significant change in rejection was observed as a function of pH. Thus, pH-responsive NF membranes may be designed by surface modification [25].

10.3.1.2 Interfacial Polymerization

A silicone-coated TFC NF membrane composed of PAN/polyamide/poly(dimethylsiloxane) (PDMS) for the separation of the fatty acid dissolved in organic solvents was interfacially prepared by reacting trimesoyl chloride (TMC) and PDMS with an aqueous phase containing piperazine (PIP) and m-phenylenediamine (MPD). The effects of the monomer blends ratio PIP/MPD and monomer concentration on membrane performance such as solvent permeation (water, alcohols, ketones and hexane) and organic materials rejection rate (poly(ethylene glycol) 200 and oleic acid) were investigated by Kim and Lee [26]. Low concentration of the monomer and high content of the PDMS were needed for the high permeation of the solvents. The membrane surface properties (hydrophilic or hydrophobic) studied by contact angle and zeta potential measurement were an important factor on the solvent permeation. The membranes showed high permeation of the hydrophobic solvent (hexane) and good rejection rate of the oleic acid dissolved in methanol and acetone.

Utilizing an interfacial polymerization technique for the preparation of a polymeric composite NF membrane, Chen et al. [27] achieved both high permeation flux of water and high salt rejection. Synthesis conditions, such as concentration of monomer, reaction time and swelling agent, significantly
affected the separation performance of composite membranes. The composite polyamide membrane had a permeation rate of \(~2–5\) gallon ft\(^{-2}\) day\(^{-1}\) (\(~3.5–8.5\) L m\(^{-2}\) h\(^{-1}\)) and a salt rejection rate of \(~94–99\%\) when 200 ppm aqueous salt solution was fed at 200 psi and 25 °C. Also, a higher performance NF membrane could be prepared by suitably swelling the support matrix in the period of polymerization. The results of various feed concentrations showed that permeate flux decreased with increasing salt concentration in the feed solution. This result may have been due to concentration polarization on the surface of polyamide membranes. The separation performance of polyamide membranes showed an almost independent relationship with operation pressure until it was up to 200 psi.

Lin et al. [28] prepared four TFC polyamide negatively charged NF membranes (NF-PS-1, NF-PS-2, NF-PS-3 and NF-PS-4) via the interfacial polymerization technique, which involved the formation of a polyamide thin film at the interfacial PS microporous substrate between two immiscible liquid phases, an aqueous phase containing PIP and an organic phase containing TMC (0.25, 0.50, 1.00 and 2.00 wt%). Correlations of the intrinsic properties of these four NF filtration membranes (in regard to the physical structures, surface negative charge density, pure water flux, pore size and the NF filtration performances) on the composition of the weight per cent of TMC in the organic phase were investigated. Experimental results clearly demonstrated that NF membrane prepared using 1.0 wt% TMC in hexane phase (i.e. NF-PS-3) gave a much higher salt rejection on salt-containing negative divalent salts like Na\(_2\)SO\(_4\) and MgSO\(_4\); the maximum rejections of Na\(_2\)SO\(_4\) and MgSO\(_4\) were both 99.6% for NF-PS-3 (1.0 wt% TMC), while the rejections of Na\(_2\)SO\(_4\) and MgSO\(_4\) for the other three NF membranes were in the order of NF-PS-2 (0.50 wt% TMC) > NF-PS-1 (0.25 wt% TMC) > NF-PS-4 (2.00 wt% TMC). The effects of the pH of the feed and the applied filtration pressure on the MgSO\(_4\) rejection were also investigated for this series of NF membranes.

NF composite membrane was prepared by interfacial polymerization of 1,6-hexylenediamine, \(\sigma\)-phenylenediamine or PIP with TMC on the surface of PS support [29]. Meanwhile, two PS support membranes with different MWCO were introduced into this experiment, hoping to find the influence of porous substrates on the prepared membrane performance. Furthermore, the water flux and salt rejection rate of those three kinds of newly prepared NF composite membranes were compared by water filtration experiment. In order to make interfacial polymerization much more effective, kinds of reaction ratios between PIP and TMC were designed. The results show that PIP reacts better with TMC than with the other two chemical medicines, and the salt rejection rate of poly(PIP) NF composite membranes can reach 55% under laboratory conditions; however, the effects of PS supports on NF performances were varied when different polyamines were put to use and PS support membrane M (the one with higher MWCO) was preferred to prepare the poly(PIP).

NF membranes consisting of a composite barrier layer prepared by interfacial polymerization of polyamide around the ultrafine cellulose nanofibers (CNs) layer in a thin-film nanofibrous composite scaffold were demonstrated by Wang et al. [30]. Two interfacial polymerization pathways (termed IP and IP-R), regarding the arrangement of the aqueous and organic phases, were investigated. It was found that interfacial polymerization with the aqueous phase above the organic phase (IP-R) yielded better filtration performance; that is, IP-R-based membranes exhibited a higher MgCl\(_2\) rejection than IP-based membranes. Transmission electron microscopy observation indicated that the denser part of the barrier layer was on the CN layer surface of IP-R-based membranes, whereas this portion was deeply immersed in the CN layer of IP-based membranes. To investigate the structure and property relationship of the composite barrier layer, both IP- and IP-R-based membranes were treated with 1% TMC in hexane. After treatment, the rejection of NaCl was found to increase from 74% to 91% for IP-R-based membranes, whereas it remained unchanged (\(~75\%) for IP-based membranes. This behaviour can be explained by the decrease in pore size due to the cross-linking of TMC and...
secondary amino groups in the barrier layer of IP-R-based membranes, while the permeability in IP-based membranes was probably mainly controlled by the water passage through channels formed at the interface between CNs and polymer matrix in the barrier layer of IP-based membranes, which is not dependent on the cross-linking reaction.

10.3.1.3 Composite

Huang et al. [31] prepared a novel composite NF membrane by overcoating the PAN UF membrane with a graft copolymer of trimethylallyl ammonium chloride onto a chitosan (GCTACC) thin layer. The effects of membrane preparation techniques and operating conditions on the performance of the composite membrane were studied. The results indicate that a composite NF membrane from 1.0 wt% GCTACC casting solution, vaporized for 2 h at 50 °C, cross-linked for 20 h at 50 °C and pH approximately 12 with ethanol/epichlorohydrin (50/0.45 wt/wt) had optimum performance. The resultant GCTACC–PAN composite membrane was positively charged. Scanning electron microscopy showed its asymmetric and composite features. At 25 °C and 30 L h⁻¹ of cycling flow, the permeability of pure water through this membrane was 6.3 L h⁻¹ m⁻² MPa⁻¹. At 25 °C, 1.2 MPa and 30 L h⁻¹ of cycling flow the rejection of 1000 mg L⁻¹ MgCl₂, CaCl₂, MgSO₄, Na₂SO₄ and NaCl solutions was 0.976, 0.972, 0.897, 0.65 and 0.407 respectively, with fluxes of 6.8 L h⁻¹ m⁻², 6.12 L h⁻¹ m⁻², 6.12 L h⁻¹ m⁻², 5.57 L h⁻¹ m⁻² and 5.51 L h⁻¹ m⁻² respectively. The order of rejection of different salts follows the decreasing order of MgCl₂, CaCl₂, MgSO₄, NaCl, KCl, Na₂SO₄ and K₂SO₄, which reveals the characteristics of the positively charged NF membrane. In addition, the curve for the streaming potential also illustrates the positively charged characteristics of this membrane, with a pressure osmotic coefficient of 11.7 mV MPa⁻¹.

Miao et al. [32] developed N,O-carboxymethyl chitosan (NOCC) composite NF membranes cross-linked by epichlorohydrin using a method of coating and crosslinking, where an epichlorohydrin/ethanol 96.7% (0.067 M KOH) solution was used as the cross-linking agent. The structure and the morphology of the resulting membrane were characterized by attenuated total reflection (ATR) infrared spectroscopy and environmental scanning electron microscopy. The effects of preparation conditions on the rejection performance of the resulting composite membrane were also investigated. At 20 °C and 0.40 MPa the rejections of the resulting membrane to Na₂SO₄ and NaCl solutions (1000 mg L⁻¹) were 90.4% and 27.4% respectively, and the permeate fluxes were 7.9 kg m⁻² h⁻¹ and 10.8 kg m⁻² h⁻¹ respectively. The rejections of this kind of NOCC–PSF composite NF membrane to the inorganic electrolyte solutions decreased in the order of Na₂SO₄, NaCl, MgSO₄ and MgCl₂.

Van der Bruggen et al. [33] provided an in-depth outline of synthesis parameters for NF membranes made of PES combined with a polyamide top layer. The top layer of an NF membrane is assumed to dominate the mass transfer resistance, but sublayers may also contribute significantly to the resistance. This is partly due to the higher thickness, combined with the narrow pores, which should prevent intrusion of the top layer during synthesis.

Starting from a study of synthesis parameters determining the performance of a PES membrane, the use of such membranes as a sublayer for a composite PES–polyamide membrane were described. An integrally skinned asymmetric PES membrane with a very thin, microporous skin layer was prepared by either dry- or wet-phase inversion processes, such as solvent evaporation, precipitation from the vapour phase, precipitation by controlled evaporation, thermal precipitation and immersion precipitation. In this way, the membrane obtained can reject solutes with molecular mass down to ~500, depending on the synthesis method. The choice of the two monomer–solvent combinations, the composition of both phases (i.e. concentration and additives), the manufacturing conditions (i.e. temperature of solutions, immersion time, curing temperature and time), and the structure and chemical properties of the support membrane were discussed with respect to their effect on formation of
macrovoids, membrane permeability and the eventual membrane morphology. A typical example of an integrally skinned asymmetric CN membrane found suitable as a support for NF membranes is shown in Figure 10.2. For the first time, a comprehensive explanation was derived for the impact of non-woven fabric wetting pretreatment, initial casting film thickness and relative air humidity on the resulting PES support structure and performance.

Top layers made of polyamide were added to these membranes; the characteristics of the sublayers were related to the performance of the eventual NF membrane. TFC membranes are comprised of an ultrathin film typically made of polyamide, which is coated over a porous support membrane typically made of PES. Several optimal casting conditions as well as possible further improvements were identified. For the PA layer synthesis, three different interfacial polymerization methods, seven different drying methods and the effect of curing time were studied. Methods for fine tuning and optimizing NF membranes were demonstrated.

Pourjafar et al. [34] investigated using the L₁₆ orthogonal array of the Taguchi method that is applied to determine the optimum condition of three controlling factors – that is, poly(vinyl alcohol) (PVA), glutaraldehyde and TiO₂ nanoparticle concentration – for preparing PVA–PES composite membrane. PES UF membrane was prepared via the immersion precipitation technique and subsequently was used as the support layer. Different PVA–PES composite membranes were fabricated at various PVA concentrations, glutaraldehyde concentration as the cross-linking agent and nanosized TiO₂ as membrane surface and performance modifier. The membranes were characterized in terms of morphology, surface properties and filtration performance via scanning electron microscopy, atomic force microscopy, X-ray diffraction, contact angle and crossflow filtration. Filtration tests were done on yeast industrial wastewater with chemical oxygen demand (COD) level of 11 500 mg L⁻¹. The Taguchi approach was employed to determine the optimum condition and achieve the best permeate flux and COD removal. As two series of data were examined, two optimized membranes were obtained from permeate flux and COD level points of view. According to the surface analysis, TiO₂ nanoparticles were successfully coated on the surface of both optimized membranes. The comparison between two optimized membranes showed that the membrane optimized from the COD level point of view had an efficiency of about 98%, while the membrane optimized from the permeate flux point of view had about 97% output. The long-term flux measurements indicated that the permeate flux of
the membrane optimized from the flux point of view was approximately 8 L m$^{-2}$ h$^{-1}$, while for the membrane optimized from the COD point of view it was about 2.5 L m$^{-2}$ h$^{-1}$. Therefore, the membrane optimized from the permeate flux point of view was more beneficial and affordable.

Shenvi et al. [35] tried to prepare composite membrane having chitosan as the active layer supported on poly(1,4-phenylene ether ether sulfone) (PPEES) membrane. The chitosan layer was cross-linked by glutaraldehyde in two different concentrations. The scanning electron microscopy images and hydraulic permeability coefficient revealed the UF nature of the neat PPEES membrane. This was used as a new support material for the casting of the chitosan layer in order to obtain composite membranes. The composite nature of the PPEES–chitosan membranes was confirmed by field emission scanning electron microscopy and differential scanning calorimetry analysis. The infrared spectroscopy results confirmed the cross-linking of the chitosan surface by glutaraldehyde. The changes in the hydrophobic nature of the PPEES membrane surface due to deposition of chitosan active layer followed by cross-linking were studied by their contact angle measurement and water flux study. From their studies, PPEES was proved to be a good support membrane for preparation of composite membranes. Increase in glutaraldehyde concentration increased the salt rejection of the membrane up to 34% for NaCl and 53% for MgSO$_4$ with a simultaneous decrease in the flux values. The hydraulic permeability coefficient values confirmed that the membranes prepared were in the NF range.

TFC NF membranes with improved acid stability were fabricated by Yu et al. through the interfacial polymerization of TMC, naphthalene-1,3,6-trisulfonylchloride (NTSC) and PIP on a porous PSF support membrane by varying the NTSC content in TMC-organic solution [36]. The physicochemical characteristics of the membranes were analysed by ATR-FTIR, streaming potential measurement and surface contact-angle measurement, the permeation properties were evaluated through crossflow permeation tests, and the acid stability was investigated through both static acid soaking tests and long-term permeation tests under acidic condition. As the NTSC content in TMC-organic solution increased, it was found that the membrane surface became more hydrophilic and negatively charged, the pure water permeability and MWCO of the NF membrane formed increased from 5.5 to 10.6 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ and about 360 to 660 Da respectively, while the rejection rate to Na$_2$SO$_4$ first increased from 98.2 to 98.7% and then declined to a lower value of 97.8%. After soaking in 8 w/v% H$_2$SO$_4$ for 30 days or filtration with 4.9 w/v% H$_2$SO$_4$ for 60 days, the TFC membranes prepared from TMC and NTSC showed little performance change, while serious performance deterioration occurred with the TFC membrane prepared from TMC.

10.3.1.4 Hollow Fibre

He et al. [37] prepared a new type of NF membrane is reported by coating a sulfonated poly(ether ether ketone) (SPEEK) layer on top of a PSF support. The membranes were characterized by dextran mixtures, salt solutions and negatively charged dyes. The SPEEK-coated NF membranes showed MWCO for dextran in the range of UF; however, there was a rather high rejection for sodium sulfate; retention for salts was in the order of RNa$_2$SO$_4$ > RNaCl > RMgCl$_2$; in addition, the membranes showed a 97–100% retention to the organic dyes. The rejection rates were improved by an increase in the coating thickness and the polymer concentration in the coating solution at the penalty of permeability decrease. Furthermore, it was found that pore penetration of SPEEK into the support membrane effectively constrained the swelling rate of SPEEK and increased the retention. The Donnan–steric pore model was used to describe the transport properties of the membrane. Modelling identified a very tortuous passage within the active separation layer.

Deng et al. [38] prepared three-bore hollow fibre charged NF membranes by interfacial polymerization. The results showed that the flux and rejection of NF membrane prepared in this study increased with increasing operating pressure. The water flux decreased and rejection for obvious dyes
increased as the solute concentration increased. The separation factor for a mixture of xylene
orange–NaCl decreased when NaCl concentration in solution increased, and it could reach as high
as 18. In addition, three-bore hollow fibre charged NF membrane has excellent stability for strong
acid (pH 3), strong alkali (pH 11) and high temperature solution (80 °C).

Hollow-fibre NF membranes can withstand much higher foulant concentrations than their spiral-
wound counterparts and can be used in water purification without pretreatment. Still, the preparation
of hollow-fibre NF membranes is much less established. De Grooth et al. [39] demonstrated the design
of a hollow-fibre NF membrane with excellent rejection properties by alternately coating a porous UF
membrane with a polycation, a polyzwitterion and a polyanion. On model surfaces, they showed
for the first time that the polyzwitterion poly-N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,
N-dimethylammonium betaine can be incorporated into traditional polyelectrolyte multilayers based
on poly(styrenesulfonate) and poly(diallyldimethylammonium chloride). Furthermore, work on
model surfaces allowed a good characterization of, and insight into, the layer build-up and helped
to establish the optimal membrane coating conditions. Membranes coated with these multilayers
have high salt rejection of up to 42% NaCl, 72% CaCl2 and 98% Na2SO4 with permeabilities of
3.7–4.5 L m⁻² h⁻¹ bar⁻¹. In addition to the salt rejections, the rejection of six distinctively different
micropollutants, with molecular weights between 215 and 362 g mol⁻¹, was investigated. Depending
on the terminating layer, the incorporation of the polyzwitterion in the multilayer results in NF mem-
branes that show excellent retentions for both positively and negatively charged micropollutants, a
behaviour that is attributed to dielectric exclusion of the solutes. Their approach of combining model
surfaces with membrane performance measurements provides unique insights into the properties of
polyzwitterion-containing multilayers and their applications.

10.3.1.5 Hybrid Membrane

A new siloxane monomer, 3-(3-(diethoxy(2-(5-(4-(10-ethoxy-4-hydroxy-2,2-dimethyl-11-oxa-
ammonio-6-aza-10-silatridecan-10-yl)phenyl)-1,3,4-oxadiazol-2-ylthio)ethyl)silyl)propylamino)-2-
hydroxy-N,N,N-trimethylpropan-1-aminium chloride (OA), was synthesized by reported 3-(4-(5-
(2-((3-aminopropyl)diethoxysilyl)ethylthio)-1,3,4-oxadiazol-2-yl)phenyl)diethoxysilyl)propan-1-amine
and glycidyltrimethylammonium chloride by an epoxide ring-opening reaction by Singh et al. [40].
OA–PVA hybrid antibiofouling NF membranes were prepared by acid-catalysed sol–gel followed by
formal cross-linking. Membranes showed a wormlike arrangement and self-assembled layered morphol-
gy with varying OA content. Hybrid NF membrane, especially OA-6, showed low surface roughness,
high hydrophilic nature, low biofouling, high cross-linking density, thermal and mechanical stability,
solvent- and chlorine-tolerant nature, along with good permeability and salt rejection. Prepared
OA-6 hybrid NF membrane can be used efficiently for desalting and purification of water with about
2.0 g L⁻¹ salt content (groundwater in major part of India). The method described provides a novel route
for producing antibiofouling membranes for diversified applications.

Metal–organic frameworks (MOFs) have emerged as porous solids of a superior type for the fab-
rication of membranes. However, it is still challenging to prepare a uniformly dispersed robust
MOF hybrid membrane. Zhang et al. [41] proposed a simple and powerful strategy – namely,
coordination-driven in situ self-assembly – for the fabrication of MOF hybrid membranes. On the
basis of the coordination interactions between metal ions and ligands and/or the functional groups
of the organic polymer, this method was confirmed to be feasible for the production of a stable mem-
brane with greatly improved MOF-particle dispersion in and compatibility with the polymer, thus pro-
viding outstanding separation ability. As an experimental proof of concept, a high-quality ZIF-8–poly
(styrenesulfonate) membrane was fabricated that showed excellent performance in NF and the sep-
aration of dyes from water.
Zhang et al. [42] tried to develop novel organic–inorganic hybrid composite NF membranes based on PVA–aminopropyl triethoxysilane (APES), which exhibit a rejection of 98.5% and a water flux of 13.5 L m$^{-2}$ h$^{-1}$ for a feed containing 2000 ppm Na$_2$SO$_4$ at 2.0 MPa at best-optimized APES ratio and thermal cross-linking time. No irreversible changes in membrane performance were observed after prolonged exposure (up to several weeks) of PVA–APES-1.0 membrane to the solutions with a pH in the range of 0–14. Moreover, after exposure to different acid solutions for 150 days, the Na$_2$SO$_4$ rejection of the composite membrane could still be maintained above 98%, and with an appropriate water flux. Notably, non-toxic solvent is used during the membrane preparation, showing enough green chemistry technology for environmental protection. A combination of high salt rejection, appropriate water flux, improved acid/alkali stability and environmentally friendly production route indicates that these PVA–APES-xx membranes may be good candidate materials for NF in treating industrial wastewater at extreme pH values.

10.3.1.6 Solvent-Resistant Membranes

Alternating deposition of oppositely charged polyelectrolytes can create stable solvent-resistant NF membranes with very high flux and selectivity. A new combination of polyelectrolytes (poly(diallyl-dimethylammonium chloride) and SPEEK) is reported by Li et al. from which supported membranes consisting of 5, 10, 15 and 20 bilayers were prepared via the layer-by-layer method. The morphology of the membranes was studied in detail by scanning electron microscopy and atomic force microscopy, showing rougher membrane surfaces with increasing bilayer number. For the first time, polyelectrolyte-complex-based membranes were also applied in the filtration of organic solvents, where they form an excellent new tool to study the role of charges in solvent filtrations. Owing to Donnan exclusion, the multilayered polyelectrolyte-complex membranes showed very good rejections up to 99% for charged solutes in the pressure-driven filtration of isopropanol solutions. Moreover, they were found to show excellent prospective use in polar aprotic solvents, like dimethylformamide and tetrahydrofuran, which have been extremely troublesome so far for most existing solvent-resistant RNF membranes [43].

Basu et al. [44] investigated the incorporation of MOFs as fillers in PDMS membranes. Mixed matrix membranes with MOFs [Cu$_3$(BTC)$_2$], MIL-47, MIL-53(Al) and ZIF-8 as dispersed phases were synthesized and characterized. The membranes were applied in solvent-resistant NF, more in particular in the separation of Rose Bengal from isopropanol. The membranes showed increased permeance but lower retention compared with unfilled membranes. Membranes were characterized with scanning electron microscopy, where poor adhesion of the fillers to PDMS was observed. Chemical modification of the fillers with N-methyl-N-(trimethylsilyl)-trifluoroacetamide allowed the synthesis of defect-free membranes with higher retention of Rose Bengal, due to good interaction with fillers and decreased membrane swelling.

Organic solvent NF is an emerging membrane separation process with the potential to replace traditional separation techniques. Its advantages include lower energy consumption than alternatives such as distillation, easy up-scaling and flexibility. However, manufacturing organic solvent NF membranes involves a number of stages contributing toward the discharge of hazardous chemicals as waste. Thus, the environmental advantages of employing organic solvent NF are to some extent cancelled out by the waste released during organic solvent NF membrane production. The paper by Soroko et al. describes a process for the preparation of polyimide integrally skinned asymmetric organic solvent NF membranes with adjustable MWCO. Previously reported methods for producing polyimide-based organic solvent NF membranes were modified by Soroko et al. without compromising the performance of the membranes. The toxic solvents used to form polymer dope solution (i.e. dimethylformamide–1,4-dioxane) are replaced by an environmentally friendly dimethyl sulfoxide.
(DMSO)–acetone solvent system. In order to further diminish the environmental impact, isopropanol was successfully replaced with water in the cross-linking step. Scanning electron microscope images revealed that membranes with spongy matrix without macrovoids were obtained regardless of the DMSO/acetone ratio [45].

10.3.2 Module for Nanofiltration

Spiral-wound and tubular modules are applied to NF. See http://en.wikipedia.org/wiki/Nanofiltration#Spiral_Wound_Module.

10.3.2.1 Spiral-Wound Module
Spiral-wound modules are the most commonly used style of module and are ‘standardized’ design, available in a range of standard diameters (2.5”, 4” and 8”) to fit standard pressure vessels that can hold several modules in series connected by O-rings. The module uses flat sheets wrapped around a central tube. The membranes are glued along three edges over a permeate spacer to form ‘leaves’. The permeate spacer supports the membrane and conducts the permeate to the central permeate tube. Between each leaf, a mesh like feed spacer is inserted [46,47]. The reason for the mesh-like dimension of the spacer is to provide a hydrodynamic environment near the surface of the membrane that discourages concentration polarization. Once the leaves have been wound around the central tube, the module is wrapped in a casing layer and caps placed on the end of the cylinder to prevent ‘telescoping’ that can occur in high flow-rate and pressure conditions.

10.3.2.2 Tubular Module
Tubular modules look similar to shell and tube heat exchangers with bundles of tubes with the active surface of the membrane on the inside. Flow through the tubes is normally turbulent, ensuring low concentration polarization but also increasing energy costs. The tubes can either be self-supporting or supported by insertion into perforated metal tubes. This module design is limited for NF by the pressure they can withstand before bursting, limiting the maximum flux possible [48,49]. Owing to both the high energy operating costs of turbulent flow and the limiting burst pressure, tubular modules are more suited to ‘dirty’ applications where feeds have particulates, such as filtering raw water to gain potable water in the Fyne process. The membranes can be easily cleaned through a ‘pigging’ technique in which foam balls are squeezed through the tubes, scouring the caked deposits [50].

10.4 Concentration Polarization and Membrane Fouling in Nanofiltration

See Van der Bruggen and Geens [5].

10.4.1 Concentration Polarization in Nanofiltration
Concentration polarization describes the accumulation of the species being retained close to the surface of the membrane which reduces separation capabilities. It occurs because the particles are convected towards the membrane with the solvent and its magnitude is the balance between this convection caused by solvent flux and the particle transport away from the membrane due to the
concentration gradient (predominantly caused by diffusion.) Although concentration polarization is easily reversible, it can lead to fouling of the membrane [46,51].

10.4.2 Membrane Fouling in Nanofiltration

A problem often encountered in practical applications of NF is the decrease of the water flux for real feed solutions in comparison with the pure water flux. Flux decline can be caused by membrane fouling [52]. Fouling is caused by precipitation of inorganic components such as CaCO₃ or CaSO₄ [53,54], deposition of organic compounds, or possibly growth of bacteria on the membrane surface (biofouling) [55]. Fouling can be defined as irreversible flux decline that can only be removed, for example, by chemical cleaning. When flux decline disappears by simply changing the feed solution to pure water, the phenomenon is reversible and should therefore not be considered as fouling.

Both reversible flux decline and fouling cause practical problems in the application of NF: For a given membrane surface, the yield of permeate decreases; the energy consumption increases because higher pressures are needed to obtain the same flow rate; cleaning procedures need additional chemical reagents; and the lifetime of the membrane decreases. Furthermore, the rejection of different components might change. It might be expected that rejections generally increase when flux decline occurs, for example, because of pore narrowing, but this is not always the case.

Flux decline due to the presence of organic compounds in the feed solution was, for example, encountered in NF of surface water containing high concentrations of natural organic matter (NOM) [56,57], where interactions between organic compounds and the membrane material (in a hollow-fibre module) even lead to the formation of a cake layer. This was also reported for groundwaters and for surface waters during NF with spiral-wound membranes [58]. It is usually accepted that flux decline in aqueous solutions containing organic molecules is mainly caused by adsorption, possibly enhanced by pore blocking [59,60]. Adsorption on NF membranes has been related to high-performance liquid chromatography characteristics [61,62]. Similar problems have been reported for UF membranes [63] and for RO membranes [64–66]. For UF, it was found that molecular size is the most important factor determining flux decline, whereas in RO different factors reflecting hydrophobicity play a role.

Toxic cyanotoxins such as microcystins represent a human health risk in water bodies. NF is an effective technology to remove these microcontaminants from drinking water. However, long-term operational sustainability is necessary because of decreases in membrane fluxes over time and increasing operation costs. The rejection of NOM is a key issue regarding membrane fouling and flux decline, and is also of great importance in the water industry due to its relationship with public health. Therefore, the study of Teixeira and Sousa aimed to analyse the effect of microcystins and NOM properties on membrane fouling and to understand the fouling mechanisms, using a series of experiments with different water types. Results showed that NF was capable of reducing low molecular weight NOM fractions from water and that these fractions were responsible for flux decline and membrane fouling. The adsorption of NOM onto the membrane surface was reduced in the presence of microcystins due to the hydrophobic character of microcystins, which are the first to be adsorbed on the membrane surface. Microcystins contributed to the rejection of smaller natural organic fractions by blocking the membrane pores and reducing NOM adsorption onto the membrane pores [67].

10.4.3 Antifouling in Nanofiltration

UF membranes, often employed in membrane bioreactors, exhibit high susceptibility to fouling by extracellular polymeric substances. As potential alternatives, commercial polyvinylidene fluoride
(PVDF) UF membranes were coated with the amphiphilic graft copolymer PVDF-graft-poly(oxyethylene) methacrylate to create TFC NF membranes by Asatekin et al. Pure water permeabilities up to 56 L m$^{-2}$ h$^{-1}$ MPa$^{-1}$ were obtained at pressures of 0.21 MPa (30 psi). The new TFC NF membranes exhibited no irreversible fouling in 10-day dead-end filtration studies of model organic foulants bovine serum albumin, sodium alginate and humic acid at concentrations of 1000 mg L$^{-1}$ and above. Dead-end filtration of activated sludge from a membrane bioreactor (1750 mg L$^{-1}$ volatile suspended solids) resulted in constant flux throughout the 16 h filtration period. Fouling performance of the TFC NF membrane and effluent water quality were substantially improved in all cases over that for the base PVDF UF membrane. Utilizing the atomic force microscope colloid probe technique, the measured interaction force profiles indicated the presence of repulsive steric interactions, which likely prevent the attachment of foulants to the TFC NF membrane. Similarly, the adhesion (pull-off) curves reveal the absence of foulant adhesion to the TFC NF membrane surface, even in the presence of divalent calcium ions. In contrast, when such force measurements are carried out with the base PVDF UF membrane, substantial adhesion forces were registered [68].

Li et al. successfully synthesized and grafted a new kind of fluorinated polyamine onto the polyamide membrane surface to fabricate an antifouling NF membrane with low surface free energy [69]. The surface composition of the fluorinated polyamide NF membrane was confirmed by FTIR and X-ray photoelectron spectroscopy. The membrane cross-section morphology was observed by a field emission scanning electron microscopy. The presence of perfluoroalkyl groups on the membrane surface significantly lowered the surface free energy from 60.0 to 44.4 mJ m$^{-2}$. The filtration experiment results indicated that the surface fluorination did not lower the separation performance of the polyamide NF membrane significantly. The antifouling experiment results demonstrated that the fluorinated polyamide NF membranes exhibited superior antifouling property – that is, high flux recovery ratio (~98.5%) and low total flux decline ratio (~11%) – during protein aqueous solution and humic acid aqueous solution filtration.

Li et al. [70] also developed a facile method for fabricating antifouling and high-flux NF membranes based on bioinspired polydopamine (PDA). PES UF membrane as the support was first deposited with a thin PDA layer and then chemically modified by a new kind of fluorinated polyamine via Michael addition reaction between fluorinated polyamine and quinone groups of PDA. PDA coating significantly reduced the pore sizes of the PES support membrane and endowed the NF membrane with high separation performance (flux about 46.1 L m$^{-2}$ h$^{-1}$ under 0.1 MPa, MWCO of about 780 Da). The grafted fluorinated polyamine on the PDA layer could form low free energy microdomains to impede the accumulation/coalescence of foulants and lower the adhesion force between foulants and the membrane, rendering the membrane surface with prominent fouling-release property. When foulant solutions (including bovine serum albumin, oil and humic acid) were filtered, the resultant NF membrane exhibited excellent antifouling properties (the minimal value of total flux decline ratio was ~8.9%, and the flux recovery ratio reached 98.6%). It is also found that the structural stability of the NF membrane could be significantly enhanced due to the covalent bond and other intermolecular interactions between the PDA layer and the PES support.

NF membranes are continually sought for their unique physical and chemical properties, which allow filtration of electrolytes, dyes and other substances. Hebbar et al. [71] prepared NF membranes from a flat sheet polyetherimide–hydrolysed poly(isobutylene-alt-maleic anhydride) (PIAM) blend membranes. The main aim was to explore the effect of addition of PIAM on morphological features and permeation properties of the membranes. The presence of dicarboxylic acid functionality leads to an enhancement in the hydrophilicity and antifouling properties. The results revealed that increasing the content of hydrolysed PIAM decreases the pore size of the membranes and subsequently increases the electrolyte rejection. The polyetherimide–hydrolysed PIAM composition (80:20) showed
reasonably good salt rejection (sodium sulfate of 1000 ppm) of up to 76% with a pure water flux of 11.8 L m$^{-2}$ h$^{-1}$ at 0.4 MPa transmembrane pressure. This study provides a simple and effective approach to producing negatively charged NF membranes for water desalination applications with low energy consumption.

A simple two-step surface modification method of polyamide NF membrane, involving the activation of amide groups by formaldehyde and the subsequent cerium (Ce(IV))-induced graft polymerization of zwitterionic 3-(methacryloylamino) propyl-dimethyl-(3-sulfopropyl) ammonium hydroxide (MPDSAH) monomers, was employed to improve membrane antifouling property [72]. The membranes before and after modification were characterized by ATR-FTIR, scanning electron microscopy and atomic force microscopy. The changes in both surface chemical composition and morphology of membranes confirmed the successful graft polymerizations of MPDSAH onto polyamide NF membrane. The static water contact-angle measurements showed that surface hydrophilicity of the modified membranes was significantly enhanced. As the MPDSAH concentration increased, the water flux of grafted membrane decreased gradually, while salt rejection increased slightly. The fouling experiments with bovine serum albumin solution demonstrated that modified membranes exhibited better resistance to protein fouling.

10.5 Technology

Industrial applications of NF are quite common in the food and dairy sector, in chemical processing, in the pulp and paper industry, and in textiles, although the chief application continues to be in the treatment of fresh, process and waste waters.

10.5.1 Treatment of Fresh, Process and Waste Waters

Kim et al. [75] chemically modified a commercially available thin TFC polyamide NF membrane to improve its rejection capacity for selected organic micropollutants categorized as endocrine disrupting chemicals and pharmaceutically active compounds: bisphenol-A, ibuprofen and salicylic acid. The raw NF membrane was altered using the following modification sequence: graft polymerization (methacrylic acid (MA) membrane); cross-linking of grafted polymer chains (ethylene diamine (ED) membrane); and substitution of functional groups (succinic acid (SA) membrane). ATR-FTIR was used to verify each modification in the sequence: the formation of amide bonds; graft polymerization and cross-linking; and increased carboxylic acids on the modified membrane. Based on zeta potential and contact-angle measurements, graft polymerization increased the negative charge and hydrophilicity of the raw membrane, while cross-linking replaced carboxylic acid with amide bonds, which made the modified membrane almost neutral at pH 6.5. The water fluxes of the ED and SA membranes were similar to that of the raw membrane; however, the water flux of the MA membranes varied with polymerization time (the membrane polymerized for 15 min revealed ≥20% higher flux than the raw membrane). Bisphenol-A rejection by the raw membrane was substantially improved from 74% to ≥95% after this series of modifications. However, the rejection capacity of the ED membrane for ibuprofen and salicylic acid was slightly reduced compared with those of the MA membrane, which was polymerized for 15 min, due to the lack of an electrical repulsion mechanism. The SA membrane recovered its negative surface charge and showed a clear enhancement in the rejection of all pollutants.
An integrated NF–membrane crystallization system was tested for the removal of sodium sulfate from aqueous wastes originated by the production process of base raw materials (Ni–MH) for special rechargeable batteries. NF experiments on NF90-2540 FilmTec™ modules showed high rejection values to sodium sulfate (>99%) when operated at pressure of 3.45 × 10^6 Pa; it was possible to achieve a maximum permeate recovery factor of 50% when starting from 60 g L^−1 Na_2SO_4 feed solution. The membrane crystallizer, operated downstream to the pre-concentration NF unit, was able to produce thenardite crystals (the anhydrous form of sodium sulfate) grown from slurry with density up to 21 kg m^−3; the solid product exhibited narrow size distribution (coefficient of variation ~30%). Polypropylene hollow-fibre membranes showed a hydrophobic character stable over 2 days of continuous operation [74].

Al-Rashdi et al. [75] investigated the rejection of heavy metal ions using a commercial NF membrane (NF270). The effect of feed pH, pressure and metal concentration on the metal rejections and permeate flux and in some cases permeate pH was explored. The results showed that with all metals examined (except As(III)), when the feed pH is below the isoelectric point the rejection increased. NF270 rejected almost 100% of copper ions at low concentrations, but decreased to 58% at the highest concentration examined. Using 1000 mg L^−1 concentration level, pH 1.5 ± 0.2 and 4 bar the rejection was 99%, 89% and 74% for cadmium, manganese and lead respectively. However, at pH above the isoelectric point the average rejections decreased. NF270 was unable to retain As(III). The metals caused a flux decline due to membrane fouling in the following order of severity: Cu^{2+} > Cd^{2+} ≈ Mn^{2+} > Pb^{2+} ≈ As^{3+}. The correlation between adsorbed amounts of the metals onto NF270 with the normalized flux shows that as the amount increased the normalized flux decreased, except for arsenic, which had a higher deposited amount and higher flux. The root-mean-square roughness as obtained by atomic force microscopy showed that roughness was decreased by membrane fouling.

The municipal wastewater treated by biological methods was used for further treatment by the NF method for wastewater reuse. For this purpose, different NF membranes, such as CK, NF-90 and NF-270, were employed. The quality analysis of product water was carried out using various analytical techniques. The results revealed that the NF-90 membrane can produce the best water quality compared with the other two membranes. The CK membrane also showed a good rejection property after NF-90 membrane, but its big inconvenience is that it gave a lower water flux. Despite the good water flux by NF-270, the permeate quality obtained with this membrane was not as good as obtained with the NF-90 and CK membranes [76].

Orecki and Tomaszewska [77] investigated the possibility of oily wastewater treatment using the NF process. The NF studies were carried out with a permeate obtained from UF (used for the treatment of the oily wastewater from metal industry). The influence of transmembrane pressure on a permeate flux and the degree of the rejection of oil and inorganic compounds was investigated. The studies on the NF treatment of oily wastewater demonstrated a high effectiveness of the rejection of oil and inorganic compounds. The permeate obtained from the treatment was free of oil. Moreover, the retention coefficient of the inorganic compounds was higher than 75% for all the cations examined (Na^+, K^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+}) and higher than 95% for sulfates. Therefore, the permeate obtained in the NF process can be reused for fresh emulsion preparation.

Khosravi et al. [78] evaluated the use of a membrane bioreactor for wastewater treatment from the Mazandaran pulp and paper industry. The qualification of wastewater and the characteristics of this industry’s wastewater were determined by different experiments, such as chemical oxygen demand, biological oxygen demand, colour, densitometry, viscometry and thermogravimetry/differential thermal analysis. Also, the colour-creating agents in the wastewater investigated were characterized. Then, the flux, retention and permeate quality of various NF and low-pressure RO membranes were investigated at two temperatures and by using a low-shear (DSS Labstak M20®) and a high-shear filter
The overall aim was to study the suitability of NF in purification of the discharge water from external activated sludge processes in the pulp and paper industry for reuse in the paper manufacturing process and to compare the results with NF of paper machine process waters. The discharge waters were nanofiltered at a higher flux than paper machine process waters. The permeate was almost free of colour and organic compounds but contained significantly more inorganic compounds than the permeate from the filtration of process waters. To successfully remove monovalent anions and inorganic carbon from the discharge water a low-pressure RO membrane such as the TFC ULP membrane is needed. With that membrane the permeate flux is lower than for NF membranes but the permeate quality is significantly better when considering inorganic ions such as sodium, chloride, nitrate and inorganic carbon (bicarbonate). The permeate flux was two times higher in the high-shear filter than in the low-shear filter but the retentions were significantly lower.

10.5.2 Food, Dairy and Beverage

Food industry applications are quite numerous. In the dairy sector, NF is used to concentrate whey and permeates from other whey treatments, and in the recycling of clean-in-place solutions. In the processing of sugar, dextrose syrup and thin sugar juice are concentrated by NF, while ion-exchange brines are demineralized. NF is used for degumming of solutions in the edible oil processing sector, for continuous cheese production and in the production of alternative sweeteners.

The process waters of the dairy industry that issue from the starting, equilibrating, interrupting and rinsing steps of the different plant units contribute, in addition to the cleaning in place, to the effluent production. Their treatment by a membrane is aimed to concentrate waste organic matter and to use permeate as disposable water for reuse, lowering both the load and volume effluent and the total water consumption of dairy plants. Consequently, Balannec et al. [79] focused on the concentration of 1/3 diluted skimmed milk (COD ≈ 36 g O₂ per litre) to about 1/1 milk (volume reduction factor, VRF 3) with nine NF and RO membranes by dead-end filtration. COD was the selected criterion for permeate quality; that is, rejection of organic milk components assigned to lactose. High COD rejection (>99%) was achieved whatever the membrane and the feed concentration. Rejections of divalent cations >90% were too high for being in accordance with negative rejection of chloride at VRF 3 using NF membranes. The negatively charged proteins at pH 6.6 were likely entrapped in a soft gel that was observed at the end of the run of dead-end filtration. This gel was reversibly removed by a flush with tap water. Dead-end filtration appears to be a useful tool to show the relative content of permeate and the occurrence of a limiting flux upon concentration involving a gel formation. At the end of run (VRF 3) with an initial highly charged feed, the COD of permeate was always far away from the quality of water for human consumption (total organic carbon TOC < 2 mg L⁻¹), but the RO permeate can be released as waste. Water quality close to vapour condensates, issuing from milk and whey drying steps, is needed for reuse in boiler feed; it would likely be reached with an RO + RO cascade and possibly with a single RO with a low charged feed.

In dairy plants, the process waters generated during the starting, equilibrating, interrupting and rinsing steps contribute to the production of effluents. They correspond to milk products (milk, whey, cream) diluted with water without chemicals. The treatment of these dairy process waters by NF or RO operations was proposed to concentrate dairy matter and to produce purified water for reuse in the dairy plant. The Vourch et al. study reports one-stage and two-stage (NF + RO and RO + RO) spiral-wound membrane treatments with five model process waters representative of the main composition variations observed in dairies. Performances (permeate flux, milk components rejection, purified water characteristics) of the different operations were compared. Discussion was focused on the comparison between quality of produced waters and vapour condensates (from product drying and
evaporation processes) reused in dairy plants. Accordingly, both TOC and conductivity of water treated by a single RO or by NF + RO operations were convenient for reuse as heating, cooling, cleaning and boiler feed water. With the two-stage RO + RO process, a more purified water complying with the TOC drinking water limit was achieved [80].

The effects of NF and evaporation concentration technologies on the physiochemical properties of milk protein concentrate (MPC) during processing were evaluated by Cao et al. [81]. Skim milk, ultrafiltered milk, evaporated milk, nanofiltered milk, evaporated MPC, and nanofiltered MPC samples were collected at different processing stages. Chemical composition, microstructure of casein micelles, free sulfhydryl content and surface hydrophobicity of the samples were determined. The insolubility index of MPC was also determined. Casein micelles aggregated compactly after evaporation, while surface hydrophobicity increased and free sulfhydryl content decreased in evaporated milk compared with skim milk. However, the microstructure of the casein micelles was relatively undisturbed after NF, with reduced surface hydrophobicity and free sulfhydryl content. No significant difference was found in chemical composition between the two MPC preparations: approximately 61.40% protein and 28.49% lactose. In addition, the particulate microstructures of both MPCs were similar. However, the insolubility index of evaporated MPC was significantly (0.58 mL) higher than that of nanofiltered MPC. So NF may be an effective way to improve the solubility of MPC products.

In the fruit juice industry, membrane technology is used mainly to clarify the juice by means of UF and microfiltration and to concentrate it by means of NF and RO. Echavarría et al. [82] looked at enzyme immobilization techniques to improve filtration performance and operation methods to quantify fouling. Membrane fouling is a critical issue and inhibits the broader application of membranes in the fruit production industry. Pectin and its derivatives form a gel-like structure over the membrane surface, thereby reducing the permeate flux. In order to degrade pectin, the raw juice is usually subjected to an enzymatic treatment with pectinase, which hydrolyses pectin and causes its protein complexes to flocculate. The resulting juice has reduced viscosity and a much lower pectin content, which is advantageous in the subsequent filtration processes.

The brewing industry is a large consumer of groundwater for brewing, rinsing and cooling purposes. As regulations become more and more stringent and the cost of water increases, water recycling gains interest. Braeken et al. [83] investigated the possibilities of NF for the treatment of brewery wastewater streams in view of recycling. Four different water streams (wastewater after biological treatment, bottle rinsing water, rinsing water of the brewing room and rinsing water of the bright beer reservoir) were filtered with four different NF membranes (UTC-20, UTC-60, Desal-HL-51 and Desal-5-DK). The results for the biologically treated wastewater were the most promising. For the other streams, rejection of organics was insufficient to obtain the required quality, mainly due to the high concentrations of organics such as ethanol in the feed water. Over the periods considered (3 h) only moderate flux decline (10–40%) was observed for most membranes and feed solutions. For Desal-5-DK at high pH, an increase of the flux was observed.

### 10.5.3 Chemical Processing

Livingston et al. [84] described ideas together with preliminary experimental results for applying solvent NF to liquid-phase organic synthesis reactions. Membranes for organic solvent NF only became available during the 1990s and, to date, have been applied primarily to food processing (vegetable oil processing, in particular) and refinery processes. Applications to organic synthesis, even at a laboratory feasibility level, are few. However, these membranes have great potential to improve the environmental performance of many liquid-phase synthesis reactions by reducing the need for complex solvent-handling operations. Examples that are shown to be feasible are solvent exchanges, where
it is desired to swap a high molecular weight molecule from one solvent to another between separate stages in a complex synthesis, and recycle and reuse of homogeneous catalysts. In solvent exchanges, NF is shown to provide a fast and effective means of swapping from a high boiling point solvent to a solvent with a lower boiling point – this is a difficult operation by means of distillation. Solvent NF is shown to be able to separate two distinct types of homogeneous catalysts – phase transfer catalysts and organometallic catalysts – from their respective reaction products. In both cases the application of organic solvent NF allowed several reuses of the same catalyst. Catalyst stability is shown to be an essential requirement for this technique to be effective. Finally, they presented a discussion of scale-up aspects, including membrane flux and process economics.

NF and RO are well-established membrane technologies for applications involving aqueous streams. The principles of NF transport (diffusion, convection and Donnan exclusion) are effectively used to develop novel membrane materials and applications in an aqueous medium. Use of NF in a nonaqueous medium holds strong potential for the food, refining and pharmaceutical industries because of the low energy costs involved with such membrane processes. Further understanding and development of solvent-resistant NF membranes provides opportunities for various hybrid processing, ranging from reactor-membrane to distillation-membrane combinations. Bhanushali and Bhattacharyya [85] provide a comprehensive overview of the literature results and their studies in the area of nonaqueous systems. For solvent-based systems, potential membrane swelling and solvent-solute coupling needs to be considered for membrane design and transport theories. A simplified transport theory for pure solvents was developed using solvent (molar volume, viscosity) and membrane properties (membrane surface energy). This model was verified with literature data for both hydrophilic and hydrophobic membranes. Membrane characterization and preconditioning aspects need to be given serious consideration for evaluating membrane performance. In addition to permeability and separation results, they report on some novel applications of NF in nonaqueous solvents.

Keraani et al. [86] aimed at integrating a green separation process without phase change, namely NF, with olefin metathesis to recover the homogeneous catalyst. As the commercially available Hoveyda II catalyst was not sufficiently retained by the membrane, a set of homogeneous ruthenium-based catalysts were prepared to enhance the recovery of the catalyst by solvent-resistant commercial membranes made of polyimide (Starmem 228). The molecular weights of the catalysts were gradually increased from 627 to 2195 g mol$^{-1}$, and recovery was found to increase from around 70% to 90% both in toluene and dimethyl carbonate. The most retained catalyst was then engaged in a series of model ring-closing metathesis reactions associated with a final NF step to recover and recycle the catalyst. Up to five cycles could be performed before a deterioration in the performance of the process was observed.

Membrane technologies are increasingly becoming useful components of pharmaceutical production processes. For some time, membrane separation technologies of RO, UF and microfiltration have been used to concentrate and purify both small and large molecules. More recent applications of membrane technologies cover a broad range of separation, concentration and purification needs. For example, pharmaceutical waste streams can be treated by NF or pervaporation to detoxify them and/or reduce the volume of waste requiring incineration. Solvent vapours can be removed/recovered from nitrogen/air emission by vapour permeation. Enantiomeric/other isomeric mixtures can be separated by liquid membranes or membrane-based multiphase extractive enzymatic resolution. NF or pervaporation can be used to enhance synthesis reaction conversion. High-performance tangential flow filtration can be used to fractionate protein mixtures whose molecular sieves used to integrate clarification and chromatographic processes for downstream processing of biomolecules. Sirkar [87] reviews attempts to provide a perspective on these developments in laboratories, pilot plants and commercial applications.
Darvishmanesh et al. [88] explored the possibility of developing a sustainable extraction method for use in pharmaceutical production, based on purification with membrane processes. Two types of commercial polymeric organic solvent NF membranes (StarMem™122 and DuraMem™150) were selected and tested for their abilities to recover the solvent from a pharmaceutical–solvent mixture (5, 10, 50 mg L\(^{-1}\)). Five different pharmaceutical compounds were selected: imatinib mesylate, riluzole, donepezil HCl, atenolol and alprazolam. Solvents tested in the experiment were those used in the manufacturing process: methanol, ethanol, isopropanol and ethyl acetate. An acceptable performance (rejection over 90%) was obtained for DuraMem150 in all tested pharmaceutical and solvent mixtures except for isopropanol. No flux was observed for isopropanol over the DuraMem150 due to its high viscosity. No separation was observed by using StarMem122 for imatinib mesylate in isopropanol (over 80%). Commercially available solvent-resistant NF membranes (StarMem122 and DuraMem150) showed promising performances as alternative tools to traditional separation units, such as distillation columns for the recovery of solvents. Furthermore, to evaluate the potential of solvent-resistant NF as a substitution for traditional solvent recovery, a model was developed for NF membrane units and implemented in a common process simulation software (Aspen Plus). These models were based on the pore flow mechanism and describe a single membrane module. A membrane module is not available in Aspen Plus and in its Model Library. In the Darvishmanesh et al. study, this shortcoming was overcome through implementation of the NF membrane module within the Aspen Custom Modeler link to Aspen Plus. The model was tested for two model solutes (Disperse orange 3 and Disperse red 19), since the pharmaceutical physical properties are not included in the Aspen Properties Database. The results presented confirmed the value of the Aspen Custom Modeler as a simulation tool for the use of NF as a novel and sustainable tool in pharmaceutical manufacturing.

10.5.4 Pulp, Paper and Textile Industry

UF and NF with high-shear cross-rotational (CR) filters have been utilized for cleaning of clear filtrates and effluents from the pulp and paper industry. The aim of a study by Mänttääri and Nyström [89] was to find out how different NF membranes operate under high-shear conditions. The filtration efficiency of the membranes was evaluated by measuring flux, retention and fouling under various recovery and pH conditions. High fluxes (approximately 100 L m\(^{-2}\) h\(^{-1}\)) for NF membranes were measured when circulation waters from the paper machine were filtered under neutral conditions. In the filtration of discharge of external activated sludge treatment plants, Mänttääri and Nyström [89] measured fluxes around 150 L m\(^{-2}\) h\(^{-1}\) even at a concentration factor of 12. The best NF membranes removed over 80% of the organic carbon and of the conductivity and almost completely eliminated the colour. With acidic waters, fluxes and retentions were significantly lower. The NF270 membrane from Dow and the Desal-5 membranes from Osmonics had the highest flux and retention properties. However, the Desal-5 membrane lost its retention properties slowly, which restricts its use in the high-shear CR filter. CR-NF can be used in the pulp and paper industry without feed pretreatment by UF. This increases the attractiveness of high-shear CR-NF.

Membrane filtration as an internal purification method, ‘the kidney’, in the pulp and paper industry is discussed by Nuortila-Jokinen et al. Membrane filtration is economically competitive and a very versatile process. It can be used to remove the enriched organic and/or inorganic loads either partially or totally from, for example, the mechanical pulping and paper-making water circuits and it can be applied to various points within the process. With the so-called shear-enhanced membrane modules, very high fluxes have been obtained: in UF about 400 L m\(^{-2}\) h\(^{-1}\) and in NF fluxes almost 200 L m\(^{-2}\) h\(^{-1}\). Depending on the membrane, suspended solids (microfiltration), polysaccharides, extractives and
high molar mass lignous substances (UF) and multivalent salts (NF) can be removed. UF permeate can well be used in paper machine showers to replace fresh water. The quality of the NF permeate is significantly higher than that of UF. The membrane processes can be enhanced by various pretreatment techniques to produce higher permeate fluxes and to eliminate membrane fouling. Such pretreatment methods are, for example, chemical treatment, ozonation and biological treatment. The most cost-effective processes were chemical flocculation, pH adjustment and thermophilic aerobic biological treatment [90].

Afons and De Pinh carried out a systematic investigation of the NF of alkaline bleaching effluent (E1) from the pulp and paper industry through a first assessment of NF of model systems; namely, solutions of salts (NaCl and Na2SO4) and organic solutes (glucose, saccharose and raffinose) which develop membrane–solute(s) interactions similar to those developed by the bleaching effluent. The ampholytic polymer of the membrane active layer, under controlled feed conditions, develops a surface charge distribution which determines the membrane performance. The verification of the effects of the anion valence and the feed concentration on the salts rejections, in accordance with the Donnan exclusion principle, is an important feature of this work. For the bleaching effluent, the NF performance is strongly dependent on the pH due to the influence of this parameter on the membrane surface charge. The contribution of this work toward the optimization of the NF operating conditions would allow for future scale-up of this separation process for E1 effluent purification and water recovery in the pulp and paper industry [91].

The textile industry is a large water consumer: dyeing, rinsing and follow-up treatment of textiles use large amounts of freshwater. As regulations become more and more stringent and the cost of fresh water increases, reclamation of wastewater becomes more and more attractive. Van der Bruggen et al. [92] explored the possibility of using NF to improve the wastewater quality to the standards that are used for the dyeing of wool. Four different samples from the wastewater treatment sequence of a textile factory were filtrated with three different NF membranes (NF70, UTC-20 and NTR 7450). The samples were a used and untreated metal complex dye bath, a used and untreated acid dye bath, a sample from the storage tank (containing a diluted mixture of the previous baths), and the effluent of the biological treatment. NF was possible for all samples, but the biologically treated dye baths showed a more efficient colour removal. For direct NF of used dye baths, two membrane passages would be needed to provide the required permeate quality. Flux decline due to adsorption of organic material on the membrane decreased the membrane capacity by up to 73%, but the process water flux reached a stable value in all experiments. The flux decline was less important for the biologically treated water. The effect of flux decline was only partly reversible; the effect of osmotic pressure on the process water flux is fully reversible. It was found that flux decline is largely concentration dependent: higher concentrations of organic compounds always caused lower process water fluxes.

The main environmental problem of textile industries is the high water consumption for their processes. Thus, it is very important to reuse wastewater, especially in areas with a water scarcity, such as Comunidad Valenciana in Spain. The goal of Bes-Piá et al. [93] is wastewater reuse combining chemical neutralization, physicochemical treatment and membranes. Neutralization studies were conducted in order to select the most appropriate neutralizing agent in terms of conductivity of the neutralized wastewater. For the physicochemical treatment, four coagulants from the Cibaâ Company (Mangasol 5389, Mangasol 6348, Žetag 7103 and Alcyl 955) were compared by carrying out jar tests using different concentrations and pH values. The experimental tests were made according to the statistics program Statgraphics. After that, NF experiments on the physico-chemically treated wastewater were performed in a laboratory plant equipped with a pressure vessel containing one spiral-wound membrane element (A = 2.51 m²). The operating conditions were transmembrane pressure of 20 bar, cross-flow velocity of 1.66 m s⁻¹ and a temperature of 25 °C. The membrane tested was
the Desal DK2540 from Osmonics. Physicochemical experiments showed that the Zetag 7130 coagulant achieved higher reductions in COD and turbidity. In addition, the sludge volume was lower than 100 mL L$^{-1}$. NF experiments showed that permeates, COD and conductivity were around 100 mg L$^{-1}$ and 1000 μS cm$^{-1}$ respectively, with a volume concentration factor of 2.5. As a result, the combination of physicochemical treatment and NF provided treated water with good enough quality to be reused in the industry.

Masmoudi et al. report that textile effluents are considered among the most polluted wastewaters all over the world. Among different textile processes, dyeing is the operation that produces the most important amounts of chemical pollution. Many studies have been carried out toward the treatment of these hazardous effluents, and a variety of techniques have been applied for this aim. Masmoudi et al. treated the effluents coming from different steps of the dyeing cycle following different mixtures of baths using membrane technology. NF experiments were performed for colour removal, but membrane fouling was still a major limitation. To enhance NF performances, microfiltration was carried out as pretreatment to NF. The results showed around 99% of colour and turbidity removal and also an important decrease in COD, chloride and salts contents with an improvement in the microfiltration and NF stabilized fluxes of different mixtures compared with that corresponding to the dyeing effluent treated separately. In order to accomplish a full reuse cycle, dyeing experiments were performed using the combined system (microfiltration–NF) permeates. The results were evaluated regarding total colour difference between samples and a standard test done with fresh water [94].

10.5.5 Nanofiltration in Organic Solvents

Othman et al. [95] investigated the potential of incorporating polymeric solvent-resistant NF membranes for biodiesel separation processes. Eight types of commercial polymeric NF membranes (Solsep 030705, Solsep 030306F, Starmem 240, Starmem 120, Desal-DL, Desal-DK MPF-34 and MPF-44) were chosen and screened for their abilities to separate the methyl-esters-rich effluent (biodiesel) from the mixture of the homogeneous catalyst, free glycerine and excess methanol after the transesterification process at various separation pressures and constant temperature. Scanning electron microscope and FTIR spectroscopy were used to examine any changes to all the membranes studied. In order to enhance the solvent-resistant NF membrane performance, the transesterification product properties were modified by reducing the alkalinity value. Results showed that for three membranes (Solsep 030705, Solsep 030306F, Starmem 240), the permeability of transesterification product after the alkalinity modification increased linearly with the operation pressures. The other five membranes (Starmem 120, Desal-DL, Desal-DK, MPF-44, MPF-34) gave dismal results. Out of the eight tested membranes, it was found that Solsep 030705 membrane gave the most promising result. Analysis of the used membranes showed minor differences in functional groups after the application.

References


11

Ultrafiltration

11.1 Principle of Ultrafiltration

Principles of ultrafiltration (UF) are shown in Figure 11.1. Low molecular weight solutes such as inorganic salts and organic low molecular weight compounds can be permeated with solvent through a UF membrane, but high molecular weight solutes, such as protein and polysaccharides, cannot pass through the membrane. With UF, since separable materials by UF are polymer solutes, an osmotic pressure is created which is much less powerful than that create in reverse osmosis. Consequently, in general, the operating pressure is up to 300 kPa.

11.2 Fundamental Analysis of Ultrafiltration

11.2.1 Phenomenological Treatment of Membrane Permeation

Since the permeation phenomenon in UF is a nonequilibrium one, its fundamental principle is explained by the thermodynamics of nonequilibrium.

Phenomenological equations are generally represented as follows:

\[
J_i = L_{ii}X_i + L_{ij}X_j \tag{11.1}
\]

\[
J_j = L_{ji}X_j + L_{jj}X_i \tag{11.2}
\]

where \( J_i \) and \( J_j \) are fluxes of \( i \) and \( j \) component respectively. \( X_i \) and \( X_j \) are conjugate powers for \( J_i \) and \( J_j \) respectively. \( L_{ii}, L_{jj}, L_{ij}, L_{ji} \) are phenomenological coefficients. The powers \( X_i \) and \( X_j \) correspond to the slopes of physicochemical potential \( \mu_i \) and \( \mu_j \) in nonequilibrium thermodynamics respectively:

\[
X_i = -\text{grad} \; \bar{\mu}_i \tag{11.3}
\]

\[
X_j = -\text{grad} \; \bar{\mu}_j \tag{11.4}
\]

Reciprocal relations of Onsager between phenomenological coefficients are established:

\[
L_{ij} = L_{ji} \tag{11.5}
\]
Kedem and Katchalsy [1] derived the following equations for the membrane permeation phenomenon of those relationships:

\[ L_v = L_{PD} \Delta p + L_{PD} \Delta \pi \] (11.6)

\[ J_D = L_{DP} \Delta p + L_{DP} \Delta \pi \] (11.7)

where \( J_v \) is the volume flux of solution, \( J_D \) is diffusion flux of solute, \( \Delta p \) and \( \Delta \pi \) are the pressure difference and osmotic pressure difference respectively.

The reflection coefficient, \( \sigma \) is the coefficient \( L_{PD} \) divided by the filtration coefficient \( L_f \):

\[ \sigma = \frac{L_{DP}}{L_f} = -\frac{L_{PD}}{L_P} \] (11.8)

where \( L_f \) is the volume flux per pressure defined by

\[ L_f = -L_P = -\left( \frac{J_v}{\Delta p} \right)_{\Delta \pi = 0} \] (11.9)

Consequently, Equation 11.6 is given by

\[ J_v = L_P (\Delta p - \sigma \Delta \pi) \] (11.10)

where \( L_P \) is the permeation coefficient of pure water.

The reflection coefficient \( \sigma \) represents the semipermeability of membrane. When \( \sigma = 1 \), the solute is completely rejected by the membrane, and the volume flux \( J_v \) is proportional to \( \Delta p - \Delta \pi \). On the other hand, when \( \sigma = 0 \) the solute is freely permeated through the membrane and the volume flux is not affected by the osmotic pressure and is proportional to \( \Delta p \).

When the solute permeation coefficient \( w \) defined by Equation 11.11 is used, the permeation flux of solute \( J_s \) is given by Equation 11.12:

\[ w = -\left( \frac{J_v}{\Delta \pi} \right)_{J_v = 0} = -\bar{C}_S (L_D + \sigma^2 L_f) \] (11.11)

\[ J_s = (1 - \sigma) \bar{C}_S J_v - w \Delta \pi \] (11.12)

where \( \bar{C}_S \) is the average concentration of solute between both sides of the membrane.

Spiegler and Kedem [2] applied Equations 11.10 and 11.12 to a microsection of the membrane thickness direction and integrated it about the membrane thickness, and consequently derived Equations 11.13 and 11.14:

\[ J_v = L_P (\Delta p - \sigma \Delta \pi) \] (11.13)

\[ R = -\frac{C_p}{C_m} = \frac{(1 - F) \sigma}{1 - \sigma F} \] (11.14)

where

\[ F = \exp \left[ -\frac{J_v (1 - \sigma)}{P} \right] \] (11.15)
and where \( C_p \) and \( C_m \) are the permeate and feed concentration, \( P \) is the solute permeation coefficient on the basis of concentration and \( R \) is the rejection of solute. The transport equations in the membrane permeation of Equations 11.13–11.15 represent the membrane characteristics by three transport coefficients: the pure water permeation coefficient \( L_p \), the reflection coefficient \( \sigma \) and the permeation coefficient of solute \( P \).

11.2.2 Pore Model

The description of membrane properties based on the membrane structure was accomplished by assuming that the UF membrane consists of pores. That is, the pore model as the permeation and separation model which is due to a ‘sieving mechanism’ was proposed [3].

In the pore model, it is assumed that the membrane has cylindrical pores of radius \( r_p \) and length \( \Delta x \), those pores penetrate a membrane, a solute is a ball body of radius \( r_s \) and the flow of solution in the pore is Poiseuille flow.

From this model, the aforementioned three transport coefficients are as follows:

\[
L_p = \frac{r_p^2 A_k}{8 \mu_p \Delta x} \tag{11.16}
\]

\[
\sigma = 1 - S_F \left(1 + \frac{16}{9} q^2\right) \tag{11.17}
\]

\[
P = D S_D \frac{A_k}{\Delta x} \tag{11.18}
\]

where

\[
S_F = 2(1 - q)^2 - (1 - q)^4 \tag{11.19}
\]

\[
S_D = (1 - q)^2 \tag{11.20}
\]

\[
q = - \frac{r_s}{r_p} \tag{11.21}
\]

\( D \) is diffusion coefficient, \( A_k \) is the opening ratio of all pore cross-sections per unit area, namely the opening ratio of the membrane surface. \( \mu_p \) is the viscosity of the permeation solution. When it is assumed that the solute is a spherical body, the radius of solute \( r_s \) can be used as Stokes radius:

\[
r_s = \frac{kT}{6\pi \mu_t D} \tag{11.22}
\]

where \( \mu_t \) is the viscosity of feed solution and \( k \) is Boltzmann constant.

11.2.3 Rejection Rate and Concentration Polarization

The rejection rate of solute \( R_0 \) in the UF is given using concentrations of the feed solution \( C_f \) and permeate \( C_p \) obtained as the experimental values, as shown by the following equation:

\[
R_0 = 1 - \frac{C_p}{C_f} \tag{11.23}
\]
When a solution is treated by the membrane separation technique, the solute concentration on the membrane surface $C_m$ is higher than $C_f$. This phenomenon is called concentration polarization. Therefore, the membrane separates solution of the concentration of $C_m$ to $C_p$. $R_0$ which was defined in Equation 11.23, is the apparent rejection rate; the true rejection rate of the membrane $R$ is defined as

$$ R = 1 - \frac{C_p}{C_m} \tag{11.24} $$

Since the concentration of solute on the membrane surface $C_m$ cannot be measured, a concentration polarization expression such as the following, based on the model shown in Figure 11.2, and $C_m$ is calculated:

$$ \frac{C_m - C_p}{C_f - C_p} = \exp \left( \frac{J_v}{k} \right) \tag{11.25} $$

where $J_v$ is the volume flux of solution and $k$ is the mass transfer coefficient of solute in the concentration polarization layer, which is defined as

$$ k = \frac{D}{\delta} \tag{11.26} $$

The $k$ value is experimentally determined by the flux change method [3] and also from a correlation equation [4,5] of the mass transfer computationally.

### 11.2.4 Concentration Magnification and Rejection Rate

See Hashimoto’s ‘UF method’ [6].

We will think about concentration magnification and rejection rate in the UF of three kinds of the following materials:

- material A, where $R_0 = 0\%$
- material B, where $0 < R_0 < 100\%$
- material C, where $R_0 = 100\%$.

Since A can be freely permeated through the membrane, we have following equation:

$$ C_{FA_i} = C_{FA_f} = \text{constant} \tag{11.27} $$

where $C_{FA_i}$ and $C_{FA_f}$ are the concentrations of material A in the feed solution before and after UF.

The volume of feed solution is decreased from $V_{F_i}$ to $V_{F_f}$, and when the concentration of material C in the feed solution is $C_{FC_i}$ and the concentration in $V_{F_i}$ is $C_{FC_f}$, we obtain the following equation:

$$ C_{FC_i} = \frac{V_{F_i} C_{FC_i}}{V_{F_f}} = X C_{FC_i} \tag{11.28} $$
where $X (= V_F / V_{Fi})$ is the concentration magnification. When a solution contains only material A and material C – for example, a solution consist of protein and salts – then from Equations 11.27 and 11.28 the relationship between the concentration and the volume can be estimated.

In material B the following equations are obtained:

\[
V_P = V_{Fi} - V_{Ff}
\]

\[
C_{FB} V_{Fi} = S_{FBi}
\]

where $V_P$ is the volume of solution, $C_{FBi}$ is the concentration of material B in the feed solution, and $S_{FBi}$ is the existing amount of material B in the feed solution.

When the amount of permeated material B is $S_{PB}$ we get

\[
\frac{dS_{PB}}{dV_P} = \frac{(S_{FBi} - S_{PB})(1 - R_0)}{V_{Fi} - V_P}
\]

Consequently, we obtain

\[
S_{PB} = S_{FBi} \left[ 1 - \left( 1 - \frac{V_P}{V_{Fi}} \right)^{1 - R_0} \right]
\]

By modifying Equation 11.32, the concentration of material B in the concentrate $V_{Fi}$ and solute amount of material B $S_{FBi}$ are obtained:

\[
\frac{C_{FBi}}{C_{FBi}} = X^{R_0}
\]

\[
\frac{S_{FBi}}{S_{FBi}} = \left( \frac{1}{X} \right)^{1 - R_0}
\]

When $R_0$ is a variable, using Equations 11.33 and 11.34, we get the results given in Figures 11.3 and 11.4.

From these figures, since $R_0$ (0%) and $R_0$ (100%) are related to material A and material C respectively, we can evaluate for a particular concentration magnification what the concentration ratio is.

When the ratio of permeated water is the recovery percentage $K$, the relationship between $X$ and $K$ is as follows:

\[
X = \frac{1}{1 - K}
\]

When the concentration of material B in the permeate is $C_{PB}$, Equations 11.33 and 11.34 are given by Equations 11.36 and 11.37 respectively:

\[
\frac{C_{PB}}{C_{FBi}} = \frac{X}{X - 1} \left( 1 - X^{R_0 - 1} \right) = \frac{1}{K} \left[ 1 - (1 - K)^{1 - R_0} \right]
\]

\[
\frac{S_{PB}}{S_{FBi}} = 1 - \left( \frac{1}{X} \right)^{1 - R_0} = 1 - (1 - K)^{1 - R_0}
\]

These equations suggest that the amount and concentration of material B in the concentrated solution and in the permeate can be estimated by measurements.
Figure 11.3 Relationship between the concentration of material B and the concentration magnification. Source: [6]. Reproduced with permission of Kodansha Scientific.

Figure 11.4 Relationship between the solute concentration of material B and the concentration magnification. Source: [6]. Reproduced with permission of Kodansha Scientific.
11.2.5 Molecular Weight Cut-off

The permeation and separation characteristics of solutions containing solutes of various molecular weights through UF are measured and the relation between the rejection and the molecular weight is determined. In general, figures with the profiles of A and B membranes as shown in Figure 11.5 are obtained. Membranes A and B have the same rejections (50%) for a molecular weight of 1000, but the rejections for the solutes of low and high molecular weights are different. This difference is attributed to the fact that the preparation of membranes with the same pore size in the membrane preparation process is difficult; namely, there is a distribution in the pore size. Ideally, the appearance of membranes should be like the C membrane, with a sharp molecular weight cut-off (MWCO). This expectation can be achieved by setting precise membrane preparation conditions (such as the temperature and humidity) in the membrane preparation and improving membrane materials (such as the preparation of polymer membrane materials of narrow molecular weight distribution).

In measurements of MWCO in UF materials, standard materials are selected which are spherical in solution and for which concentration measurement is easy with low concentration. Examples are $\gamma$-globulin (MW 160,000), serum albumin (MW 67,000), cytochrome C (MW 13,000), vitamin B$_{12}$ (MW 1355), raffinose (MW 504), sucrose (MW 342) and sodium chloride (MW 58.5). Also, water-soluble polymers with various molecular weights, such as poly(ethylene glycol) (PEG), poly(vinyl pyrrolidone) and dextrin (DX), are used [7,8].

Ohya and co-workers [9–13] used PEGs and DXs as standard solutes to determine the MWCO properties of the UF, carrying out the evaluation using gel permeation chromatography. Yanagishita et al. [14] estimated the MWCO properties of a UF membrane using single-, three- and five-component PEG mixture systems.

A solution that is used for MWCO measurement should be a dilute solution as much as possible so that it is hard to be influenced by concentration polarization. Also, since the molecular shape in solution is dominant in the separation by UF, careful attention should be paid only molecular weight. It

Using Equations 11.16–11.22 derived in the pore model of UF in Section 11.2.4, the rejection of a membrane for which the pore radius of the membrane $r_p$, all pore cross-sections per unit membrane

---

**Figure 11.5** Relationship between the molecular weight and the rejection of solute in UF.
area $A_k$ and the length of the pore $\Delta x$ are known can be quantitatively estimated regardless of the kind of solute [3]. A quantitative evaluation by $r_p$ and $A_k/\Delta x$ is suggested, whereas the rejection performance of the membrane is evaluated with MWCO.

### 11.2.6 Batch-Style Concentration

The examination of the rejection state is usually carried out by batch-style operation. When the amount of the initial liquid $V_{F_i}$ is concentrated to $V_{F_f}$, the concentration of a molecular group of material C is increased according to Equation 11.28. Namely, it is proportional to concentration magnification. On the other hand, the molecular group of material B permeates some way through the membrane with concentration, and it is concentrated, staying as shown in Equation 11.33. Therefore, the concentration of material B in the permeate changes with the concentration magnification. Therefore, $V_p (= V_{F_i} - V_{F_f})$ is permeated and the mean concentration of material B in the permeate $C_{PB}$ is measured, and apparent rejection $R_a$ is defined as

$$R_a = 1 - \frac{C_{PB}}{C_{FB_0}}$$

Consequently, we obtain

$$R_a = \frac{1}{X-1} \left( X^{R_0} - 1 \right)$$

Because, using this equation, the rejection $R_0$ is found from an apparent rejection at a certain concentration magnification, Equations 11.33 and 11.34 demand that the concentration of material B and solute quantity change if they change concentration magnification. The concentration of material C is constant, as can be seen from Equation 11.21.

In Section 11.2.5 the behaviour of materials A, B and C was investigated. However, in addition, these are mixed practically and the concentrations of the three kinds of materials are not known. In addition, the concentrations of material A, B, and C are not dilute, such as the treatment using solution theory. Since there are interactions between solute molecules, we do not know what their theoretical values are even if we can have those ratios. The approximate amount of each of the three materials can be classified roughly by UF by dividing the complicated solution system into two systems that are easier to check.

In the initial solution, when A, B and C have concentrations $C_{FA_0}$, $C_{FB_0}$ and $C_{FC_0}$ the total concentration is $C_{F_i}$ and this doubles $X$; in the concentrate the concentrations of B and C materials are $C_{FB}$ and $C_{FC}$ and the total concentration is $C_{F}$; and in the permeate the concentrations of B and C materials are $C_{PB}$ and $C_{PC}$ and the total concentration is $C_{P}$. This leads to the following equations:

$$\begin{align*}
C_{FA_0} + C_{FB_0} + C_{FC_0} &= C_{F_0} \\
C_{FA} + C_{FB} + C_{FC} &= XC_{FA_0} + (X)^{R_0} + C_{FC_0} = C_{F} \\
C_{PB} + C_{PC} + C_{FC_0} &= \frac{X}{X-1} \left[ 1 - X^{-(1-R_0)} \right] C_{FB_0} + C_{FC_0} = C_{P} 
\end{align*}$$

(11.40)

Because the right sides of these three equations are obtained by measurements, the four unknowns $C_{FA_0}, F_{FB_0}, C_{FC_0}$ and $R_0$ can be calculated when the measurement values of two kinds of $X$ are obtained. When selectivity by the gel layer is constant, this analytical method is effective, and helps the consideration with an analysis value and the analysis value of real data.
In the consideration of the case of decreasing the volume of feed solution from $V_{F_i}$ to $V_{F_f}$, the concentrations of materials A, B and C are shown by Equations 11.27, 11.33 and 11.28 respectively.

11.3 Membranes for Ultrafiltration

There are two kinds of organic membranes used: polymers and inorganic membranes using inorganic materials represented by ceramics.

11.3.1 Organic Membranes

These membranes are used in a wide variety of separation processes. They are made from various materials, including regenerated cellulose, cellulose acetate (CA), cellulose nitrate, polyacrylonitrile, poly(vinylidene fluoride) polyimide, polysulfone, polyethersulfone, and so on. They are used in medical applications, such as in artificial dialysis, and in the food manufacturing process in fruit juice concentration and in the sanitization of mineral water. Because they are lighter than inorganic membranes, they are easy to handle, are generally cheap and it is easy to prepare various module membranes, but their usable temperature range is small and their chemical resistance is weak.

11.3.2 Inorganic Membrane

Inorganic membrane has a pore size distribution that is sharper than an organic thin membrane, and can be used at elevated temperature and pressure, and the durability to medicinal solution washing is high. After mixing it with binders, and having moulded ceramic particles such as alumina, mullite and titania, it is easy to form a porous structure with high ratio surface area by hardening it at a high temperature. A tubular shape with coarse particles is formed, and asymmetric ceramic separation membranes can be prepared by coating several layers with fine particles on this tubular support. Inorganic membranes are relatively expensive and not high in strength.

11.4 Ultrafiltration Modes

UF processes can be operated in various different modes depending on the requirements of the process. The more commonly used modes are (1) batch concentration, (2) multistage continuous concentration, (3) batch diafiltration, (4) continuous diafiltration and (5) feed and bleed type operation.

11.4.1 Batch Concentration

A concentration process refers to the selective removal of a solvent from a solution (e.g. removal of water from a protein solution). This can be achieved by using a membrane which totally retains the solute while allowing unhindered passage of solvent. A set-up used for batch concentration is shown in Figure 11.6. A batch concentration process is...
usually operated at constant transmembrane pressure (TMP). Owing to the continuous increase of solute concentration in the feed, the permeate flux declines with time. Batch concentration is considered to be an efficient way of processing material since the membrane has the lowest possible exposure to the feed.

11.4.2 Multistage Continuous Concentration

Concentration can also be carried out in a continuous manner, but a single membrane module gives a very low concentration factor. The concentration factor is defined as the solute concentration in the product divided by that in the feed. A multistage process is preferred for a continuous operation, as shown in Figure 11.7.

11.4.3 Batch Diafiltration

Diafiltration is used for separating two solutes from one another (e.g. separation of a salt from a protein, or indeed separation of one protein from another). The membrane used should allow easy passage of the solute desired in the permeate while substantially retaining the other solute. A set-up used for batch diafiltration is shown in Figure 11.8.

11.4.4 Continuous Diafiltration

The solvent lost with the permeate is replenished using fresh solvent (also called diafiltration buffer). Diafiltration can also be carried out in a continuous fashion using the set-up shown in Figure 11.9.
The feed and bleed type operation is used for both concentration and diafiltration. It involves the intermittent bleeding of the retentate stream, as shown in Figure 11.10. Such an operation can give very high productivity and selectivity under highly optimized conditions.

11.5 Concentration Polarization and Fouling in Ultrafiltration

11.5.1 Concentration Polarization in Ultrafiltration

Concentration polarization has been defined to be an accumulation of solute species at the upstream surface of the membrane [15] and is considered to be a hydrodynamic/diffusion phenomenon [16]
This can be alleviated by operating the system at a higher velocity (if the system can tolerate it) [17]. Concentration polarization appears to be present to some degree in any membrane processing because of the fundamental limitations of mass transfer and the existence of a boundary layer.

The permeation rate of water $J_w$ through the membrane is represented by

$$J_w = \bar{C}_w D_w \frac{\bar{V}_w}{R T} \frac{\Delta P - \Delta \pi}{t_m}$$

where $\bar{C}_w$ is the mean water content of the membrane, $\bar{D}_w$ is mean diffusion coefficient of water in the membrane, $\bar{V}_w$ is the partial molar volume of free water in the membrane, $\Delta P$ is the pressure difference between both sides of membrane, $\Delta \pi$ is the difference of osmotic pressure between both sides of the membrane, $R$ is the gas constant, $T$ is the absolute temperature in the operation, and $t_m$ is the membrane thickness.

When the solute which is rejected by the membrane exists in the feed solution, the concentration polarization layer of this solute is made on the membrane surface. Consequently, the permeation rate of water is limited. As shown in Figure 11.11, in the steady state, because the quantity of solute entering into the concentration polarization layer is equal to the quantity of solute going away from the polarization layer by diffusion, the following equation results:

$$JC_S = D_S \frac{dC_S}{dx}$$

When boundary conditions: $C_S = C_w$ at $x = 0$ and $C_S = C_F$ at $x = \delta_i$ are applied to Equation 11.42 and integrated, we obtain

$$J_S = \frac{D}{\delta_i} \ln \frac{C_w}{C_F} = k_S \ln \frac{C_w}{C_F} \quad \text{or} \quad k_S \ln \frac{C_w - C_p}{C_F - C_p}$$

where $\delta_i$ is the thickness of concentration polarization layer and $k_S$ is the mass transfer coefficient.

From Equation 11.43 it is found that $J$ is proportional to $k_S$, inversely proportional to $\delta_i$, and decreased with increasing in $\ln C_F$. When experimental data of the permeation rate is arranged, we can understand the fact that the relation of $J \sim \ln(C_F - C_p)$ is used is due to this equation.

![Figure 11.11 Permeation model of UF membrane: (a) with concentration polarization; (b) with gel layer. Source: [6]. Reproduced with permission of Kodansha Scientific.](image-url)
Lee et al. [18] investigated concentration polarization in UF of soluble oil, and the characteristics of the gel obtained at the end of the experiments were analysed. It was found that the oil content of the gel was approximately 40 vol.% and was almost independent of pressure. The gel was a concentrated oil–water emulsion. Membrane fouling was also analysed in terms of critical surface tension, wettability of the membrane and capillary pressure. Fouling was mainly due to adsorption of oil on the membrane structure, which modified the critical surface tension and the wettability, as well as the effective pore diameter, resulting in reduced membrane permeability. The regeneration of fouled membrane was examined with micellar solutions of the system sodium dodecyl sulfate–n-pentanol, which was found to be very efficient and useful with respect to both economics and performance.

The retention characteristics of UF membranes are delineated through comparison of the combined viscous flow and frictional model with the Ferry–Faxen equation. The MWCO concept is discussed by Jonsson using calculations of how sharp cut-off curves one can expect of UF membranes with uniform pore sizes and how heteroporosity will affect such curves. Experimental retention–flux curves for different macromolecules were measured. From these data the MWCO curves at varying pressure levels can be determined and by comparing with the model an average pore radius can be calculated. Permeate flux is often more or less pressure independent, which has been explained by a gel layer formation at the membrane surface. However, it has been shown that for many types of macromolecules it is rather an osmotic pressure of the concentrated boundary layer that is responsible for the special flux–pressure relationship [19].

Flux reductions experienced during UF are due either to concentration polarization or fouling. It is usually difficult to distinguish between these two phenomena, but by using a turbulence-promoting module it is possible to determine the reversibility of a flux reduction, and thus distinguish between concentration polarization and fouling. By using a turbulence-promoting module, it is also possible to distinguish between different cases of fouling. In the paper by Jönsson, fouling caused by the deposition of material at the surface of the membrane is illustrated by results from tests with a silica sol, and fouling due to interactions in the membrane matrix is illustrated by results from UF of a low-molecular organic solute [20].

Adsorption has been found to be significant in UF by mixed matrix membrane. Removal of very low molecular weight solutes compared with the MWCO of the membrane is facilitated by adsorption. Modelling of the adsorption coupled with concentration polarization is presented based on the mathematical approach developed by Gekas et al. [21] from first principles. However, extensive modifications were included in theoretical development, including those suggested by Ruiz-Bevia et al. [22]. The developed model captured the rejection dynamics with the help of retention factor. The model equations were solved under the framework of boundary layer analysis, using the integral approach. Effects of the adsorption isotherm and the different parameters affecting the system performance were also investigated. Further, experimental validation of the model results with two different mixed matrix UF studies was also elucidated [23].

Nowadays, there are attempts to develop new membrane separation cells to minimize the concentration polarization phenomenon. An efficient contact between the fluid and the membrane is fundamental to reach this objective. In the study Miranda and Campos, the hydrodynamic characteristics of a liquid jet impinging perpendicularly to a flat and round-shaped membrane are explored. The jet flow is confined by a conical wall extended from the jet nozzle to a short distance above the membrane. The momentum and mass transport equations in the laminar regime are solved numerically by a finite-difference scheme. The solution depends on Reynolds (Re) and Schmidt (Sc) numbers and on two new dimensionless groups, $\Pi_v$ and $\Pi_{\pi 0}$. $\Pi_v$ represents the ratio between the permeate velocity through a non-polarized membrane surface and the average jet velocity at the cell inlet, and $\Pi_{\pi 0}$ is the ratio between the osmotic pressure over a non-polarized membrane surface and the static pressure.
difference across the membrane. The concentration polarization is investigated in wide ranges of values of these groups, and new indexes are defined to quantify the polarization level. For increasing values of \( \text{Re} \), \( \text{Sc} \) and \( \Pi_v \), the polarization level and the concentration at the membrane surface increase. For increasing values of \( \Pi_{\pi0} \) the polarization level increases, but the concentration at the membrane surface tends to the bulk concentration. The suction effects on the velocity profiles in the layer over the membrane are also analysed. A compact module of jet cells is proposed [24].

11.5.2 Fouling in Ultrafiltration

Fouling involves the adsorption or trapping of particles (foulants) that are present in the fluid being transported across the membrane and can be a physical and/or chemical phenomenon. Some typical foulants are proteins, lipids, bacteria and so on. The basic mechanisms of fouling have been studied by a number of researchers [25–27]. The general consensus appears to be that fouling may be due to one or more of the following mechanisms. (1) Formation of a dynamic membrane (surface layer or filter cake) on the front face of the membrane. In UF, fouling occurs predominantly on the membrane surface where the dynamic membrane controls membrane behaviour. (2) Fouling within the membrane structure. There is evidence [28,29] that protein deposits within the membrane pores as well as on the surface. In UF, the amount of protein deposited within the membrane pores is small compared with that on the membrane surface. However, in microfiltration (MF) there is greater deposition within the pores, and internal fouling appears to dominate within large pores. (3) Fouling at the pore entrance. A number of authors [30–32] have considered that the deposition of materials on the surface of the membrane must have in some way obstructed the pore entrances. The loss of effective membrane surface porosity is dependent upon the size of the depositing molecules and the pore size.

A clear distinction must be made between concentration polarization and membrane fouling. Concentration polarization leads to gel formation when the concentration at the membrane surface reaches the solubility limits of the macrosolute. The main difference between gel formation and membrane fouling is that the gel layer is formed on the membrane surface, whereas the fouling layer is formed by solute–membrane interactions and is more closely bound to the membrane surface. Fouling is an irreversible adsorption of macromolecules, whereas gel formation is reversible because of the low interactive forces between the macromolecules in the gel [33].

Deposits formed on the membrane during UF of aqueous solutions of individual whey proteins were examined under a scanning electron microscope. \( \gamma \)-Globulin formed granules which agglomerated and stacked into layers to form a porous matrix on the membrane. \( \beta \)-Lactoglobulin and bovine serum albumin both formed sheets on the membrane and formed multimers which were identified by sodium dodecyl sulfate gel electrophoresis. \( \beta \)-Lactoglobulin also formed strands where deposits were not thick. \( \alpha \)-Lactalbumin formed smooth spherical particles which did not hinder water permeation greatly. Studies of UF rate indicated that \( \beta \)-lactoglobulin and \( \gamma \)-globulin were most significant in causing permeation flux decline by surface fouling [34].

UF of high-purity-grade bovine serum albumin was carried out by Meireles et al. under various temperature between 5 and 30 °C and at various cross-flow velocities, pressures, and concentrations with the aim of studying protein denaturation and its consequences on the process [35]. Three different pump heads were tested. Denaturation of proteins in solution was monitored by laser light scattering and size exclusion chromatography. The rate of protein denaturation increases with temperature, cross-flow and time. It was observed that membrane fouling was different depending on whether denaturation had occurred or not. Under high-concentration polarization, denaturation can occur in the boundary layer if the wall concentration exceeds 400 g L\(^{-1}\). It is shown how the residence time,
operating temperature and pressure play an important part in membrane fouling. This can provide guidelines for process design and control.

Yamagiwa *et al.* [36] first investigated the effectiveness of surfactant precoat treatment of a polysulfone ultrafilter for reduction of membrane fouling in UF of antifoam. Fifteen different surfactants, including alcohols and synthetic nonionic surfactants, were tested. In general, pretreatment with non-ionic surfactant gave a larger flux than that with alcohol did. The flux increase by pretreatment with nonionic surfactant depended on a hydrophile–lipophile balance (HLB) value and type of hydrophobic tail. The most effective surfactant for reducing antifoam fouling among the 15 surfactants was Brij-58, which has an HLB value of 16 and a straight alkyl hydrophobic chain. The UF flux of the membrane treated with Brij-58 was almost three times larger than that of untreated membrane. The precoat treatment with Brij-58 was the most effective for reducing antifoam fouling in terms of rejection properties. Furthermore, flux was also improved by the surfactant pretreatment in UF of model process streams, such as fermentation media, broth and yeast suspension with or without antifoam. The surfactant Brij-58 was found to be more effective for reducing membrane fouling in UF of model stream YG compared with ethanol or Brij-35. The mean flux increase by the pretreatment with Brij-58 was about 80% in UF of the model stream without antifoam. When antifoam was added to the model stream, flux was almost doubled by the pretreatment with Brij-58. The effectiveness of surfactant precoat treatment for reducing membrane fouling was also confirmed in terms of rejection properties.

Membrane filtration (MF and UF) has become an accepted process for drinking water treatment, but membrane fouling remains a significant problem. Howe and Clark [37] systematically investigated the mechanisms and components in natural waters that contribute to fouling. Natural waters from five sources were filtered in a bench-top filtration system. A sequential filtration process was used in most experiments. The first filtration steps removed specific components from the water, and the later filtration steps investigated membrane fouling by the remaining components. Particulate matter (larger than 0.45 μm) was relatively unimportant in fouling compared with dissolved matter. Very small colloids, ranging from about 3 to 20 nm in diameter, appeared to be important membrane foulants based on this experimental protocol. The colloidal foulants included both inorganic and organic matter, but the greatest fraction of material was organic. When the colloidal fraction of material was removed, the remaining dissolved organic matter (DOM), which was smaller than about 3 nm and included about 85–90% of the total DOM, caused very little fouling. Thus, although other studies have identified DOM as a major foulant during filtration of natural waters, the work by Howe and Clark shows that a small fraction of DOM may be responsible for fouling. Adsorption was demonstrated to be an important mechanism for fouling by colloids.

The fouling of UF membranes by natural organic matter (NOM), isolated from a potable surface water source, was studied with an emphasis on elucidating fouling modes and the role of aggregates. NOM size was related to membrane pore sizes using parallel membrane fractionation and size exclusion chromatography, such analyses confirmed the predominance of low MW species and identified the presence of aggregates in concentrated NOM solutions. Cake formation was the dominant mode of fouling by the unfiltered feed, which contained aggregates. This was identified by a constant rate of increase in membrane resistance with permeate throughput and was independent of pore size over a 10–1000 kDa MWCO range. Prefiltration (to remove aggregates) and dilution (to reduce aggregate concentration) reduced the rate of increase in membrane resistance for the low MWCO membranes but did not change the fouling mode. In contrast, such pretreatment prevented cake formation on the larger MWCO membranes and shifted the mode of fouling to pore blockage. The data lend support for the idea that an initial fouling layer of large aggregates can catalyse the fouling by lower molecular weight species. The fouling layer could be removed from the large MWCO membranes by backwashing, but the lower MWCO membranes exhibited some irreversible fouling, suggesting that low
molecular weight species penetrated into the pore structure. A combined pore blockage–cake formation model described the data well and provided insight into how fouling modes evolve during filtration [38].

UF of whey is a major membrane-based process in the dairy industry. However, commercialization of this application has been limited by membrane fouling, which has a detrimental influence on the permeation rate. There are a number of different chemical and physical cleaning methods currently used for cleaning a fouled membrane. It has been suggested that the cleaning frequency and the severity of such cleaning procedures control the membrane lifetime. The development of an optimal cleaning strategy should therefore have a direct implication on the process economics. In this regard, the use of ultrasound has attracted considerable interest as an alternative approach to the conventional methods. Muthukumaran et al. studied the ultrasonic cleaning of polysulfone UF membranes fouled with dairy whey solutions. The effects of a number of cleaning process parameters were examined in the presence of ultrasound and results compared with the conventional operation. Experiments were conducted using a small, single sheet-membrane unit that was immersed totally within an ultrasonic bath. Results show that ultrasonic cleaning improves the cleaning efficiency under all experimental conditions. The ultrasonic effect is more significant in the absence of surfactant, but is less influenced by temperature and TMP. Their results suggest that the ultrasonic energy acts primarily by increasing the turbulence within the cleaning solution [39].

UF is an emerging technology for drinking water production, but a main challenge remains the lack of understanding about fouling. Jermann et al. [40] investigated the impact of molecular interactions between different NOM compounds on UF fouling mechanisms. They performed dead-end filtration experiments with individual and mixed humic acid and alginate (polysaccharide). Alginate showed detrimental, but mostly reversible, flux decline and high solute retention. Their results indicate that this was caused by pore blocking transformed into cake building and weak molecular foulant–membrane and foulant–foulant interactions. In the presence of calcium, aggravated fouling was observed, related to complexation of alginate and its subsequently induced gel formation. With humic acid, more severe irreversible fouling occurred due to humic acid adsorption. Minor adsorption of alginate onto the membrane was also observed, which probably caused the substantial irreversible flux decline. The fouling characteristics in the mixtures reflected a combination of the individual humic acid and alginate experiments, and they concluded that the individual fouling mechanisms mutually influence each other. A model elucidates this interplay of the individual fouling mechanisms via hydrophobic and electrostatic interactions. In their study, such an interplay resulted in an alginate cake, or gel in the presence of calcium, which is relatively irreversibly adsorbed onto the membrane by humic acid associations. The study showed the importance of mutual influences between various foulants for improved understanding of fouling phenomena. Furthermore, it showed that substances with a minor individual influence might have a large impact in mixed systems, such as natural water.

Exploring reasonable ways to remove foulant is of great importance in order to allow sustainable operation of UF membranes in water/wastewater treatment technology. Compounds of organic and inorganic origin largely contribute to irreversible fouling. The study by Yu et al. attempted to remove the problem of UF membrane fouling by using four different enzymes: alpha-amylase, lipase, cellulase and protease. This investigation showed that none of these enzymes was found to be effective for the removal of foulant when used alone. However, when these enzymes were used in combination with NaOH and citric acid, about 90% cleaning was achieved. The addition of nonionic surfactant to the enzymatic solution appears to increase the efficiency of flux recovery by reducing the adhesion of foulant species to the membrane surface through the decrease of contact angle. Field-emission gun scanning electron microscopy, Fourier transform infrared spectroscopy and atomic force microscopy techniques were employed to qualitatively illustrate the foulant characteristics. The surface roughness
through atomic force microscopy was used to explain the potential mechanism for the enzymatic cleaning [41].

Yu et al. compared pre-coagulation enhanced by KMnO₄ before UF (KCUF) with normal pre-coagulation by alum (CUF) in the UF of water from the Songhua River, China. The TMP with KCUF was much lower than that when alum alone was used. With KCUF, a slower increment of TMP occurred, even under conditions of high river water turbidity. The results also showed that the removal of chemical oxygen demand (COD), U₂₅₄ and total organic carbon were appreciably higher after adding 0.5 mg L⁻¹ KMnO₄ compared with CUF. Although assimilable organic carbon (AOC) was increased by permanganate treatment, the AOC of the permeate from KCUF was nearly the same as that from CUF, showing that the cake layer on the surface of KCUF membrane could adsorb small molecules more effectively than that of CUF. This result was confirmed by the apparent molecular weight distribution measured by size exclusion chromatography. It was shown that flocs formed by KMnO₄ and alum were larger than those formed only by alum, causing higher removal of flocs and higher permeation flux. Lower NOM was found in the permeate from the KCUF systems because oxidation and adsorption of organic matter on the flocs occurred. The membrane was partly clogged by organic matter or other materials, including some small flocs [42].

Fine iron oxide particles (IOPs) are effective in removing NOM that causes membrane fouling in water treatment, but the separation of used IOPs is problematic. Cui and Choo [43] studied the fabrication and use of granular iron oxide adsorbents, in combination with UF (UF) membranes while investigating the NOM removal efficiency and fouling control. Sulfonated styrene–divinylbenzene copolymer beads were coated with two types of iron oxides (ferrihydrite and magnetite) and their performances were compared with that of fine IOPs. A significant amount of iron oxide coating (52–63 mg of iron per gram of bead) was achieved by means of electrostatic binding and hydrolysis of iron ions. Iron-oxide-coated polymer (IOCP) beads were able to remove some amounts (~20%) of dissolved organic carbon comparable to that achieved by IOPs within a short period of time (<15 min). Regenerated IOCPs exhibited the same sorption capacity as the fresh ones. The integrated IOCP–UF system operation with a 15 min empty bed contact time and 10 h cyclic regeneration maintained the 20% dissolved organic carbon removal with no sign of significant membrane fouling. In contrast, a sharp TMP build-up occurred in the UF system when no iron oxide pretreatment was applied, regardless of the types of membranes tested. Iron oxide adsorbed the NOM fraction with molecular weights of >1000 kDa, which is believed to be responsible for severe UF fouling.

Polymeric mesocomposite membranes were prepared via wet-phase inversion processes by incorporating surfactant-templated mesoporous silica particles, denoted MSP-1, into polysulfone matrices formed with and without PEG as a molecular porogen. Transmission electron microscopy and N₂ adsorption–desorption measurements showed higher surface area (354 m² g⁻¹), smaller average pore size (53 nm) and larger pore volume (2.92 cm³ g⁻¹) with a narrower pore size distribution (26 nm width at half-maximum) for surfactant-templated mesoporous silica particles compared with those of precipitated commercially available mesoporous silica, HiSil. The distinct morphological changes induced by PEG and by MSP-1 were redundant from the membrane performance point of view as they translated into similar performance gains that were not additive, pointing to the potential use of mesoporous additive as an alternative porogen. The higher hydrophilicity and unique structural features of MSP-1 resulted in enhanced performance of the prepared membranes compared with MSP-free controls and HiSil-based mesocomposites. Mechanical properties of mesocomposites and neat polysulfone membranes were comparable. Electron microscopy coupled with flux and rejection measurements were used to investigate the influence of polymer content, MSP loading, and the presence of porogen on the structure and separation properties of mesocomposite membranes. Mesocomposite membranes showed increased water flux and dextran rejection. For UF membranes, the figure of
merit, operationally defined as the product of water flux and rejection of 12 kDa dextran, increased by a factor of 2.8 (for membranes cast with a porogen) and 6.3 (in the absence of porogen) upon incorporation of the mesoporous additive at a loading of 10 wt%. Enhancement factors were 3.7 and 11.2 for less permeable membranes cast from mixtures with higher (20 wt%) polymer content. Fouling tests with humic acid solutions demonstrated that mesocomposite membranes experienced lower flux decline and showed higher rejections [44].

11.6 Ultrafiltration Technology

As indicated in ‘About Ultrafiltration: A Versatile and Economical Solution’ at http://www.kochmembrane.com/Learning-Center/Technologies/What-is-Ultrafiltration.aspx, UF is a pressure-driven process that removes emulsified oils, metal hydroxides, colloids, emulsions, dispersed material, suspended solids and other large molecular weight materials from water and other solutions. UF membranes are characterized by their MWCO as shown in Figure 11.12.

UF excels at the clarification of solutions containing suspended solids, bacteria and high concentrations of macromolecules, including oil and water, fruit juice, milk and whey, electrocoat paints, pharmaceuticals, poly(vinyl alcohol) and indigo, potable water and tertiary wastewater.

11.6.1 Modules of Ultrafiltration

Depending on the shape and material of the membrane, different modules can be used for the UF process [45]. Commercially available designs in UF modules vary according to the required hydrodynamic and economic constraints, as well as the mechanical stability of the system under particular operating pressures [46]. The main modules used in industry are plate and frame, spiral-wound, tubular and hollow-fibre module.

11.6.1.1 Plate-and-Frame Module

This module uses a membrane placed on a flat plate separated by a mesh-like material. The feed is passed through the system from which permeate is separated and collected from the edge of the plate. Channel length can range from 10 to 60 cm and channel heights from 0.5 to 1 mm [47]. This module

![Figure 11.12](Image) Relationship between UF membrane and separation species.
provides low volume hold-up, relatively easy replacement of the membrane and the ability to feed viscous solutions because of the low channel height, unique to this particular design [46].

11.6.1.2 Spiral-Wound Module
This module is composed of a combination of flat membrane sheets separated by a thin meshed spacer material which serves as a porous plastic screen support. These sheets are rolled around a central perforated tube and fitted into a tubular steel pressure vessel casing. The feed solution passes over the membrane surface and the permeate spirals into the central collection tube. Spiral-wound modules are a compact and cheap alternative in UF design, offer a high volumetric throughput and can also be easily cleaned [46]. However, they are limited by the thin channels, where feed solutions with suspended solids can result in partial blockage of the membrane pores [47].

11.6.1.3 Tubular Module
The tubular module design uses polymeric membranes cast on the inside of plastic or porous paper components with diameters typically in the range of 5–25 mm with lengths from 0.6 to 6.4 m [48]. Multiple tubes are housed in a PVC or steel shell. The feed of the module is passed through the tubes, accommodating radial transfer of permeate to the shell side. This design allows for easy cleaning; however, the main drawbacks are its low permeability, high volume hold-up within the membrane and low packing density [46,48].

11.6.1.4 Hollow-Fibre Module
This module is conceptually similar to the tubular module with a shell and tube arrangement. A single module can consist of 50 to thousands of hollow fibres and therefore is self-supporting, unlike the tubular design. The diameter of each fibre ranges from 0.2 to 3 mm, with the feed flowing in the tube and the product permeate collected radially on the outside. The advantage of having self-supporting membranes is the ease with which they can be cleaned owing to their ability to be backflushed. However, replacement costs are high, as one faulty fibre will require the whole bundle to be replaced. Considering the tubes are of small diameter, using this design also makes the system prone to blockage [47].

11.7 Ultrafiltration Applications

11.7.1 Drinking Water
UF of river water for drinking water production was performed with hollow fibre membranes in a crossflow filtration system with frequent membrane backwashing by Nakatsuka et al. [49]. The effects of membrane material, operating conditions and raw water quality on UF behaviour were investigated. The permeate flux for the hydrophilic CA membranes was much higher than that of the hydrophobic polyethersulfone membrane, a phenomenon which was explained by membrane fouling due to the adsorption of substances in raw water on and in the pores of the membranes. In order to maintain the high and stable flux for the CA membrane, the operating backwashing pressure should be more than twice as high as the filtration pressure. It was also shown that efficient removal of organic compounds from raw water was accomplished by the fouled CA membrane.

UF is a promising process to produce qualified drinking water. The application of UF for drinking water production has undergone accelerated development during the past decade. Membrane fouling
may be the main obstacle for wider implementation of UF, which usually causes higher costs of energy, operation and maintenance. Fouling is formed due to pore blocking, pore stricting and cake formation. Pretreatments (e.g. coagulation, adsorption, and pre-oxidation) can in various degrees alleviate the fouling by pre-reacting with the foulants in the feed water. However, adverse effects from the pretreatment are also claimed. Moreover, modest operation methods (e.g. running modes, rinsing modes, chemical cleaning, and air scouring) can effectively obtain the fouling reduction. In the report by Gao et al., fouling control in UF technology for drinking water production is reviewed in terms of different effective pretreatments and operation methods. Specific mechanisms and future research required are discussed [50].

During cleaning steps, UF membranes are mechanically and chemically stressed. This can result in membrane degradations, failures and shutdowns for membrane replacement, therefore affecting the production rate of the process and its sustainability. These phenomena raise the problem of necessary optimization of the cleaning procedures that have to tackle simultaneously the best cleaning efficiency and the less detrimental procedures for the membranes. Despite the fact that ageing is becoming a major issue between end-users, membrane manufacturers and chemical product suppliers, there is considerably less literature dedicated to membrane ageing than to cleaning. Regula et al. [51] first briefly reviewed articles dedicated to ageing damage involving NaOCl and commercial detergents (especially on polysulfone UF membrane). Then, their study details an innovative way in which the ‘designs of experiments’ are used to provide additional data that help with a thorough understanding of membrane ageing. Thus, contrary to the accelerated ageing approach that is commonly used in membrane-ageing research (concentration per time of contact: $c \times t$ parameter), designs of experiments were used to organize the best ageing experiments in order to achieve a relevant establishment of an ageing pattern. The results show that this scientific approach provides a satisfying and reliable pattern to simulate membrane ageing as a function of the chosen chemical parameters.

11.7.2 Protein Concentration

Devereux et al. examined the scale-up is of hollow-fibre UF for the concentration of isoelectrically precipitated soya protein. Membrane flux performance is described for protein concentrations up to 150 kg m$^{-3}$ using a model based on individual resistances to permeate flux. Parameters involved in the prediction of this resistance include the precipitate particle size and the rejection by the membrane of the remaining soluble protein. Flux prediction for precipitate suspensions of total protein concentrations greater than 150 kg m$^{-3}$ is difficult due to the presence of significant amounts of soluble protein. This gives rise to increased resistance due to the build-up of soluble protein at the membrane surface. However, at these high protein concentrations, greater flux rates (up to three times at a protein concentration of 200 kg m$^{-3}$) are obtained if the major part of the protein is in the precipitated rather than in the soluble form. The major limitation on membrane performance with respect to protein precipitates arises from the rheological properties of concentrated suspensions of protein precipitate. High apparent viscosities and yield stresses of the retentate lead to cessation of flow over the membrane surface and a sharp decline in flux. Improvement of membrane performance for concentration of protein precipitate suspensions may be achieved by careful choice of the geometry of the hollow-fibre membrane cartridge and associated pipework [52].

An electro-UF process was proposed and developed for concentrating protein solution rapidly by applying an electric field and employing a membrane with a higher nominal MWCO (NMWCO) than the molecular weight of protein to be concentrated. In this process, the high NMWCO membrane was used to achieve a high permeate flux, while the adoption of an electric field was used to obtain a high rejection of the target protein by manipulating the electrophoretic effect. Bovine serum albumin was
used as a model protein, and 50 and 100 kDa NMWCO polysulfone membranes were used for bovine serum albumin concentration. The effects of membrane NMWCO, electric field strength, feed concentration on permeate flux and protein rejection were examined. The experimental results showed that the concentration time required for a target protein concentration could be significantly shortened when an electric field was applied and a membrane with higher NMWCO was used. When a 3000 V m$^{-1}$ electric field was applied and the 100 kDa NMWCO polysulfone membrane was used, the concentration time for concentrating 0.5 g L$^{-1}$ bovine serum albumin solution to around 1.0 g L$^{-1}$ decreased by 80% compared with the process with a 50 kDa membrane without electric field, suggesting that this electro-UF concentration process is a viable alternative to conventional UF process and a promising method for concentrating dilute protein solutions [53].

Whey is a liquid by-product of the dairy industry produced during the manufacture of cheeses and casein. As a raw material, it has many applications in food technology due to the functional and nutritional properties of its proteins. Membrane technology, especially UF, has been used in the dairy industry to produce whey-protein concentrates, because this technology allows the selective concentration of the proteins in relation to the other components. In this context, the objective of the work of Baldasso et al. was to concentrate and to purify the whey proteins using UF in association with discontinuous diafiltration. The two strategies were tested by changing the volumetric-concentration factor, the diafiltration water volume and the number of diafiltration steps. The results showed that the UF process is adequate for the production of protein concentrates; in the best experimental strategy, the protein concentrate obtained was greater than 70% by weight (dry basis) [54].

11.7.3 Enzyme Recovery

The patent of Trutnovsky and Paletta describes a method and device for producing low molecular weight products, especially for determining the concentration of low molecular weight biological substances, by means of enzyme reaction, characterized by the fact that, after the reaction is complete, the used enzyme is separated from the low molecular weight substances of the reaction mixture by means of UF, conducted into a circulation system, especially a continuous circulation system, and used again for enzymatic production of low molecular weight substances [55].

An enzymatic process of cellulose hydrolysis based mainly on the use of membrane techniques was studied by Pizzichin et al. The proposed flow sheet assumed that during cellulose hydrolysis the enzyme is continuously separated from glucose and cellobiose and is recycled in the cellulose reaction vessel by membrane UF. The UF of Celluclast enzyme by Novo was performed in a DDS column module assembled with flat polysulfone membranes. Membrane polarization effects were studied in the 0.1–5% w/v enzyme concentration range under varying pressures up to 600 kPa. A partial loss of enzymatic activity was observed as a consequence of the UF and membrane washing operations [56].

Wu et al. [57] designed to improve the traditional scouring procedure using a solution of sodium silicate, sodium carbonate, H$_2$O$_2$, surfactant, and so on as a refining agent for degumming machine-drawn raw silk sheet and raw silk from the cocoon shell of the silkworm *Bombyx mori*. The raw silk sheet was scoured first in strongly alkaline electrolysed water (pH $\geq$ 11.5) consisting mainly of hydroxyl ions by boiling for 30 min and then treated by the traditional scouring procedure (without alkaline compounds), resulting in refined silk floss. The recycled strongly alkaline electrolysed water containing sericin was separated by UF into a retentate with a range of high molecular mass values accounting for 10% (w/w) of the cocoon shell and the filtrate was separated by nanofiltration into a purified H$_2$O filtrate and a retentate containing oligopeptides and free amino acids, which can be used directly as food additives or in biological growth media. The UF retentate was hydrolysed by papain under three different conditions into three groups of sericin peptides with high, middle or low molecular mass.
Sodium dodecyl sulfate–polyacrylamide gel electrophoresis and gel permeation high-performance liquid chromatography showed the molecular mass of these sericin peptides was in the range 0.2–60, 0.2–30 and 0.2–15 kDa. These clean products have a variety of applications, including coating materials for surface modification, cell culture media and food additives. The procedure they described could be applied to the manufacture of silk floss quilts and the process of refining raw silk, which results in three clean products of the silk protein fibroin (i.e. stripped of sericin) and reduces environmental pollution from scouring waste containing sericin.

11.7.4 Wastewater

The wastewaters generated in fishmeal production (average flow rates of 1100 m$^3$ h$^{-1}$ for a plant capacity of 100 tons of fish per hour) contain a high organic load, and therefore they should not be discharged directly into the sea without effective treatment in order to prevent a negative impact on the environment. On the other hand, these effluents contain a large amount of potentially valuable proteins. These proteins can be concentrated by means of UF and recycled into the fishmeal process, improving its quality and the economic benefits from the raw material, whereas the treated water can be discharged into the sea or reused in the plant. Owing to the high concentration of suspended matter in these effluents, MF pretreatment is required. An extensive review of the application of pressure-driven membrane separation processes in the treatment of seafood-processing effluents and recovery of proteins therein is presented by Afonso and Borquez. Two effluents from a fishmeal plant located in Talcahuano, Chile, were characterized and microfiltrated with a Whatman filter No. 1. A mineral tubular membrane, Carbosep M2 (MWCO, 15 kDa, internal diameter, 6 mm; length, 1.2 m) was used in the UF experiments. The operating conditions were optimized in total recirculation mode, and the subsequent concentration experiments were carried out at 4 bar, 4 m s$^{-1}$, ambient temperature and natural pH. The results show that UF reduces the organic load from the fishmeal wastewaters and allows the recovery of valuable raw materials comprising proteins. Moreover, they point out that further investigation should be dedicated to the use of UF membranes of lower MWCO – or even nanofiltration membranes – in order to achieve complete recovery of the proteins contained in these effluents. Although the membrane undergoes severe fouling, it can easily be cleaned through a caustic washing [58].

Akdemir and Ozer [59] give a promising treatment method for olive oil mill wastewater (OMWW). Although the same steps of this method have been used in different studies before, the flow scheme is novel. The membrane filtration of pretreated OMWW was investigated by using two UF membranes in this study. Pretreatment steps were pH adjustment (pH 2) and cartridge filter filtration, and pH adjustment (pH 6) and cartridge filter filtration. Each step of cartridge filter filtration was a batch process and the effluent from the filter was recycled back to the OMWW tank. Pretreated OMWW was sent to the feed vessel of the experimental set-up. Recovery of olive oil in the OMWW was realized by collecting it from the top of the pretreated OMWW. UF membranes used were JW and MW membranes supplied by Osmonics. The effects of the main operating parameters (TMP, feed flow rate, pH and membrane type) on the permeate flux and membrane fouling were examined. The effectiveness of the different membranes and operating conditions was evaluated using retention coefficients calculated from COD and total organic carbon of experimental studies. The highest permeate flux (25.9 L m$^{-2}$ h$^{-1}$) was obtained using the MW membrane under operational conditions of 200 L h$^{-1}$ flow rate and TMP of 4 bar, while the highest removals were obtained at 100 L h$^{-1}$ flow rate and TMP of 1 bar. COD, total organic carbon, suspended solids, and oil and grease concentrations of MW membrane effluent were 6400 mg L$^{-1}$, 2592 mg L$^{-1}$, 320 mg L$^{-1}$ and 270 mg L$^{-1}$ respectively.
Poultry processing plants use relatively high amounts of water, with an average consumption of 26.5 L per bird during primary and secondary processing of live birds to meat. The used water contains proteins, fats, carbohydrates from meat, blood, skin and feathers, resulting in much higher biological oxygen demand and COD. Hence, the processors are required to remove the majority of the soluble and particulate matter in the wastewater prior to discharge from the plant. Treatments for poultry wastewater include screening, diatomaceous earth filtration, ozonation and chlorine dioxide. Food safety and inspection service regulations allow reconditioned water to replace potable water in prescribed ratios. Recycling of poultry wastewater by UF improves the quality of recycled water and provides a solution to water resource limitations. UF is basically a pressure-driven process that separates on the basis of molecular diameter. Membrane bioreactors that integrate biological degradation of waste products with membrane filtration are also quite effective in removing organic and inorganic contaminants as well as biological entities from wastewater. Value-added products like crude proteins could be separated through UF from poultry wastewater, subsequently reducing the COD. Ongoing research in membrane separation techniques involves exploration of new membrane materials and of new module design configurations to address issues of membrane fouling and treatment of waste streams containing high suspended solids or viscous wastes [60].

11.7.5 Recycling of Water

Drinking water is becoming a scarce resource in many areas, and both use of water and wastewater outlet are of major ecological and economical importance in many countries. Consumption and discharge may be considerably minimized by means of water reuse. The food industry has a large consumption of water, but until now very limited reuse has taken place due to legislation constraints and hygienic concerns. The legal space for use of water of qualities other than drinking water has been opened with the current legislation. This will, however, in many cases require careful analyses of individual cases based on a thorough understanding of the hazards involved in order to avoid compromising the safety of the food product and thereby the health of consumers. Implementation of water reuse practices in the food industry presents a great challenge for both companies and public health authorities regarding knowledge, technical expertise and documentation. Casani et al. discuss the regulatory, technological, monitoring, verification and ethical aspects associated with microbiologically safe reuse of water in the food industry and give some examples of the challenges ahead and possible approaches [61].

In daily life a large amount of water is used for the cleaning of bottles from the beverage industry. If the amount of fresh water used can be reduced by membrane technology to at least 50% of the starting values, the total costs can be reduced too. Scharnagl et al. used different types of membranes, ranging from UF down to reverse osmosis. The membrane properties were studied under crossflow conditions with varying flow rates and different TMPs. For quality assessment, the COD, conductivity, hardness degree of water, and nitrate amount of both feed and permeate solutions were measured during the experiments. The most characteristic parameters for the calculation of the energy consumption were permeate flux, energy demand of the pumps and the cleaning procedures and chemicals for membrane recovery. First, the experiments were performed at laboratory scale with a small membrane test cell and different types of washing waters. With these basic results a small pilot plant for continuous operation was built. The feed stream could be controlled from 10 up to 400 L h\(^{-1}\) and the TMP could rise to 70 bar. During this part, energy consumption and the cleaning possibilities of the membrane system were also studied. The water quality of the first part of the experiments could be confirmed, and the energy and performance data were used for designing a pilot plant to be connected directly
into the water stream of the washing process where the system was to be tested under real conditions. Based on the experiments it was calculated that the amount of fresh water can be reduced by at least 55% by connecting a membrane system into the washing machine [62].

The beer brewing process often generates large amounts of wastewater effluent and solid wastes that must be disposed of or treated in the least costly and safest way so as to meet the strict discharge regulations that are set by government entities to protect life (both human and animal) and the environment. It is widely estimated that for every 1 L of beer that is brewed, close to 10 L of water is used; mostly for the brewing, rinsing and cooling processes. Thereafter, this water must be disposed of or safely treated for reuse, which is often costly and problematic for most breweries. As a result, many brewers are today searching for: (1) ways to cut down on this water usage during the beer brewing process, and/or (2) means to cost-effectively and safely treat the brewery wastewater for reuse. Based on the available documented literature, the paper by Simate et al. provides a review assessment of the current status of the brewery wastewater treatment processes, including potential applications for reuse. Key challenges for both brewery wastewater treatment and reuse are also discussed in the paper and include recommendations for future developments [63].

An attempt was made to examine the effect of applied pressure on membrane fouling that might influence the potential use of UF membrane in treating as well as recovering the bioresources, namely protein and carbohydrate from complex feed like palm oil mill effluent. Palm oil mill effluent was first subjected to physical pretreatment processes, consisting of depth and surface filtration in order to remove the total suspended solids. The pretreatment processes enabled the reduction of total suspended solids, turbidity, total dissolved solid and COD by up to 97.3%, 88.2%, 3.1% and 46.9% respectively. Protein (45.3%) and carbohydrate (41.5%) that are retained as insoluble matters together with suspended solids might be used as fertilizer or animal feed by-products. Then, poly-sulfone UF membrane of 20 kDa was used in the UF membrane study. This study indicated that the applied pressure imposed a direct effect on fouling, permeate flux, protein and carbohydrate recovery, as well as wastewater treatment. In total, the permeate flux decreased with filtration time until it reached steady-state values. Beyond a certain applied pressure between 0.6 and 0.8 MPa, the increase in permeate flux with pressure was negligible and insignificant. The highest applied pressure (0.8 MPa) encouraged the formation of fouling up to 85.8% but at the same time enabled the recovery of protein and carbohydrate up to 61.4% and 76.4% respectively. The highest reduction of total suspended solids, turbidity, total dissolved solid and COD also occurred at 0.8 MPa by up to 97.7%, 88.5%, 6.5% and 57.0%. The study revealed that it is possible to have appropriate control of applied pressure in order to favour fouling that would, in turn, lead to better rejection of other solutes present in the feed [64].

11.7.6 Produced Water

A hydrophilic UF membrane was pilot tested by Lee and Frankiewicz for its ability to clean oilfield produced water over a 4 month period at a West Texas location. The UF membrane has a pore size of 0.01 μm and was operated in a crossflow mode to maintain surface cleanliness. The pilot skid included desanding and deoiling hydrocyclones as pretreatment devices. Process variables investigated included the permeate flow to reject flow ratio, membrane cleaning frequency, and the effect of feed water quality on membrane performance. Based on this test, design criteria were determined and operating costs estimated for a full-scale facility. The pilot skid routinely discharged permeate water with total oil and grease <2 mg L⁻¹. The effectiveness of pretreatment was essential to maintaining membrane permeability. During the test, the hydrocyclones’ solid and oil removal
efficiencies averaged 73% and 54% respectively. Emulsified oil droplets were found to be carrying 5–10 μm oil-coated solids into the membrane unit. Based upon this pilot test program, the operating cost for a full-scale membrane unit, to produce 25 000 BPD of permeate water with <2 mg L\(^{-1}\) residual oil, is estimated at 9.7 cents/bbl. Overall water recovery would exceed 98%. The successful implementation of this technology is dependent on the water quality fed to the membrane unit. The preferred specifications for the UF membrane feed water are <50 ppm oil and <15 ppm solids [65].

The reuse of wastewater from the dairy industry was investigated by Sarkar et al. using coagulation, adsorption and membrane separation. The dairy industry was chosen as it requires huge volumes of water. In recent times, development of newer membranes with high flux/rejection characteristics have increased the probability of water reuse and recycling to a greater extent. In this investigation, thorough pretreatment studies were done using different types of coagulants categorized as inorganic, polymeric and organic having biological origins. The coagulant treatment was performed at a variety of pH values using different dosages and it was followed by activated charcoal treatment. The combined effects of these two pretreatment methodologies were evaluated. The colour and the odour were removed completely and permanently after charcoal treatment. The pretreated water was passed through a crossflow reverse osmosis membrane system and the permeate water was found to have very good quality. This was compared with the process water used by the dairy farm and was found that the water can be recycled or reused [66].

11.7.7 Oil and Gas Wastewater Treatment

The gas injection technique was introduced to achieve flux improvement in crossflow UF of oil emulsion. Using nitrogen gas injection, homogeneous liquid-phase oil–water emulsion was changed to a heterogeneous gas–liquid phase. The injected gas causes a positive effect of promoting turbulence, but it also has negative effect of decreasing the effective membrane area due to the partial occupation of membrane pores by bubbles. The efficiency of the gas injection was found to be dependent on bubble fractions in the mixture: at sufficient bubble fractions a higher flux was observed, but at lower bubble fractions the flux rather decreased compared with that without gas injection. An attempt was made to explain the mechanisms for the dual aspects of gas injection. A turbulence dampening effect was also observed when the dependence of mass transfer coefficient on crossflow rate was investigated with gas injection [67].

The oil industry produces large volumes of wastewater, including oil-well produced water brought to the surface during oil drilling and refinery wastewater. These streams are difficult to treat due to large concentrations of oil. UF is very promising for their treatment to remove oil, but has been limited by economic obstacles due to severe membrane fouling. In a study by Asatekin et al., novel UF membranes incorporating the amphiphilic comb copolymer additive polyacrylonitrile-graft-poly(ethylene oxide) (PAN-g-PEO) were found to exhibit complete resistance to irreversible fouling by several classes of organic foulants [68]. This work focused on application of these novel UF membranes to the treatment of oily wastewater feed streams, employing three industrial samples of oil-well produced water and refinery wastewater. UF membranes cast with 20 wt% PAN-g-PEO in polyacrylonitrile achieved removals of dispersed and free oils of over 96% based on COD for produced water samples, comparable to a polyacrylonitrile UF commercial membrane control. For refinery wastewater treatment, the COD removal values were substantially lower, between 42 and 44%, due to higher contents of dissolved organics. Comb copolymer modified membranes showed significantly better fouling resistance than controls, recovering fully their initial fluxes after
a simulated backwash for each of the three wastewater samples tested. The results indicate that UF membranes incorporating PAN-g-PEO can be cleaned completely by physical methods alone, which should extend membrane lifetimes substantially and improve the process economics to treatment of oil-contaminated waters [69].

### 11.7.8 Recovery of Electrodeposition Paint

The patent by Arimori et al. provides a system for recovery of an electrodeposition paint wherein the loss of the electrodeposition paint is not increased even if the number of steps of the multistage recovery and washing process for a film filtration filtrate is reduced. A system for recovery of an electrodeposition paint, which supplies the film filtration filtrate of electrodeposition bath liquid into the final stage washing tank of film filtration filtrate multistage recovery and washing tanks, is characterized in that the filtrate obtained by carrying out the film-filtration of the liquid in the final stage washing tank is supplied into said final stage washing tank, and the concentrated liquid is supplied into an electrodeposition bath and/or a washing tank other than the final stage washing tank [70].

### 11.7.9 Pulp and Paper

The pulp and paper industries have been trying different technologies to reduce fresh water consumption in paper mills. This has led to a fast development of new wastewater treatment technologies for industrial reuse. Lately, water-soluble polymeric ligands have shown to be powerful substances to remove trace metals from industrial wastewater through UF. In the study by Vieira et al., poly(ethyleneimine) and poly(vinyl alcohol) were used as water-soluble polymeric macroligands. The UF experiments were carried out in stirred dead-end cells. The membrane used was formed from poly(vinylidene fluoride). The performance of water-soluble polymeric ligands was evaluated by determining metal removal and COD. In general, the complexation–UF process was efficient for metal removal from wastewater, leading to a better effluent quality when compared with UF without any ligands addition [71].

A process for metals removal from totally chlorine-free wastewater using water-soluble polymeric ligands in combination with UF was investigated by Tavares et al. [72]. The polymeric ligands addition, contact time between the polymeric ligands and the wastewater, and pH were evaluated. The UF experiments were carried out in dead-end stirred cells and the pressure applied was controlled by nitrogen gas. The membranes used were made from poly(vinylidene fluoride) by the phase inversion method. Wastewater from the ‘Klabin’ Pulp and Paper Industry was used. The performance of water-soluble polymeric ligands poly(vinyl alcohol) and poly(ethyleneimine) was evaluated by determining metal, colour, turbidity and COD removal. In general, the complexation–UF process was efficient in the removal of those parameters from wastewater, leading to a better effluent quality when compared with UF without any ligands addition.

Permeate is a part of the stream generated in the UF process. This stream could be utilized due to its composition in low molecular compounds. Serrano et al. [73] used different combinations to study the use of UF permeate as a preliminary step in pulp and paper production. The results showed that the use of UF permeate, obtained from the black liquor of olive tree pruning fractionation, as cooking liquor instead of the preliminary step is an excellent option, with yields of 35.6% and physical properties of paper sheets similar to those obtained by the use of green traditional liquor (0.599 kN g$^{-1}$ burst index and 1.076 mN m$^{-1}$ tear index).
11.7.10 Chemical Solutions

In many developing countries, access to safe drinking water is not available to all the population. As a response to this, the AQUAPOT project\(^1\) developed a water treatment facility based on UF technology able to be used in developing countries and working in Ecuador and Mozambique. Up to now, the major problem detected in the field application of UF in drinking water production from surface water has been membrane fouling and its cleaning. To study the consequences that lack of cleaning and maintenance of the installation can have over the membranes, AQUAPOT has simulated fouling over UF membrane that suffered from an irreversible fouling after long-term filtration of surface water. The experimental study of Arnal et al. included characterization of the foulant layer and chemicals test (under static and dynamic conditions) to remove membrane fouling, with moderate results for chemicals solutions tested. In this study, air bubbles were used as an alternative, cost-effective and environmentally friendly membrane cleaning technique to remove severe fouling. The work describes the experimental procedure performed in the physico-chemical test with chemical solutions bubbled with air, and the main results obtained when comparing the permeability values before and after cleaning the membrane [74].

Water treatment using UF membranes is gaining popularity worldwide, but the problem of membrane fouling needs to be addressed. So Yamamura et al. [75] investigated the characteristics of membrane foulants by conducting two long-term filtration experiments using surface water from the Chitose River. The membrane was made of polyacrylonitrile and had an MWCO of 100 kDa. The experiments were conducted in February 2004 (winter operation, run 1) and October 2005 (summer operation, run 2), when feed water characteristics were considerably different. Despite this, rates of physically irreversible fouling were similar. By measuring pure water permeability before and after chemical cleaning, they found that acidic or chelate solutions were most effective for cleaning the membrane from run 1, whereas an alkaline solution was more effective for that from run 2. Analysis of the chemical solutions that worked effectively to cancel the fouling revealed that acidic cleaning in run 1 extracted iron, carbohydrate and humic acid, while alkaline cleaning in run 2 extracted carbohydrates. These results indicate that the iron, carbohydrates and humic acid caused the physically irreversible fouling in run 1, and carbohydrates were mainly responsible in run 2. Based on the findings obtained in this study, it was suggested that the most important foulants and the most effective chemical cleaning agents may differ substantially between seasons.

11.7.11 Saccharification

Extruded cassava starch was continuously hydrolysed with glucoamylase in a UF reactor. With a residence time of 2.5 h, the optimum enzyme concentration was 1200 Novo AG units 100 g\(^{-1}\) substrate solids. This resulted in low glucose rejections by the Amicon YM-5 membrane and essentially pure glucose in the reactor permeate solids. Starch conversions were 64% at 22 °C and 97% at 55 °C. Productivity of the UF reactor (glucose produced per unit enzyme) was 10–11 times better than a batch reactor over a 24 h operating period [76].

Enzyme hydrolysis of maltodextrine by a fungal α-amylase for the production of maltose syrup was carried out by Grześkowiak-Przywecka and Słomińska with simultaneous use of a stirred tank reactor and a ceramic UF membrane with various MWCOs. The study was carried out with using the hydrolysate obtained from the most chemically purified starch – potato starch. The factors examined were

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\(^1\) "AQUAPOT" is the name of a project that is the brainchild of Valencia Polytechnic Professor José Miguel Arnal; the project’s purpose is to provide safe drinking water for people in emerging countries.
MWCO, enzyme dosage, residence time, TMP, carbohydrate composition and retention factor. The optimal dosage of enzyme was 2.65 FAU g\textsuperscript{-1} DS. The maximal maltose content in the permeate with using a 5 kDa cut-off was 63%. Steady-state of hydrolysis was achieved after 2–3 h reaction [77].

Lubiewski et al. [78] defined the physicochemical parameters of a reaction system that alter the effectiveness of a continuous recycle membrane reactor during potato starch hydrolysis. The enzymatic hydrolysis of starch in a UF reaction system proceeded with a continuous decrease in the permeate flux, accompanied by an increase in dry substance content in both the permeate and retentate fractions. The decrease in the permeate flux was caused by an increase in feed viscosity. If a prehydrolysis process was conducted, it was possible to enzymatically hydrolyse potato starch in solutions with concentrations up to 20%. A quasi-steady state of starch enzymatic hydrolysis was reached in the UF reaction system by alternately supplementing it with starch solution and water.

11.7.12 Wine Production

Attaining biological stability in wine has been a problem for winemakers for centuries. The main methods for preventing microbes from destroying wine have been the addition of chemicals, such as sulfur dioxide and potassium sorbate, and UF. These methods are less than satisfactory. Chemicals can only be used to a certain level before they affect the taste of the wine or cause allergy reactions in the drinker. UF will remove the microbes but it also removes taste and body from the wine. Previous attempts at pasteurization of wine have been marginally successful because of the subsequent spoilage of the wine in less than optimum winery storage and less than total kill of the microbes. Medaglia devised a method to eliminate these problems and have the wine ready to bottle in a pasteurized state, and designed the equipment to do this in the winery. The method consists of two elements which differ from previous attempts in two significant ways. First, enough heat and time to kill all microbes in the wine were used, and then this treated wine was poured into the tank or barrel. In this way both the wine and the container holding the wine were sanitized [79].

11.7.13 Blood Filtration

UF is a medical therapy that removes excess water, salt and metabolic decomposition products (such as urea, creatinine, and vitamin B\textsubscript{12}) from the bodies of patients who have a condition called fluid overload and keeps proteins such as albumin.

For application as artificial kidneys, the UF, hydrolysis and adsorption characteristics of semipermeable cellulose nitrate membranes containing urease, styilestone and activated charcoal, which were prepared by the use of mixed solvents of \textit{n}-propyl alcohol and N,N-dimethyl formamide, were investigated under various conditions by Tamura et al. It was observed that the UF rate, the hydrolysis and the adsorption characteristics using aqueous solutions of urea and disodium phenoltetramophthalein sulfonate (BSP) as a feed solution were significantly influenced by the solvent composition in the casting solution, the evaporation period, the additional amount of activated charcoal and the operating temperature and pressure. When a mixture of albumin, sodium chloride, urea, creatinine, BSP and vitamin B\textsubscript{12} was used as a model for blood, the UF rate was high (2.5 × 10\textsuperscript{-5} g cm\textsuperscript{-2} s\textsuperscript{-1}) and urea, creatinine, BSP and vitamin B\textsubscript{12} were removed, and also albumin was completely rejected [80].

Figure 11.13 shows the effects of the UF period on the UF rate, the hydrolysis of urea, the ion exchange capability, the adsorption and the rejection fraction. As can be seen from the figure, the UF rate decreased. This result can be attributed to the combined factors of the blockage of pores in the membrane, namely the compaction of membrane, and the concentration polarization of albumin molecules. The hydrolysis fraction of urea was always 100% and the ammonium ion was
completely adsorbed throughout this UF period. The hydrolysis fraction of the adsorbed sodium ion eventually approaches a constant value, and the albumin was perfectly rejected. These results can be interpreted as the membrane being able to function as an artificial kidney [81].

Uragami et al. [82] developed antithrombogenic blood filtration membranes, which were prepared with polyanion complex formation immersing quarternized chitosan membranes

\[
q\text{-Chitosan (I)}
\]

\[
\begin{align*}
\text{CH}_3\text{OH} & \\
\text{OH} & \\
{+\text{N(\text{CH}_3)_3}}\text{Cl} & \\
\text{m} & \\
\end{align*}
\]

(I) cross-linked with diethylene glycol diglycidyl ether

\[
\text{H}_2\text{C} \rightleftharpoons \text{CH} \rightleftharpoons \text{O} \left\{ \text{CH}_2 \rightleftharpoons \text{CH}_2 \text{O} \right\}_2 \text{CH} \rightleftharpoons \text{CH}_2
\]

Diethylene glycol diglycidyl ether (II)

**Figure 11.13** Effects of ultrafiltration period on the characteristics of the system membrane: cellulose nitrate/urease/stylite/activated charcoal. Operating conditions: 40 °C, 0.5 kg cm−2, pH 7.2. Feed mixture: sodium chloride 900 mg dl−1, urea 60 mg dl−1, BSP 10 mg dl−1, vitamin B12 10 mg dl−1, albumin 1 g dl−1 adsorption fraction of ammonium ion. ☑️: albumin, ☐: NaCl ☐: urea, ☐: adsorption fraction of NH₄⁺ ion, ☐: BSP, ☐: vitamin B₁₂; ☐: creatimine, ☐: ultrafiltration rate.
As can be seen from Figure 11.14, UF rates of those heparinized chitosan membranes decreased with an increase of the degree of heparinization. Also, those membranes could perfectly permeate solutes of low molecular weight, such as urea, creatinine and vitamin B$_{12}$, which are waste matters, and completely reject protein such as albumin, which is an active component. In addition, no thrombus was macroscopically observed on the heparinized chitosan membranes in vivo. These results suggest that heparinized chitosan membranes combine both high filtration ability and good antithrombogenicity.

**Figure 11.14** Relationship among the degree of heparinization of chitosan membranes, UF characteristics and water contents. ○, △, ■, ✓ and ◆ are the permeation rate for aqueous urea, creatinine, glucose, BSP, vitamin B$_{12}$ and albumin respectively. ■ is the rejection for urea, creatinine, glucose BSP and vitamin B$_{12}$. ■ is the rejection for albumin. ○ is the water content. Operating condition are 37 °C, 1 kg cm$^{-2}$. Source: [82].
References


12

Microfiltration

12.1 Principle of Microfiltration

The principle of microfiltration (MF) is shown in Figure 12.1. Low molecular weight solutes such as inorganic salts, organic low molecular weight compounds and polymer solutes can be permeated with solvent through a MF membrane, but large molecules such as colon bacillus, staphylococcus and AIDS virus cannot pass through the MF membrane. With MF, since separable materials by MF are large molecules, an osmotic pressure is created which is much less powerful than that created in ultrafiltration (UF). Consequently, in general, the operating pressure is less than 200 kPa.

MF usually serves as a pretreatment for other separation processes, such as UF, and a post-treatment for granular media filtration. The typical particle size used for MF ranges from about 0.1 to 10 μm. In terms of approximate molecular weight, these membranes can separate macromolecules generally less than 100 000 g mol$^{-1}$.

Membrane filtration processes can be distinguished by three major characteristics: driving force, retentate stream and permeate streams. The MF process is pressure driven with suspended particles and water as retentate and dissolved solutes plus water as permeate. The use of hydraulic pressure accelerates the separation process by increasing the flux of the liquid stream but does not affect the chemical composition of the species in the retentate and product streams [1].

MF membranes can generally operate in one of two configurations: dead-end and crossflow filtration. Most of us have performed dead-end filtration in the laboratory using a circular piece of filter paper and funnel. In dead-end filtration, the fluid is passed through tangentially with respect to the membrane [2]. Part of the feed stream containing the treated liquid is collected below the filter, while parts of the water are passed through the membrane untreated. Crossflow filtration is understood to be a unit operation rather than a process, as shown in Figure 12.2a. In crossflow filtration shown in Figure 12.2b, all of the process fluid flows and all particles larger than the pore sizes of the membrane are stopped at its surface. All of the feed water is treated at once subject to cake formation [2]. This process is mostly used for batch or semi-continuous filtration of low concentrated solutions [3].

Munir reported hybrid-flow filtration [4]. The hybrid flow process combines the dead-end and the crossflow principle. As in crossflow filtration, tubular membranes with the filtration layer on the inside wall are used. The filtration process has two phases: the production phase and the flushing phase. During the production phase, the tubes are closed on one side and a dead-end filtration is performed. During the flushing phase, the tube is open on both sides and the fraction that did not pass through the membranes is removed in order to clean the membrane surface as in crossflow filtration. This filtration technique is especially suitable for treating water streams containing suspended solids in low concentrations (polishing).
12.2 Fundamental Analysis of Microfiltration

12.2.1 Dead-end Filtration

Cake layer is formed in proportion to the quantity of permeate on the membrane surface in MF operation of dead-end filtration. Change with time of the permeation flux is modelled in an expression of Ruth et al. [5] like general cake filtration.

A model illustration of dead-end filtration is shown in Figure 12.3. When particle concentration in the feed (particle suspension) is expressed in volume of the wet cake provided for quantity of unit filtration liquid $C_b$, the cake thickness $L_c$ is given as

$$L_c = \frac{V C_b}{A} \tag{12.1}$$

where $A$ and $V$ are membrane area and amount of permeate respectively.
According to Darcy’s law, the water flux through the particle layer is proportional to the pressure difference and inversely proportional to the coefficient of viscosity of the water and the thickness of the particle layer:

\[ J_v = \frac{K \Delta P}{\mu L_c + L_m} \tag{12.2} \]

where \( J_v \) is the water permeation flux, \( \Delta P \) is the pressure difference, \( L_c \) is the cake thickness, \( L_m \) is the permeation resistance of the membrane, \( K \) is the permeation resistance of the cake layer and \( \mu \) is the viscosity of water. The \( L_m \) value in Equation 12.2 is converted into corresponding cake thickness. Since the relationship between water permeation flux and amount of permeate is

\[ J_v \frac{dV}{dt} = A \tag{12.3} \]

Equation 12.2 is renewed and the following equation is obtained:

\[ \frac{dV}{dt} = \frac{AK\Delta P}{\mu} \frac{1}{L_c + L_m} \tag{12.4} \]

When the amount of permeate to form a cake thickness equivalent to filter material resistance is \( V_0 \), Equation 12.5 is given and consequently Equation 12.6 is provided:

\[ L_m = \frac{V_0 C_b}{A} \tag{12.5} \]

\[ \frac{dV}{dt} = \frac{A^2 K \Delta P}{C_b \mu} \frac{1}{V + V_0} = \frac{K}{2(V + V_0)} \tag{12.6} \]

When this expression is a differential equation about \( V \) and removes this in an initial condition, we obtain

\[ (V + V_0)^2 = K(t + t_0) \quad (t_0 = V_0^2 / K) \tag{12.7} \]
In other words:

\[ V = \sqrt{Kt + V_0^2 - V_0} \]  

Equation 12.7 is called the filtration equation of Ruth, and \( K \) and \( V_0 \) are filtration constants. When the filtration resistance of cake \( K \) and the \( V_0 \) value that is related to the filtration resistance of the membrane are found, the filtration process is expressed as a model. But this expression can also be applied to constant-pressure filtration, because \( \Delta P \) is included in \( K \).

### 12.2.2 Crossflow Filtration

A model illustration of crossflow filtration is shown in Figure 12.4.

The permeation flux is the same as Equation 12.2. Change of the thickness of the cake layer with time is expressed as Equation 12.9 by considering both sedimentation rate \( J_vC_b \) by volume flow of cake and peel rate \( J^*C_b \) by crossflow:

\[
\frac{dL_c}{dt} = J_vC_b - J^*C_b \tag{12.9}
\]

The following differential equation is obtained when \( J_v \) is removed from Equations 12.2 and 12.9:

\[
\frac{dL_c}{dt} = \left( \frac{K\Delta PC_b}{\mu} \right) \left( \frac{1}{L_c + L_m} \right) - J^*C_b \tag{12.10}
\]

The steady-state value of permeation flux \( J_{vss} \) is given as follows:

\[
J_{vss}C_b = J^*C_b \tag{12.11}
\]

From this differential equation, cake thickness and change of the permeation flux with time in the crossflow filtration can be calculated. In addition, the analysis solution is as follows:

\[
- \frac{L_c}{J^*C_b} - \frac{C_1}{(J^*C_b)^2} \ln \left( \frac{J^*C_bL_c + J^*C_bL_m - C_1}{J^*C_bL_m - C_1} \right) = t \tag{12.12}
\]

where \( C_1 = \frac{K\Delta PC_b}{\mu} \).

![Figure 12.4 Model illustration of crossflow filtration.](image-url)
12.3 Membranes for Microfiltration

12.3.1 Membrane Materials

Organic membranes are made using a diverse range of polymers, including cellulose acetate, polysulfone, polyvinylidene fluoride (PVDF), polyethersulfone (PES) and polyamide. These are most commonly used due to their flexibility and chemical properties [2]. Inorganic membranes are usually composed of sintered metal or porous alumina. They are able to be designed in various shapes, with a range of average pore sizes and permeability [1,6].

12.3.1.1 Polymer Membranes

PES powder was grafted with acrylic acid (AAc) by simultaneous $\gamma$-ray irradiation. The kinetics of the radiation-induced graft polymerization was studied and the grafted PES powder was characterized. Then, MF membranes were prepared from PES-g-PAAc powder with different degrees of grafting under the phase inversion method. The swelling behaviour and the mean pore size of MF membranes were measured, and the filtration property was tested. The results showed that the pore size and the flux of MF membranes increased with the increase in degrees of grafting. And, MF membrane properties were dependent on the pH value [7]. Most current research has focused on using ceramic MF membranes for micellar casein concentrate production, but little research has focused on the use of polymeric spiral-wound (SW) MF membranes. A method for the production of a serum protein (SP)-reduced micellar casein concentrate using SW MF was compared with a ceramic MF membrane. Pasteurized (79°C, 18 s) skim milk (1100 kg) was microfiltered at 50°C (about 3x concentration) using a 0.3 μm PVDF SW membrane, bleed-and-feed, three-stage process, using two diafiltration stages, where the retentate was diluted 1:2 with reverse osmosis water. Skim milk, permeate and retentate were analysed for SP content, and the reduction of SP from skim milk was determined. Theoretically, 68% of the SP content of skim milk can be removed using a single-stage 3x MF. If two subsequent water diafiltration stages are used, an additional 22% and 7% of the SP can be removed respectively, giving a total SP removal of 97%. Removal of SP greater than 95% has been achieved using a 0.1 μm pore size ceramic uniform transmembrane pressure (UTP) MF membrane after a three-stage MF with diafiltration process. One stage of MF plus two stages of diafiltration of 50°C skim milk using a PVDF polymeric SW 0.3 μm membrane yielded a total SP reduction of only 70.3% (stages 1, 2 and 3: 38.6%, 20.8% and 10.9% respectively). The SP removal rate for the polymeric SW MF membrane was lower in all three stages of processing (stages 1, 2 and 3: 0.05 kg m$^{-2}$ h$^{-1}$, 0.04 kg m$^{-2}$ h$^{-1}$ and 0.03 kg m$^{-2}$ h$^{-1}$ respectively) than that of the comparable ceramic UTP MF membrane (stages 1, 2 and 3: 0.30 kg m$^{-2}$ h$^{-1}$, 0.11 kg m$^{-2}$ h$^{-1}$ and 0.06 kg m$^{-2}$ h$^{-1}$ respectively), indicating that SW MF is less efficient at removing SP from 50°C skim milk than the ceramic UTP system. To estimate the number of steps required for the SW system to reach 95% SP removal, the third-stage SP removal rate (27.4% of the starting material SP content) was used to extrapolate that an additional five water diafiltration stages would be necessary, for a total of eight stages, to remove 95% of the SP from skim milk. The eight-plus stages necessary to remove >95% SP for the SW MF membrane would create more permeate and a lengthier process than required with ceramic membranes [8]. Nanofibrous membranes have been paid attention in MF. The solution blowing process is a new nanofibre fabricating method with high productivity. PVDF nanofibrous mat was successfully solution blown using a multiorifices die by Zhuang et al. [9]. The fibres were mostly 60–280 nm in diameter and three-dimensionally curly, which resulted in a loose construction with high porosity of 95.8%. The nanofibrous mat was further hot-pressed to increase its integrity. The structure and MF performance were evaluated. The results showed the crystallinity of the
membranes increased, and the porosity and pore size decreased after hot-pressing treatment. The hot-pressed membranes showed high retention ratio against microparticles and high pure water flux, which will help the solution-blown membrane find application in high-flux MF. Amphiphilic molecules have been widely used in surface modification of polymeric materials. Bile acids are natural biological compounds and possess a special facial amphiphilic structure with an unusual distribution of hydrophobic and hydrophilic regions. Based on the facial amphiphilicity, cholic acid, one of the bile acids, was utilized for the hydrophilic modification of PVDF MF membranes via the hydrophobic interactions between the hydrophobic face of cholic acid and the membrane surfaces. Ethanol, methanol and water were each used as solvent during the cholic acid adsorption procedure. Their polarity affects the cholic acid adsorption amount for similar cholic acid concentration and adsorption time. There are no changes on the membrane surface morphology after cholic acid adsorption. The hydrophilicity of PVDF membranes is greatly enhanced and the water drops permeate into the cholic-acid-modified membranes quickly after modification. All these factors are a benefit to the permeation flux of membrane for water. When the cholic acid concentration is higher than 0.088 M, the water permeation flux is doubled compared with the nascent PVDF membrane and shows a good stability during the filtration procedure. These results reveal the promising potential of facial amphiphilic bile acids for the surface modification of polymeric materials [10].

A functional terpolymer of poly(methyl methacrylate-2-hydroxyethyl methacrylate-acrylic acid) was synthesized via a radical polymerization by Ju et al. [11]. The terpolymer could be directly blended with PVDF to prepare the MF membranes via a phase separation process. The synthesized polymers were characterized by Fourier transform infrared (FTIR) and nuclear magnetic resonance proton spectra. The membrane had the typical asymmetric structure, and the hydrophilic side chains tended to aggregate on the membrane surface. The surface enrichment of amphiphilic copolymer and the morphology of the MF membranes were characterized by FTIR attenuated total reflection spectroscopy and scanning electron microscopy. The contact angle and water uptake were also tested to assess the hydrophilicity and wetting characteristics of the polymer surface. The water filtration properties were measured. It was found that the modified membranes showed excellent pH sensitivity and pH reversibility behaviour. Furthermore, the hydrophilicity of the blended membranes increased, and the membranes showed good protein antifouling property.

12.3.1.2 Inorganic Membranes

An experimental study of the interaction of the enzyme yeast alcohol dehydrogenase with MF membranes was carried out by Bowen and Gan [12]. Most measurements were made with capillary pore inorganic membranes (Anopore) with some comparative measurements being made with polymeric membranes of low protein affinity (Durapore). It was shown that the prolonged exposure of the enzyme to the inorganic membrane under low shear conditions (slow recycle) resulted in a loss of enzyme activity. Under filtration conditions, the membrane permeation rate decreased continuously with time. This decrease could be quantified using the standard blocking filtration law, which describes a decrease in pore volume due to deposition of enzyme on the walls of the pore. No significant loss in activity of permeating enzyme occurred under solution conditions where the enzyme was stable. However, a significant loss of such activity occurred under solution conditions where the enzyme was slightly unstable. The experiments indicate that the likely mechanism for activity loss is a membrane–enzyme interaction resulting from a shear-induced deformation of the enzyme structure. Two conclusions of practical importance are drawn from the work.

Crossflow membrane MF of low-pectin raw apple juice was studied using inorganic membranes (TECH SEP Carbosep®, Lyon, France) having a nominal pore size of 0.2 μm. Permeate flux was measured at different operation conditions (transmembrane pressure between 100 and 500 kPa, feed velocities
between 1 and 6 m s\(^{-1}\), and temperatures of 293, 298 and 323 K). Some concentration experiments were made in order to study the rejection of pectins and polyphenols at different volume concentration ratio values. Final stabilization tests were carried out to analyse the long-term clarified juice behaviour [13]. Crossflow MF experiments were performed with 0.5 \(\mu\)m silica particles using an inorganic membrane of 0.2 \(\mu\)m pore size. Huisman et al. [14] analysed how several physicochemical factors, such as solution pH, salt concentration and valency of the salt, influenced permeate flux and fouling tendencies. The electrostatic properties of silica particles (feed suspension) and \(\alpha\)-alumina particles (active layer of the membrane) were characterized by performing zeta potential measurements. It was found that the permeate flux is dependent on the surface charge of the suspended particles and possibly dependent on the surface charge of the membrane. High permeate fluxes were obtained at high pH and low salt concentration. Under these circumstances the repulsion between the silica particles is strong. In contrast, low filtration fluxes were measured at high salt concentration, low pH and with a \(\text{CaCl}_2\) electrolyte – that is, when the surface charges are weak and in the presence of specific cations. The net energy of interaction between the charged surfaces involved in the MF process was calculated using the DLVO theory. This gave qualitative arguments for the explanation of the observed changes in the permeate flux.

A series of structural parameters of a new composite membrane made by depositing a thin layer of titanium oxide on a cordierite support were measured by Palacio et al. An extended bubble point method was used, along with scanning electron microscopy. Afterwards, the permeate flux decline was analysed when differently charged proteinic solutions, showing no retention for a clean membrane, were permeated. Permeation experiments were performed at constant concentration and pressure for bovine serum albumin (BSA) (negatively charged at neutral pH) and lysozyme (positively charged at neutral pH) aqueous solutions. It is seen that lysozyme, in spite of its significantly smaller size, fouls the membrane more, giving a faster decline kinetics compared with the BSA within the frame of the usual models. The net surface charge of the membrane was obtained by measuring the streaming potential that appears when an electrolytic solution is permeated, whose results are interpreted in terms of a fine capillary model for the transport through the pores that takes into account the electrolyte adsorption. Different streaming potential versus electrolyte concentration behaviour was obtained, leading to positive net surface charge density for both the clean and BSA fouled membranes. This positive charge was lower for the fouled than the clean membrane, which is in accordance with the negative charge of BSA molecules at neutral pH [15].

Inorganic MF membranes with a pore size down to 0.1 mm were made by Kuiper et al. using laser interference lithography and silicon micromachining technology. The membranes have an extremely small flow resistance due to a thickness smaller than the pore size, a high porosity and a very narrow pore size distribution. They are relatively insensible to fouling, because they have a smooth surface, short pore channels and because they can be operated in crossflow configuration at very low transmembrane pressures. Experiments with yeast cell filtration of beer showed a minimal fouling tendency and a flux that was about 40 times higher than in conventional diatomaceous earth filtration. The uniform pore distribution made the membranes suitable for many other applications, like critical cell-to-cell separation, particle analysis systems, absolute filtrations and model experiments [16].

### 12.4 Fouling in Microfiltration

A major characteristic that limits the performance of MF or any membrane technology is a process known as fouling. Fouling describes the deposition and accumulation of feed components, such as suspended particles, impermeable dissolved solutes or even permeable solutes, on the membrane.
surface and/or within the pores of the membrane. Fouling of the membrane during the filtration processes decreases the flux, and thus the overall efficiency of the operation. This is indicated when the pressure drop increases to a certain point. It occurs even when operating parameters are constant (pressure, flow rate, temperature and concentration). Fouling is mostly irreversible, although a portion of the fouling layer can be reversed by cleaning for short periods of time [1].

Soluble proteins and Ca and P salts in the fouling deposit on a mineral MF membrane obtained in static conditions were analysed and compared with those found using dynamic filter conditions in a laboratory pilot installation for milk processing by Vetier et al. The serum milk proteins were retained by the porous micellar deposit under both static and dynamic conditions, resulting in progressive fouling of the dynamic micellar membrane, enabling milk to be processed with a mineral MF membrane. Ca and P salts increased fouling probably by allowing better adsorption of casein micelles on the alumina and by acting as intermicellar bonds in the deposit. Fat globules modified porosity, permeability and resistance to matter transfer of the deposit. The dynamic conditions gave a deposit of the same type and structure as with the static conditions, although made thinner by the velocity effect [17].

The fouling tendencies of seven commercial antifoam agents used with MF membranes were investigated in a stirred cell by Liew et al. [18]. Parameters such as viscosity, oil droplet size distribution, contact angle, work of adhesion $W_a$, membrane type, operating pressure and feed concentration were examined. The results show that the silicone-based antifoam G832 gave a significantly lower flux ($\leq 100 \text{ L h}^{-1} \text{ m}^{-2}$) than the polypropylene glycol antifoam PPG2000 ($1500–2500 \text{ L h}^{-1} \text{ m}^{-2}$) over the concentrations from 0.5 to 4.0 mL L$^{-1}$ at 50 kPa, 700 rpm and 25 °C. The significantly lower flux attained by the antifoam G832 was attributed to a number of factors, such as its greater viscosity ($1.25 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ compared with $1.05 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ for PPG2000), a smaller average oil droplet size (0.28 μm versus 0.65 μm) comparable to the membrane pore size distribution (0.26–0.62 μm), a higher contact angle (98° versus 51°) and a significantly larger value of work of adhesion (26.0 mN m$^{-1}$ versus 0.81 mN m$^{-1}$). The different magnitudes of membrane adsorption by these antifoam agents, as reflected by their values of work of adhesion, were also observed in the field emission scanning electronic microscopy photographs. In terms of membrane type, the inorganic Anopore alumina membrane was found to offer a higher PPG flux than the organic Millipore polyvinyl difluoride membranes (both hydrophilic and hydrophobic). Furthermore, the mixed-type antifoams (B5600, B426 and G832) were found to give an increased hydraulic resistance and fouling percentage with an increase in pressure or feed concentration. Conversely, for PPG2000, a reduction of the hydraulic resistance and fouling percentage was observed with increases of these two parameters.

Organic polymers are commonly used as coagulants or flocculants in pretreatment for MF. These high molecular weight compounds are potential membrane foulants when carried over to the MF filters. Wang et al. examined fouling of three MF membranes of different materials by three commonly used water treatment polymers: poly(diallyldimethylammonium) chloride, polyacrylamide and poly(acrylic acid-co-acrylamide) with a wide range of molecular weights. The effects of polymer molecular characteristics, membrane surface properties, solution condition and polymer concentration on membrane fouling were investigated. Results showed severe fouling of MF membranes at very low polymer concentrations, suggesting that residual polymers carried over from the coagulation/flocculation basin can contribute significantly to membrane fouling. The interactions between polymers and membranes depended strongly on the molecular size and charge of the polymer. High molecular weight, positively charged polymers caused the greatest fouling. Blockage of membrane pore openings was identified as the main fouling mechanism, with no detectable internal fouling in spite of the small molecular size of the polymers relative to the membrane pore size. Solution conditions (e.g. pH and calcium concentration) that led to larger polymer molecular or aggregate sizes resulted in greater fouling [19].
Surface deposition of polydopamine (PD) using facile aqueous-based chemistry under mild reaction conditions was accomplished on reverse osmosis, nanofiltration, UF and MF membranes. This surface treatment not only retained much of the membranes’ intrinsic pure water permeability, but also improved the fouling resistance of polypropylene MF, poly(tetrafluoroethylene) MF, PVDF MF, poly(arylene ether sulfone) UF, polysulfone UF, polyamide nanofiltration, and polyamide reverse osmosis membranes, as measured using oil–water emulsion filtration. To demonstrate the scalability of this approach, PD was applied to, and improved the fouling resistance of, membrane modules. Following PD deposition, membranes could be further modified by grafting fouling-resistant macromolecules, such as poly(ethylene glycol), to further improve fouling resistance of MF membranes [20].

Nafion–PVDF nanofibrous membranes with electrostatically negative charges on the fibre surface were fabricated via electrospinning with superior water permeability and antifouling behaviours in comparison with the conventional MF membranes [21]. The fibre diameter and the resultant pore size in the nanofibrous membranes were easily controlled through tailoring the properties of the electrospinning solutions. The electrospun Nafion–PVDF nanofibrous membranes revealed high porosities (>80%) and high densities of sulfonate groups on the membrane surface, leading to praiseworthy water permeability. Unexpectedly, the water permeability was observed as proportional to the fibre diameter and pore size in the membrane. The presence of sulfonate groups on the membrane improved the antifouling performance against negatively charged oily foulants.

Currently, there is a growing emphasis on wastewater reclamation and reuse all over the world due to restricted water resources. Among a variety of wastewater reuse technologies, the use of MF membranes is one of the popular processes because it has the ability to successfully eliminate particulates and colloidal matters. However, successful fouling control is not easy because effluents from the activated sludge process still contain small particulates and colloidal matters such as extracellular polymeric substance and soluble microbial products. On the other hand, microbubbles have advantageous properties compared with common bubbles, but there has been no reporting of the use of microbubbles in physical cleaning instead of aeration. Encouraging results were obtained by Lee et al. through the application of microbubbles for physical cleaning. In evaluation of the cleaning efficiency, the efficiency of microbubbles was observed to be twice as high as that of aeration, except during the course of the initial 30 min. Total organic carbon concentration of the membrane tank after treatment with microbubbles was more than twice as high as that after aeration for physical cleaning. The membrane cleaned with microbubbles also had the smoothest surface, with a roughness of 42.5 nm. In addition, microbubbles were found to effectively remove extracellular polymeric substance and make the structure of the gel layer loose. In particular, the microbubbles had the ability to remove proteins through the effect of pyrolytic decomposition. Therefore, in FTIR spectra of the membrane surfaces taken before and after physical cleaning, while each treatment showed similar peak positions, the peak values of the membrane treated with microbubbles were the lowest. Through various analyses, it was confirmed that microbubbles can remove foulants on the gel layer in spite of their very low shear force. This means that microbubble cleaning has full potential for use as a physical cleaning method in the wastewater reclamation process [22].

Biological activated carbon (BAC) filtration was investigated as a pretreatment for reducing the organic fouling of an MF membrane (0.1 μm PVDF) in the treatment of a biologically treated secondary effluent (BTSE) from a municipal wastewater treatment plant by Pramanik et al. [23]. BAC treatment of the BTSE resulted in a marked improvement in permeate flux, which was attributed to the effective removal of organic foulants and particulates. Although the BAC removed significantly less dissolved organic carbon than the granular activated carbon (GAC) treatment which was used as a control for comparison, it led to a markedly greater flux. This was attributed to the effective removal
of the very high molecular weight substances such as biopolymers by the BAC through biodegradation and adsorption of those molecules on the biofilm. Size exclusion chromatography showed the BAC treatment led to approximately 30% reduction in these substances, whereas the GAC did not greatly remove these molecules. The BAC treatment led to a greater reduction of loosely attached and firmly attached membrane surface foulant, and this was confirmed by attenuated total reflection FTIR spectroscopy analysis. Their study demonstrated the potential of BAC pretreatment for reducing organic fouling and thus improving flux for the MF of BTSE.

12.5 Module of Microfiltration

12.5.1 Plate-and-Frame Module
Membrane modules for dead-end flow MF are mainly plate-and-frame configurations. They possess a flat and thin-film composite sheet where the plate is asymmetric. A thin selective skin is supported on a thicker layer that has larger pores. These systems are compact and possess a sturdy design. Compared with crossflow filtration, plate-and-frame configurations possess a reduced capital expenditure; however, the operating costs will be higher. The uses of plate-and-frame modules are most applicable for smaller and simpler scale applications (laboratory) which filter dilute solutions [3].

12.5.2 Spiral-Wound Module
This particular design is used for crossflow filtration. The design involves a pleated membrane which is folded around a perforated permeate core, akin to a spiral, that is usually placed within a pressure vessel. This particular design is preferred when the solutions handled are heavily concentrated and in conditions of high temperatures and extreme pH. This particular configuration is generally used in more large-scale industrial applications of MF [3].

12.6 Microfiltration Technology
As indicated in ‘About Microfiltration: Effortless Purification of Macromolecules’ at http://www.kochmembrane.com/Learning-Center/Technologies/What-is-Microfiltration.aspx, MF has significant applications in simple dead-end filtration for water, sterile fruit juices and wine, and aseptic pharmaceuticals. However, not all applications that benefit from MF operate successfully in the dead-end mode, and a large portion of the MF market has been captured by crossflow. The most common of these is the clarification of whole-cell broths and purification processes in which macromolecules must be separated from other large molecules, proteins or cell debris. Clarification of dextrose and highly-coloured fruit juices employ MF extremely well. There are also large markets for MF crossflow filtration in wine production, milk and whey defatting, and brewing. As with UF, MF systems operate at relatively low pressures and come in a variety of configurations. MF membranes are characterized by their molecular size cut-off, as shown in Figure 12.5.

12.6.1 Water Treatment
MF and UF pilot plants were operated to produce drinking water from surface water from 1992 to 1996. MF was combined with pre-coagulation by polyaluminium chloride and was operated in a
dead-end mode using hollow-fibre polypropylene and monolith-type ceramic membranes. A UF pilot plant was operated in both crossflow and dead-end modes using hollow-fibre cellulose acetate membrane and was combined occasionally with powdered activated carbon and GAC adsorption. Turbidity in the raw water varied in the range between 1 and 100 mg L\(^{-1}\) (as standard kaolin) and was removed almost completely in all MF and UF pilot plants to less than 0.1 mg L\(^{-1}\). MF and UF removed metals such as iron, manganese and aluminium well. The background organics in the river water measured as KMnO\(_4\) demand varied in the range between 3 and 16 mg L\(^{-1}\). KMnO\(_4\) demand decreased to less than 2 mg L\(^{-1}\) and to less than 3 mg L\(^{-1}\) on the average by the coagulation–MF process and the sole UF process respectively. Combination of powdered activated carbon or GAC adsorption with UF resulted in an increased removal of the background organics and the trihalomethanes formation potential as well as the micropollutants such as pesticides. Filtration flux was controlled in the range between 1.5 and 2.5 m day\(^{-1}\) with the transmembrane pressure less than 100 kPa in most cases for MF and UF. The average water recovery varied from 99 to 85% [24]. Conventional treatment of raw water for the municipal supply of drinking water may include chemical addition, coagulation, flocculation, sedimentation, filtration and disinfection, usually with chlorine. The reason for a larger use of membrane filtration systems, such as MF and UF, in this field is mainly due, for example, to the ability of the membrane to remove pathogenic microorganisms as well as to control disinfection by-products’ precursors. Bottino et al. used MF ceramic membranes for the treatment of raw water drawn from a lake located near Genoa. The behaviour of permeate flux as a function of operating variables such as temperature, transmembrane pressure and test duration was analysed. Membrane retention towards particles, microorganisms, algae and disinfection by-products’ precursors was also investigated [25].

Oil and gas industries generate large amounts of wastewater as a by-product in both onshore and offshore production operations. This wastewater is commonly referred to as ‘produced water’ (PW). PW is very difficult to treat and its characteristics change from well to well. Treatment of this PW could improve the economic viability of these oil and gas fields and lead to a new source of water for beneficial use. Ebrahimi et al. [26] reported on a research project that evaluated the multistage treatment process of oilfield PW generated from tank dewatering with different ceramic membranes. The investigations focus on the characterization of permeate flux using various ceramic MF, UF and nanofiltration membranes as potential techniques for efficient treatment of tank dewatering PW. Results for average flux rates, flux degradation, removal of organic substances (measured as total organic carbon) and inorganic substances (measured as the electrical conductivity) and oil removal

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**Figure 12.5** Relationship between MF membrane and separation species.
efficiency are shown. A pilot study was conducted to assess the performance of a municipal wastewater reclamation plant consisting of a combined coagulation–disk filtration (CC–DF) process, MF and reverse osmosis membranes, in terms of the removal of water contaminants and changes in characteristics of effluent organic matter (EfOM). The CC–DF and MF membranes were not effective for the removal of dissolved water contaminants. However, they could partially reduce the turbidity associated with the cake layer formation by particulate materials on the membrane surfaces. Furthermore, most of the water contaminants were completely removed by the reverse osmosis membranes. Although the CC–DF process could remove approximately 20% of turbidity, the aluminium concentrations considerably increased after the CC–DF process due to the residual coagulants complexed with both carboxylic acid and alcohol functional groups of EfOM. Those aluminium–EfOM complexes had a lower negative charge and higher molecular weight (>0.1 μm pore size of the MF membranes) compared with non-complexed EfOM. These results indicate that the control of the formation of the aluminium–EfOM complexes should be considered as a key step to use the CC–DF process as a pretreatment of the MF and reverse osmosis membranes for mitigation of membrane fouling in the tested pilot plant [27].

Different processes, such as flocculation with ferric chloride (FeCl₃) and deep bed filtration (sand filtration and dual media filtration), as a pre-treatment to MF were used for seawater desalination [28]. The performance of these pretreatments was determined in terms of silt density index and modified fouling index and flux decline in MF. Flux decline of MF with seawater was 45% without any pretreatment, 42% after pretreatment of FeCl₃ flocculation, 24% after pretreatment of sand filtration with in-line coagulation and 22% after pretreatment of dual media filtration (sand and anthracite). Modified fouling index and silt density index also indicated that deep bed filtration with in-line flocculation was a better pretreatment than flocculation alone. Detailed molecular weight distribution of seawater organic matter was examined after different pretreatments. Molecular weight distribution of the initial seawater mainly ranged from 1510 Da to 130 Da. Deep bed filtration with in-line flocculation removed relatively large molecular weight of organic matter (1510–1180 Da), while the small molecular weights (less than 530 Da) were not removed. MF membranes achieve high retention of bacteria and viruses by pore-size exclusion by the diameters of the fibres in the scaffold layer. The membranes have a high permeation flux as compared with conventional commercial micro filtration membranes under the same applied pressure.

The patent of Chu et al. uses ultrafine nanofibres (fibre diameters from 3 to 50 nm and lengths from about 100 to about 5000 nm) infused into, or deposited onto, the surface of fibrous filtration media. Negatively charged ultrafine nanofibres can include polysaccharide nanofibres prepared by a 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)|NaBr|NaClO oxidation system in aqueous solution. Ultrafine polysaccharide nanofibres having a large number of carboxylate groups are produced (0.7–1.0 mmol per gram of cellulose). The carboxylate groups are negatively charged and can interact with positively charged polymers/molecules by forming a complex. Such ultrafine polysaccharide nanofibres have positive charges that are effective for the removal of bacteria and viruses through adsorption [29].

12.6.2 Dairy Industry

Merin et al. described a technique for the MF of cheese brine. Soft cheese brine with viable counts per millilitre of up to 1.2 × 10⁶ bacteria and 2.2 × 10⁴ yeasts and moulds was filtered using a pleated tangential flow filtration cartridge of 0.2 μm pore size membrane [30]. This filtration resulted in a three to four orders of magnitude reduction of bacteria and the complete rejection of yeast and mould from the permeate. Hard cheese brine with similar bacterial loads was treated with a 1.2 μm pore size
membrane cartridge and the resulting permeate contained two to three orders of magnitude fewer bacteria and no yeasts or moulds. Flux decline during the filtration was a function of the number of microorganisms and the amount of N in the brine. A cleaning procedure using enzyme and acid washes was established in order to prolong membrane performance.

Developments of crossflow MF (CFMF) in the dairy industry, some of which had just been patented, were reported by Saboya and Maubois [31]. Combination of the use of the uniform transmembrane hydraulic pressure concept (UTP) with its different ways of carrying out microfiltrate recirculation, longitudinal porosity gradient and of new ceramic membrane materials allows the differential separation of each category of milk particles. Pretreatment by CFMF of incoming milk is used for the production of low heated fluid milks having a flavour similar to that of raw milk and a shelf life three to five times longer than that of classical products. Results observed in the retention by the MF membrane of pathogenic bacterial species allow it to be said that the hygienic safety of cheeses made from raw MF milk is at least equal or even higher than that of cheeses made from pasteurized milk. Numerous other applications of CFMF were under development, such as removal of residual fat from whey or the clarification and the removal of bacteria from cheese brine, but the most promising were undoubtedly the differential separation of micellar casein and of small milk fat globules. With the products obtained on both sides of the MF membrane, dairy technology will have the possibility not only to improve yield and quality of many dairy products but also to create a diversified range of new textures.

Increasing the temperature of MF to >50 °C may allow for operation at higher fluxes and reduce the bacterial growth during MF. However, there is a concern that operating at higher temperatures could cause calcium phosphate precipitation that would lead to membrane fouling. The objective of Hurt et al. was to determine the effect of operating a 0.1 μm ceramic UTP MF unit at temperatures of 50, 55, 60 and 65 °C on membrane fouling and SP removal from skim milk with and without removal of low molecular weight soluble milk components by UF before MF at a flux of 54 kg m⁻² h⁻¹. For each replicate, 1000 kg of pasteurized skim milk was split into two batches. One batch was ultrafiltered (with diafiltration) to remove an average of 89 ± 2% of the lactose and a percentage of the soluble calcium and phosphorus. The retentate from UF was diluted back to the protein concentration of skim milk, creating the diluted UF retentate (DUR). On subsequent days, both the DUR and skim milk were run on the MF unit with the flux maintained at 54 kg m⁻² h⁻¹ and a concentration factor of 3× and the system run in recycle mode. The temperature of MF was increased in 5 °C steps from 50 to 65 °C, with a 1 h stabilization period after each increase. During the run, transmembrane pressure was monitored, and permeate and retentate samples were taken and analysed to determine if any changes in SP, calcium, or phosphorus passage through the membrane occurred. Increasing temperature of MF from 50 to 65 °C at a flux of 54 kg m⁻² h⁻¹ did not produce a large increase in membrane fouling when using either skim milk or a DUR as the MF feed type as measured by changes in transmembrane pressure. Increasing the temperature to 65 °C only caused a slight reduction in calcium concentration in the permeate (11 ± 3%) that was similar between the two MF feed types. Increasing processing temperature reduced the percentage of SP removal by the process, but the increased temperature also caused a decrease in casein contamination in the permeate with no evidence of membrane fouling [32].

12.6.3 Sterilization

Sterilization of fermentation medium involving heat may result in undesirable chemical reactions that alter nutrient concentration and yield products that interfere in the fermentation performance. Sterilization of heat-sensitive compounds usually involves separate sterilizations of carbon source and
nutrient solution. Membrane separation processes are an alternative to thermal processes, as they have many advantages, such as the possibility of continuous and modular operation and the use of moderate temperatures. In this context, the objective of the study by Faria et al. was the preparation of hollow-fibre membranes and the design of modules suitable for continuous sterilization of fermentation medium. The membrane with the best performance had a maximum pore diameter of 0.2 μm and a permeability of 42.9 L m⁻² bar⁻¹ h⁻¹ for a glucose–peptone–yeast extract medium. A module with 0.26 m² of permeation area was built with these membranes. This module was able to provide a permeate flow rate of 2.2 L h⁻¹ using a pressure difference of 0.2 bar. The collected permeate was completely sterile, thus confirming the efficiency of this process [33].

Pineapple is a very appreciated tropical fruit owing to its unique aroma and flavour. Pineapple juice was cold sterilized and clarified by CFMF associated with an enzymatic treatment. A tubular PES 0.3 μm pore size membrane with effective filtration area of 0.05 m² was used in the pilot system. Ten experiments were carried out under the same operational conditions, 25 °C and 100 kPa, in order to evaluate the cold sterilization and clarification of pineapple juice by MF. It was observed that the permeate flux did not change significantly after 15 min of processing time. It was stabilized around 100 L h⁻¹ m⁻². The clarification process was considered very efficient due to the great reduction of haze and viscosity, and by showing no significant changes in pH, acidity, sugar and soluble solid content of the juice. The permeate of the process was collected in sterile bottles inside a laminar flow station and kept under refrigeration (8 °C) for a period of 28 days. The samples were submitted to microbiological evaluations in intervals of 7 days. The microbiological analysis of the microfiltered pineapple juice showed that it was in agreement with the requirements by the Brazilian legislation for juices and drinks [34].

Thermal preservation is used by the egg industry to ensure the microbiological safety of liquid egg white (LEW); however, it does not eliminate all microorganisms and impairs some of the delicate functional properties of LEW. A pilot-scale CFMF process was designed to remove the natural microflora present in commercial LEW, obtained from a local egg-breaking plant, while maintaining the nutritional and functional properties of the LEW. LEW, containing approximately 10 (6 ± 1.7) colony-forming units (CFU) per millilitre of total aerobic bacteria, was microfiltered using a ceramic membrane with a nominal pore size of 1.4 μm, at a crossflow velocity of 6 m s⁻¹. To facilitate MF, LEW was screened, homogenized and then diluted (1 : 2, w/w) with distilled water containing 0.5% sodium chloride. Homogenized LEW was found to have a threefold lower viscosity than unhomogenized LEW. Influence of MF temperature (25 and 40 °C) and pH (6 and 9) on permeate flux, transmission of egg white nutrients across the membrane and microbial removal efficiency were evaluated. The pH had a significantly greater influence on permeate flux than temperature. Permeate flux increased by almost 148% when pH of LEW was adjusted from pH 9 to pH 6 at 40 °C. The influence of temperature on permeate flux, at a constant pH, however, was found to be inconclusive. Microbial removal efficiency was at least 5 log₁₀ CFU mL⁻¹. Total protein and sodium dodecyl sulfate polyacrylamide gel electrophoresis analysis indicated that this MF process did not alter the protein composition of the permeate, compared with that of the feed LEW, and that the foaming properties of LEW were retained in the postfiltered samples [35].

Madaeni et al. [36] investigated to establish a rationale for the cleaning of MF membranes fouled by milk. Milk was processed using a hydrophilic GVWP membrane. Fouling is the most important problem associated with the membrane-based milk sterilization process. This is mostly due to the deposition of bacteria, fats, proteins and minerals on the membrane surfaces. In the first part of this work, the factors affecting the chemical cleaning efficiency were studied. This includes the effect of concentration, temperature, cleaning time and crossflow velocity. A wide range of cleaning agents, including acids, bases and surfactant, was used. Flux recovery was employed for presenting the cleaning
efficiency. In the second part of this study, flux recovery was optimized using response-surface methodology with a face-centred central composite design. This was employed to create the mathematical model and minimize the number of experiments.

12.6.4 Virus Removal

Zhua et al. [37] investigated to determine virus removal efficiency by iron coagulation followed by MF in water treatment using the MS2 bacteriophage (~25 nm diameter) as a tracer virus. Results from these bench-scale studies were used to propose a mechanism for virus removal by iron coagulation–MF. Ferric chloride was used as coagulant, and the dosages were 0, 2, 5 and 10 mg L\(^{-1}\) as Fe(III) with pH adjusted during mixing to 6.3, 7.3 and 8.3. In the absence of iron coagulation and with less than 2 mg L\(^{-1}\) Fe, MF alone achieved less than a 0.5 log removal of MS2 virus. However, iron coagulation pretreatment dramatically improved virus removal, especially in the 5–10 mg L\(^{-1}\) Fe dose range, ultimately achieving more than 4 log removal at pH 6.3 with 10 mg L\(^{-1}\) Fe dose. For the 5 and 10 mg L\(^{-1}\) Fe dosages, decreasing pH in the 8.3–6.3 range resulted in significantly greater virus removal. For 0 and 2 mg L\(^{-1}\) Fe dosages, decreasing pH in the 8.3–6.3 range also improved virus removal, but to a lesser extent. The experimental data indicate negatively charged MS2 viruses first adsorbed onto the positively charged iron oxyhydroxide floc particles before being removed by MF. MS2 viruses were not inactivated in iron or aluminium coagulation, as evidenced by the fact that their concentrations before and after coagulation, settling and resuspension of the coagulated sludge were not statistically different.

Virus removal performance and mechanisms were investigated in a hybrid coagulation–MF system by using river water spiked with bacteriophage Qb. Virus removal increased with filtration time: the rate of virus removal was 4 log at the beginning of filtration and gradually increased to 6 log over 5 h, probably because of the growth of a cake layer that accumulated on the membrane surface. Quantification of the virus particles in the MF compartment by a combination of a polymerase chain reaction method and a plaque-forming unit method revealed that most of the virus (99.999%) in the MF compartment was entrapped in the aluminium floc and then located in the solid phase; most of the virus (99.9%) in the solid phase was inactivated. The rate of recovery of virus particles from the MF compartment decreased with filtration time: after 3 h of filtration approximately half of the virus particles in the MF compartment were not recovered by hydraulic backwashing, indicating that the virus might have been retained on the MF membrane as part of an irreversible foulant [38].

MF applied in the dairy industry for bacteria removal is an important technology for extending the shelf life of milk while maintaining or even improving its organoleptic and nutritional properties. Fernández et al. [39] reviewed the evolution of this technique over recent years and the advances currently being made in the field. The cited literature indicates the strategies used to overcome the main drawbacks of this type of operation, the most common operating conditions employed and the reduction degree of bacteria obtained.

Membranes are finding widespread applications in disinfection processes for raw water and municipal effluent reuse. Madaeni et al. [40] describe a fundamental study for transmission of mixtures of real viruses through 0.22 μm hydrophobic MF membrane. Two non-human animal viruses – foot-and-mouth disease (FMD) and infectious bovine respiratory (IBR) virus – in dilute solution were selected as viruses and challenged with the membrane. An attempt was made to address the main questions for process performance in terms of transmission (or rejection) of virus and flux, under various operating conditions, including transmembrane pressure, stirring and time. The effect of the presence of large virus (IBR, 150 nm) on rejection of small virus (FMD, 25 nm) was elucidated.
It was found that IBR virus was completely rejected by the membrane regardless of the operating conditions. The small FMD virus was significantly removed depending on the conditions being higher for lower transmembrane pressure. The presence of large IBR virus enhances the removal of small virus. Although numerous studies have focused on phages (mainly viruses of bacteria), few researchers investigated the MF capability for removal of human or animal viruses from water or wastewater. This study is an answer to the questions arising for removal of real viruses from water by MF membrane.

12.6.5 Oil Refining

The diversification of the nonfood uses of vegetable oils and the need for softer processing demands new oil refining processes. Taking advantage of the membrane technology for vegetable oil refining, the preliminary results reported by Pioch et al. concern a single dead-end or CFMF step. The influence of experimental parameters (temperature, pore size, pressure, etc.) on the flow rate of permeate and on the free fatty acids (as soap) and phosphorus retention ratios is discussed. After addition of sodium hydroxide followed by dead-end filtration the quality of the oil meets the quality standard, but the main drawback is the very poor flow rate as a consequence of the rapid fouling of membranes. Cross-flow filtration allows a higher flow rate of permeate, which shows a slow decrease after operating for several hours, with only a slight loss of quality of the processed oil compared with dead-end filtration. From this preliminary study, CFMF gives promising results for vegetable oils refining. This is the first report of simultaneous reduction of phosphorus, free fatty acids and water concentrations after a solvent-free single MF step [41].

The refining process of vegetable oils generates acidic wastewater with the following characteristics: pH (1–1.5), COD (10–30 g O₂ per litre), suspended solids (7–12 g L⁻¹) and fats (2–4 g L⁻¹). In order to reduce the effluent load and recover a fraction of the fats without using any additives, an MF (0.2–1.4 μm) process involving ceramic membranes at very low transmembrane pressure values (0.1–1 bar) was assessed. Four batches of acidic wastewater from different manufacturing runs were tested. Trials with a constant volumetric reduction ratio of 30 were carried out for periods of more than 5 h. With a 0.5 μm membrane it was possible to maintain a permeate flux of 100 L h⁻¹ m⁻² for 24 h and achieve a 91% reduction in suspended solids, a 96% reduction in fat and a COD reduction of more than 60%. In addition, the retentate thus extracted separated spontaneously into two phases, both of which could be exploited: the upper phase mainly consisting of fats as a by-product and the lower clarified phase which could be mixed into the permeate [42].

Oily wastewater is produced in oil refining processes. This waste is usually treated by a number of physical, chemical and biological techniques in water treatment units of oil refinery before being disposed in the environment or reused as agricultural water. One of the treatment techniques for oil separation from wastewater is membrane filtration. The performances of hydrophilic MF GRM and UF GRM polymeric membranes challenged with synthetic feed (gas oil dispersed in water) and oily wastewater effluent of an American Petroleum Institute unit in the refinery were investigated by Madaeni et al. [43]. A comparison was carried out under optimum conditions and in cross-flow mode on a laboratory scale. The effects of operating parameters (i.e. pressure and crossflow velocity) on flux and rejection were elucidated. The flux of the MF GRM membrane for real feed within the first 2 h of filtration was low compared with synthetic feed because of the presence of solid and colloidal particles in the real feed. The oil rejection (around 99%) for synthetic feed was higher compared with real feed. A similar trend was found for both UF GRM and MF GRM membranes.
References


13

Comparison of Pressure-Driven Membrane Separation Processes

13.1 Pressure-Driven Membrane Separation Technologies

Widely recognized as the technology of choice for superior water and wastewater treatment, membranes provide a physical barrier that effectively removes solids, viruses, bacteria and other unwanted molecules. Different types of membranes are used for softening, disinfection, organic removal, and desalination of water and wastewater and can be installed in compact, automated, modular units. Membrane filtration units can also be installed in relatively small facilities that blend into the surrounding area and can be fully automated to significantly reduce the required amount of operator attention.

Recent advances in technology have significantly reduced the cost of membrane-based systems. Installation costs are lower because membrane systems do not require large buildings or as much land as conventional systems. Operating costs are reduced since today’s membranes produce more water and remove more impurities while using less energy.

Membranes provide physical barriers that permit the passage of materials only up to a certain size, shape or character. There are four crossflow, pressure-driven membrane separation processes employed for liquid–liquid and liquid–solid separation: reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). Membranes are manufactured in a variety of configurations, including hollow fibre, spiral and tubular shapes. Each configuration offers varying degrees of separation.

1) **Reverse osmosis**  RO, sometimes called hyperfiltration, describes the tightest of these molecular-level separations. In RO, hydraulic force is applied in excess of the natural osmotic pressure of a solution to provide the driving energy for water molecules to diffuse into and through the membrane. Typical operating pressure can be in the hundreds to even a thousand pounds per square inch (25–68 bar). RO membranes are generally characterized by their ability to reject sodium chloride at given pressure, temperature and concentration conditions. Typical rejection values can be on the order of 98–99.5%.

2) **Nanofiltration**  NF is the next, more open crossflow membrane filtration type. In solutions of mixed ionic species, monovalent ions will tend to permeate the membrane, whereas divalent or multivalent species will tend to be highly rejected at the membrane interface. Since some ionic species, the monovalent ions, are transmitted through the membrane, the difference in chemical potential between the two solutions is less and therefore lower driving forces are required. Hence, typical NF operating pressures may be only one to a few hundred pounds per square inch (7–40 bar). NF membranes are generally characterized by their ability to retain a divalent ionic
species, often magnesium sulfate or calcium chloride. Since more variability in applications exist with NF, retention of magnesium sulfate might range from around 80 to 98%.

3) **Ultrafiltration**  With UF, the membranes comprise a discrete porous network. As a mixed solute solution is pumped across the membrane, smaller molecules pass through the pores while larger molecules are retained. We end up with one solution depleted of larger molecules, the permeate stream, and another enriched of larger molecules, the retentate. The open membrane structure means that mass transfer is now more flow dependent than pressure dependent, so operating pressure is further reduced. Typical operating pressures for UF are tens of pounds per square inch to a hundred or so (100–1000 kPa). Membrane classification convention shifts to atomic mass for UF membranes. Molecular weight cut-off is generally expressed in standard dalton or kilodalton units. For example, a 10 kDa membrane would highly retain molecules of that molecular mass or greater while highly permeating smaller molecules. While this system is inherently flawed since the atomic mass does nothing to describe the actual size or geometry of a molecule, it remains the standard convention for UF membrane classification.

4) **Microfiltration**  MF describes the coarsest of filtration in the crossflow membrane filtration range. Membrane porosity is, at last, conventionally depicted as a distance measure generally from a fraction of a micrometre up to a micrometre ($10^{-6}$ m) or so. Large and small molecules then can be separated from very large or complex molecular structures. Typical operating pressures for MF are a few pounds per square inch to perhaps a hundred (50–600 kPa).

The relationship between solute size in the feed and permeation and separation characteristics in pressure-driven membrane processes is shown as Figure 13.1.

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**Figure 13.1** Relationship between solute size and separation characteristics in pressure-driven membrane processes. 
- ●: suspended solids, bacteria; ●: viruses, macromolecules, colloids; ○: Multivalent ions, mid-size organic substances; ●: monovalent ions, low molecular weight substances.
UF and MF are reported as follows [1]. They are filtration processes that operate on a physical sieving separation process. They are best used for the removal of suspended solids, *Giardia*, *Cryptosporidium* and the reduction of turbidity. They are also used as a pretreatment to desalination technologies such as RO and NF.

1) **Separation scale**  
MF membrane pores are larger than UF membrane pores. MF pore diameters have a range of 0.01 to 10 μm. UF pore sizes are rated by the molecular weight of retained substances with a molecular weight range of 1000 to 100 000 Da. The smaller (tighter) MF membrane pore sizes occasionally overlap the larger (more open) UF pores. However, UF pores are generally smaller than MF pores.

2) **Separation mechanism**  
UF membranes have a skin layer on the membrane structure surface. This layer contains the pores that effect the rated separation or rejection of substances larger than the membrane pores. This creates a ‘concentration polarization’ at, or near, the membrane surface. With MF membranes, however, the concentration polarization phenomenon does not occur, as the smaller substances (smaller than the MF retained particles or bacteria) permeate the membrane.

3) **Operating pressure**  
Microfilters are usually operated below 200 kPa. Ultrafilters operate up to 300 kPa.

4) **Membrane thickness and strength**  
Mechanical strengths of membranes vary by material, structure and manufacturing process. This is true even when the membrane thicknesses are similar. Hollow-fibre UF membranes usually have a wall thickness of 150–300 μm. The wall thicknesses of MF hollow-fibre membrane manufactured with an elongation process are normally 50 to 100 μm but have similar strength properties to UF hollow fibres.

5) **Surface features**  
Scanning electron microscopy observations of the UF and MF membrane surfaces show that MF pores are clearly discernible, while the pores on the UF surface are not.

Figure 13.2 compares the relation among the solute in feed, pore size of membrane and pressure-driven membrane separation process, and Table 13.1 summarizes the characteristics in pressure-driven membrane separation processes [2].

![Figure 13.2](image-url)  
*Figure 13.2* Relationship among solute in feed, pore size of membrane and pressure-driven membrane process.
When Figures 13.1 and 13.2 and Table 13.1 are compared, the characteristics of RO, NF, UF and MF can be easily understood. The choice of the pressure-driven membrane separation process depends on the purpose to be enabled.

### Table 13.1 Characteristics in pressure-driven membrane separation processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Microfiltration</th>
<th>Ultrafiltration</th>
<th>Nanofiltration</th>
<th>Reverse osmosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Driving force, (\Delta P) (MPa)</td>
<td>0.11–0.3</td>
<td>0.15–0.5</td>
<td>0.5–1.5</td>
<td>0.5–1.5</td>
</tr>
<tr>
<td>Separation mechanism</td>
<td>Sieve</td>
<td>Sieve</td>
<td>Sieve + solution/diffusion + exclusion</td>
<td>Sieve + solution/diffusion + exclusion</td>
</tr>
<tr>
<td>Pore diameter ((\mu m))</td>
<td>(10^{-4}–10^{-3})</td>
<td>(5 \times 10^{-4}–5 \times 10^{-3})</td>
<td>(10^{-3}–3 \times 10^{-3})</td>
<td>(10^{-1}–10)</td>
</tr>
<tr>
<td>Retentate</td>
<td>Bacteria, suspended solids (MW &gt;5 \times 10^5) Da</td>
<td>Colloid, viruses, macromolecules (MW &gt; 2 \times 10^5) Da</td>
<td>Molecules, multivalent ions (5 \times 10^2 &lt; MW &lt; 2 \times 10^5) Da</td>
<td>Salts, low molecular weight compounds</td>
</tr>
<tr>
<td>Permeate</td>
<td>Water, dissolved solids</td>
<td>Water, salts, low molecular weight compounds</td>
<td>Water, monovalent salts</td>
<td>Water, solvent</td>
</tr>
</tbody>
</table>

13.2 **Problems of Reverse Osmosis and Nanofiltration**

NF and RO processes have been widely utilized for a range of desalination and deionization applications. However, pressure-based membranes have several inherent technical and economical limitations, particularly where high feed recoveries are essential. The most severe impediment to high recovery is the osmotic pressure of the feed solution that has to be overcome by the applied hydrostatic (feed) pressure. The osmotic pressure of saline solutions such as brackish water and seawater can be significant. Moreover, since the osmotic pressure is determined by the salt concentration directly at the membrane surface, it can be affected by concentration polarization, which is the build-up of salt near the surface of the membrane due to incomplete mixing of the surface boundary-layer fluid with the bulk solution, a phenomenon accentuated by high-pressure fluid passing through the membrane material. Although concentration polarization can be minimized by design and operating parameters, it can never be completely excluded and must be overcome by increased applied hydrostatic (feed) pressure, particularly as feed recovery is increased. Overcoming high osmotic pressures and concentration polarization resulting from higher recoveries requires not only substantial energy to produce the necessary higher pressures and flow rates but also additional investment in capital cost for additional membrane area and pumping capacity. It can also result in shorter useful life of the membrane due to compaction effects and enhanced fouling that can occur at higher pressures and recoveries as a result of the concentration of scaling components near the surface of the membrane. Enhanced fouling increases the required frequency of membrane cleaning, increasing labour and chemical costs, and reducing throughput. For feeds with total dissolved solids (TDS) levels typical of seawater, recoveries approaching 50% and beyond are seldom feasible; for brackish water levels of TDS, recoveries beyond 80% are rarely economical, resulting in substantial waste of pretreated feed that must be returned to the source or alternatively disposed. Consequently, pressure-based membrane systems inherently perform better at lower feed concentrations and lower recoveries in which the osmotic pressure of the
feed and its fouling and scaling potential are minimized. Furthermore, membrane process equipment size is determined according to feed or concentrate flow requirements and decreases with increased recovery rate and lower feed concentration; conversely, pressure-based membranes perform optimally, producing the best product quality and highest permeate flux rates, with low recoveries and low concentration feeds [3].

References


Forward Osmosis

14.1 Principle of Forward Osmosis

Forward osmosis (FO) is an osmotic process that, like reverse osmosis (RO), uses a semipermeable membrane to effect separation of water from dissolved solutes. The driving force for this separation is an osmotic pressure gradient, such that a ‘draw’ solution (DS) of high concentration (relative to that of the feed solution (FS)) is used to induce a net flow of water through the membrane into the DS, thus effectively separating the feed water from its solutes (see Figure 14.1a). In contrast, the RO process uses hydraulic pressure as the driving force for separation, which serves to counteract the osmotic pressure gradient that would otherwise favour water flux from the permeate to the feed (Figure 14.1b). Hence, significantly more energy is required for RO compared with FO (see http://en.wikipedia.org/wiki/Forward_osmosis).

Figure 14.2 shows a schematic diagram for a water treatment system using the FO method. This system is composed of an FO membrane, an FO membrane module, a DS, and a DS reproduction process. At first water is transferred from the FS side to the DS side through the FO membrane by osmotic pressure of the DS in the FO membrane module, and consequently the FS is concentrated and the DS is diluted. This diluted DS is separated and reproduced by the reproduction apparatus. By continuously repeating this process water treatment as desalination is carried out. The DS reproduction process accounts for most of the overall energy cost to the FO method.

As already mentioned, in the RO method it is the hydraulic pressure rather than osmotic pressure to the highly concentrated salt water side that is given and the water is moved from the salt water side to the fresh water side. On the other hand, in the FO method hydraulic pressure is not added to the system and the water is moved from the fresh water side to the salt water side using the osmotic pressure difference that occurs between highly concentrated salt water and fresh water.

In this way, the FO method is different from the RO method at the points where (1) the direction of the water movement is from the fresh water side to the salt water side and (2) the driving force for the water movement is due to an osmotic pressure difference (concentration difference).

14.2 Advantages and Problems of Forward Osmosis

In the desalination of seawater by RO, a little less than 90 atm high pressure is applied and approximately 60% recovery is obtained. Higher pressure is necessary to get a higher recovery, and therefore the running costs for things like electricity bills and large facilities such as a high-pressure pump or plumbing capable of withstanding high pressure are high. On the other hand, when an aqueous salt
solution such as MgCl$_2$ is used as a DS in FO, a driving force of 1000 atm is provided by an aqueous solute of 5 m MgCl$_2$ [1]. Thus, water conversion is possible with a high recovery of more than 80% from highly concentrated salt water solution such as the seawater under atmospheric pressure without using a high-pressure pump in FO. In addition, as with RO, one of the problems in the water processing system with the separation membrane includes a drop in processing capacity as a result of membrane fouling. However, even when the same water permeability is provided, because hydraulic pressure is not applied in FO there are less collisions of molecules with the membrane wall than in RO, and the adsorption characteristics of the membrane pollutant at the film surface are lower than for an RO membrane. Therefore, detachment of the membrane pollutant is possible by physical washing [2].

The fundamental performances which are demanded for FO membranes are follows: (1) high water permeability through the active layer, (2) low salt permeability through the active layer and (3) structure of the support layer with low internal concentration polarization (ICP). Points (1) and (2) are also

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**Figure 14.1** Principles of FO and RO.

**Figure 14.2** Schematic diagram for water treatment in FO membrane system.
required in an RO membrane, but because the osmotic pressure is a driving force in the FO process a 
support structure with a low ICP is significantly demanded. It is necessary for the DS, which plays an 
important role in the FO process, to have high osmotic pressure to give a high driving force and simulta-
taneously it is strongly demanded that a diluted DS can be reproduced by low energy in practical appli-
cation [3].

14.3 Fundamental Analysis of Forward Osmosis

The generally simple equation describing water transport in FO and RO using the relationship 
between osmotic and hydraulic pressures and water (solvent) flux is as follows:

$$J_w = A(\sigma \Delta \pi - \Delta P)$$  \hspace{1cm} (14.1)

where $J_w$ is the water flux, $A$ is the hydraulic permeability of the membrane, $\sigma$ is the reflection 
coefficient, $\Delta \pi$ is the difference in osmotic pressures on the two sides of the membrane, and $\Delta P$ is 
the difference in hydrostatic pressure. For FO, $\Delta P$ is zero; for RO, $\Delta P > \Delta \pi$.

The solute flux $J_s$ for each individual solute can be modelled by Fick’s law:

$$J_s = B \Delta c$$ \hspace{1cm} (14.2)

where $B$ is the solute permeability coefficient and $\Delta c$ is the transmembrane concentration differential 
for the solute. It is clear from this governing equation that a solute will diffuse from an area of high 
concentration to an area of low concentration. This is well known in RO, where solutes from the feed 
water diffuse to the product water; however, in the case of FO the situation can be far more 
complicated.

In FO processes, solute diffusions in both directions depending on the composition of the DS and 
the FS occur. This does two things: solutes in the DS may diffuse to the FS and solutes in the FS may 
diffuse to the DS. Clearly, this phenomenon has consequences in terms of the selection of the DS for 
any particular FO process. For instance, the loss of DS may have an impact on the FS perhaps due to 
environmental issues or contamination of the feed stream, such as in osmotic membrane bioreactors.

An additional distinction between the RO and FO processes is that the permeate water resulting 
from an RO process is in most cases fresh water ready for use. In the FO process, this is not the case. 
The membrane separation of the FO process in effect results in a ‘trade’ between the solutes of the FS 
and the DS. Depending on the concentration of solutes in the feed (which dictates the necessary con-
centration of solutes in the draw) and the intended use of the product of the FO process, this step may 
be all that is required. The FO process is also known as osmosis (see http://en.wikipedia.org/wiki/
Forward_osmosis).

14.4 Membranes and Modules for Forward Osmosis

14.4.1 Membranes for Forward Osmosis

Generally, any dense, nonporous, selectively permeable material can be used as a membrane for 
FO [1]. Membranes in flat sheet and capillary configurations have been tested for various applications 
of FO [4–8].

In the 1970s, all studies involving osmosis used RO membranes, either flat sheet or tubular, and in all 
cases researchers observed much lower flux than expected.
Several commercially available RO membranes and an in-house cellulose acetate membrane were used to treat dilute wastewater by FO using a simulated seawater DS [9,10]. Flat sheet RO membranes from Eastman and cellulose acetate hollow-fibre membranes from Dow were used to desalinate seawater by FO using glucose as the DS [4]. Cellulose acetate membranes reinforced with mineral fillers were used to evaluate whether membrane performance under RO conditions can be predicted through FO testing [7].

On the other hand, Permasep RO membranes made of an aromatic polyamide – DuPont B-9 (flat sheet) and B-10 (hollow fibre) – were applied to FO experiments and a relatively low flux of about 8 L m$^{-2}$ h$^{-1}$ at a driving force of 80 bar was obtained [5,8].

Reduction of ICP is an important point in the development of FO membrane with a high performance.

As mentioned earlier, many RO membranes were applied to FO studies but FO performance was not high. When we think about what the cause depends on, it is necessary to think about the difference between an FO membrane and an RO membrane. When existing commercial RO membranes are applied to the FO membrane process, it is very difficult to obtain a high water flux. Such a result is dependent upon the fact that RO membranes are designed in the membrane structure that is most suitable for hydraulic pressure drive [11,12]. Because it is driven under an operation pressure that is higher than the osmotic pressure of the FS by the RO method, pressure resistance is required on an RO membrane. Therefore, the support layer supporting the activity layer (AL) must be designed as a dense structure.

When the transmission direction of the water and the movement direction of the salt in Figure 14.1 is noticed, because in the RO method water and the salt is an equivalence direction, a concentration polarization (outside concentration polarization) around the active layer of the FS side reduces the water permeability. On the other hand, in the FO method the concentration polarization (ICP) in the region between the active layer and the support layer causes a reduction in the water permeability. Therefore, because the degree of density in the support layer remarkably influences the performance of water permeability in the FO method, how to control ICP is of great importance. Because the guidance of the membrane structure design for the FO method is different from the RO method, the development of a suitable separation membrane for FO drive is essential for the practical application of the FO membrane process.

The development of FO membranes with a high efficiency is significantly dependent upon the reduction of the internal concentration polarization. The problem of the ICP in the FO membrane was already proposed 20–30 years ago by Lee et al. [13] and Loeb et al. [6]. Tiraferri et al. [14] manufactured an FO membrane by a preparation method like that of an RO membrane to reduce the ICP by getting a nonwoven fabric wet with a solvent beforehand and trying to raise the porosity of the support layer by lowering the polymer concentration in the cast solution. It was confirmed that the water flux through the FO membranes increased with decreasing polymer concentration in the casting solution and a flux of about 25 L m$^{-2}$ h$^{-1}$ at a driving force of about 48 bar was obtained, and the RO membrane made for comparisons did not show high water permeability. Ma et al. [15] concluded that the structure of the support layer significantly influences the performance of water permeability through the FO membrane. Similarly, Emadzadeh et al. [16] prepared a high-performance FO membrane by adding TiO$_2$ nanoparticles in the support layer.

Because a strong pressure tightness is not demanded in an FO membrane, some approaches that are different from membrane preparation using a polysulfone ultrafiltration support membrane method seen in conventional RO membranes are possible. FO membranes with the active layer coated on a nonwoven fabric support layer were prepared and their FO membrane performances were examined [17,18]. Those FO membranes showed very high water flux of about 37 L m$^{-2}$ h$^{-1}$ at a driving force of about 24 bar.

Higa [3] reported the relationship between internal concentration and the structural parameter of a support layer in an FO membrane. As stated earlier, ICP happens because of the structure of the
support layer in the FO membrane, and there is the phenomenon that the concentration difference in the active layer decreases compared with the concentration difference of the whole membrane. Because this phenomenon causes a drop of the driving force, the water flux decreases.

As can be seen from Figure 14.3, when the AL of the membrane contacts with the FS and DS, the state of the formation of ICP is significantly different. Because the AL slightly penetrates the salt in Figure 14.3a (AL-facing-DS), the salt in the DS moves in the support layer, and the salt concentration in the support layer becomes higher than that in the FS. On the other hand, in Figure 14.3b (AL-facing-FS) water is permeated from the FS side to the support layer side and the salt concentration in the support layer is diluted; consequently, the effective osmotic pressure is lowered.

The decrease in effective osmotic pressure difference by ICP in AL-facing-FS is more remarkable than in AL-facing-DS, and AL-facing-FS decreases the FO performance. However, AL-facing-FS is often used in the real application of the FO membrane because generally a film pollutant is included in an FS. Therefore, AL-facing-FA and AL-facing-DS are called the FO and pressure retarded osmosis (PRO) mode respectively.

Figure 14.4 shows the effect of DS concentration on the water flux in AL-facing-FA and AL-facing-DS mode through an FO membrane [19]. The water flux is proportional to the osmotic pressure difference shown by the theoretical value (i.e. DS concentration), but the difference with the theoretical value grows really big with increasing DS concentration because of the influence of ICP. Also, water flux in AL-facing-FA for the same DS concentration is low because AL-facing-FA is easily affected by ICP from AL-facing-DS.

Higa also proposed a structural idea for the preparation of a suitable FO membrane [3]: the ICP in the support layer of an FO membrane is estimated as a membrane structural factor. As shown in Figure 14.5, the tortuosity factor $\tau$ in a porous support is defined by the ratio of the mean length $\lambda$ of a pore in a porous support and the thickness $d$ of the support:

$$\tau \equiv \frac{\lambda}{d}$$  \hspace{1cm} (14.3)

Porosity is the ratio of the area of the support $A$ to the total sum of the cross-section of the pores $\sum a_i$ (Equation 14.4). The membrane structural factor $S$ is defined as the value of the tortuosity factor multiplied by the thickness of the support divided by the porosity (Equation 14.5). When this $S$ value
is low, the effect of ICP is decreased. Consequently, the formation of a thinner support membrane with more pores which were formed on a straight line as much as possible is strongly demanded to obtain a higher performance FO membrane:

$$
\varepsilon \equiv \frac{\lambda}{d}
$$

$$
\varepsilon \equiv \frac{\sum a_i}{A}
$$

$$
S \equiv \frac{\tau d}{\varepsilon}
$$

14.4.2 Modules for Forward Osmosis

Fundamentally, the construction of an FO system is comprised of a semipermeable FO membrane, the feed side chamber, the DS chamber and the DS recycle chamber, as shown in Figure 14.2. Various modules are used to hold or pack FO membranes. Flat sheet, tubular, capillary and hollow-fibre
membranes are set respectively in plate–frame, spiral, tubular and hollow-fibre-type modules shown in Chapter 4. These modules are chosen depending on the particular purpose.

14.5 Technology

It is well known that pressure-driving membrane technologies such as RO, nanofiltration, ultrafiltration, microfiltration and so on are applied to water processing in many fields. In recent years the FO method, which makes an osmotic pressure difference between the DS with high osmotic pressure and the FS, has attracted much attention [1,20–23].

14.6 Application Area of Forward Osmosis Process

The FO process is applied in various fields, such as seawater desalination, wastewater treatment and water purification, pharmaceutical applications, food processing and power generation [21,22].

14.6.1 Seawater Desalination

Seawater can be desalinated by direct osmosis across a cellulose acetate membrane by using the osmotic pressure of a hypertonic glucose solution as the energy source. The resulting glucose solution is potable. This may prove useful for an emergency water supply in lifeboats [24].

A novel forward (direct) osmosis desalination process was presented by McCutcheon et al. [25]. The process uses an ammonium bicarbonate DS to extract water from a saline feed water across a semi-permeable polymeric membrane. Very large osmotic pressures generated by the highly soluble ammonium bicarbonate DS yield high water fluxes and can result in very high feed water recoveries. Upon moderate heating, ammonium bicarbonate decomposes into ammonia and carbon dioxide gases that can be separated and recycled as draw solutes, leaving the fresh product water. Experiments with a laboratory-scale FO unit utilizing a flat-sheet cellulose triacetate (CTA) membrane demonstrated high product water flux and relatively high salt rejection. The results further revealed that RO membranes are not suitable for the FO process because of relatively low product water fluxes attributed to severe ICP in the porous support and fabric layers of the RO membrane. Forward (direct) osmosis using semi-permeable polymeric membranes may be a viable alternative to RO as a lower cost and more environmentally friendly desalination technology. The driving force in the FO process described is provided by a DS comprising highly soluble gases – ammonia and carbon dioxide. Using a commercially available FO membrane, experiments conducted in a crossflow, flat-sheet membrane filtration cell yielded water fluxes ranging from 2.1 to 21.2 gal ft$^{-2}$ day$^{-1}$ (3.6–36.0 L m$^{-2}$ h$^{-1}$) for a wide range of DS and FS concentrations. It was found, however, that the experimental water fluxes were far lower than those anticipated based on available bulk osmotic pressure difference and membrane pure water permeability data. ICP was determined to be the major cause for the lower than expected water flux by analysis of the available water flux data and scanning electron microscope images of the membrane displaying a porous support layer. DS concentration was found to play a key role in this phenomenon. Sodium chloride rejection was determined to be 95–99% for most tests, with higher rejections occurring under higher water flux conditions. Desalination of very high sodium chloride FSs (simulating 75% recovery of seawater) was also deemed possible, leading to the possibility of brine discharge minimization [26]. Martinetti et al. [27] investigated vacuum-enhanced direct contact membrane distillation (VEDCMD) and FO for water recovery enhancement in desalination of brackish water.
Past studies had demonstrated that both VEDCMD and FO can be effectively utilized in the treatment of a wide range of highly concentrated FSs. In their study, two RO brine streams with total dissolved solids concentrations averaging 7500 and 17 500 mg L\(^{-1}\) were further desalinated by VEDCMD and by FO. In both processes, high water recoveries were achieved; however, recoveries were limited by precipitation of inorganic salts on the membrane surface. Various cleaning techniques were able to remove the scale layer from the membrane and restore water flux to almost initial levels. FO achieved water recoveries up to 90% from the brines and VEDCMD achieved water recoveries up to 81% from the brines. Addition of a scale inhibitor during both processes was effective at maintaining high water flux for an extended time. When considering the total water recovery (the recovery from the RO processes combined with the batch recovery from the VEDCMD or FO process), greater than 96 and 98% total recoveries were achieved for the two different brine streams.

FO is attracting increasing interest for its potential applications in desalination. In FO, permeation of contaminants from FS into DS through the semipermeable membrane can take place simultaneously with water diffusion. Understanding the contaminants transport through and rejection by the FO membrane has significant technical implications in the way clean water is separated from the diluted DS. In the Jin et al. study, a model was developed to predict boron flux in FO operation. A strong agreement between modelling results and experimental data indicates that the model developed in this study can accurately predict the boron transport through FO membranes. Furthermore, the model can guide the fabrication of improved FO membranes with decreased boron permeability and structural parameter to minimize boron flux. Both theoretical model and experimental results demonstrated that when the membrane active layer was facing the DS the boron flux was substantially greater compared with the other membrane orientation due to more severe ICP. In this investigation, for the first time, rejection of contaminants was defined in FO processes. This is critical to compare the membrane performance between different membranes and experimental conditions [28].

Seawater desalination for agricultural irrigation will be an important contributor to satisfying growing water demands in water-scarce regions. Irrigated agriculture for food production drives global water demands, which are expected to increase while available supplies are further diminished. Implementation of RO, the current leading technology for seawater desalination, has been limited in part because of high costs and energy consumption. Because of stringent boron and chloride standards for agricultural irrigation water, desalination for agriculture is more energy intensive than desalination for potable use, and additional post-treatment, such as a second-pass RO process, is required. In this perspective, Shaffer et al. introduce the concept of an integrated FO and RO process for seawater desalination. Process modelling results indicate that the integrated process can achieve boron and chloride water quality requirements for agricultural irrigation while consuming less energy than a conventional two-pass RO process. The challenges to further development of an integrated FO and RO desalination process and its potential benefits beyond energy savings are discussed [29].

FO is an emerging technology for low-energy desalination. Amongst the many other factors, temperature of the DS and FS plays an important role in influencing the performance of the FO process. In the study by Phuntsho et al., the influence of the temperature and the temperature difference on the performance of the FO process was studied in terms of water and solute fluxes. Temperature difference was maintained by elevating only one of the solutions (either DS or FS). The results indicate that water flux on average increases by up to 1.2% for every degree rise in temperature from 25 °C to 35 °C, while this rise is 2.3% from 25 °C to 45 °C. Providing a temperature difference by elevating only the DS also enhanced the water flux significantly, although it was lower than an FO process operated at isothermal conditions. However, elevating only the temperature of FS did not significantly improve the water flux, although it was higher than the FO process operated at 25 °C. This has significant implications in the FO process because the total mass of the DS requiring heat energy is significantly less than
the total FS used. The influences of temperature in the FO process, such as through changes in the thermodynamic properties of the solutions, and the various concentration polarization effects are also explained in detail [30].

The development of high-performance and well-constructed thin-film composite (TFC) hollow-fibre membranes for FO applications is presented by Sukitpaneenit and Chung [31]. The newly developed membranes consist of a functional selective polyamide layer formed by highly reproducible interfacial polymerization on a polyethersulfone (PES) hollow fibre support. Using dual-layer coextrusion technology to design and effectively control the phase inversion during membrane formation, the support was designed to possess desirable macrovoid-free and fully sponge-like morphology. Such morphology not only provides excellent membrane strength, but it has been proven to minimize ICP in an FO process, thus leading to water flux enhancement. The fabricated membranes exhibited relatively high water fluxes of 32–34 L m$^{-2}$ h$^{-1}$ and up to 57–65 L m$^{-2}$ h$^{-1}$ against a pure water feed using 2 M NaCl as the DS tested under the FO and PRO modes respectively, while consistently maintaining relatively low salt leakages below 13 g m$^{-2}$ h$^{-1}$ for all cases. With model seawater solution as the feed, the membranes could display a high water flux up to 15–18 L m$^{-2}$ h$^{-1}$, which is comparable to the best value reported for seawater desalination applications.

Qi et al. [32] focused on the recent developments of FO for desalination and the challenges it faced. Issues discussed include membrane, configuration, DS, integration with post-treatment, and energy and economic evaluation. In spite of the potential advantages of FO, there exist a number of technical barriers that impede FO’s application for water desalination. Further membrane development is needed to give high water flux, low reverse solute flux and material stability over the operating pH range. It is currently not economically viable to use NaCl as the draw solute for municipal-scale FO desalination in view of the solute loss through the membrane. Progress in post-treatment is also needed, because FO cannot stand as a single process, but has to be integrated with a post-treatment to regenerate DS and produce desalinated water that meets the required standards. An FO–RO process is technically feasible, but economically unviable due to energy consideration. In order for FO to compete with the existing RO desalination technology, a breakthrough is necessary in the three key areas of membrane development, selection of appropriate DS, and integration with a suitable post-treatment, and these need to be addressed based on a total system approach.

Thermoresponsive magnetic nanoparticles as a class of smart materials that respond to a change in temperature may be used as a draw solute to extract water from brackish or seawater by FO. A distinct advantage is the efficient regeneration of the draw solute and the recovery of water via heat-facilitated magnetic separation. However, the osmotic pressure attained by this type of DS is too low to counteract that of seawater. Zhao et al. designed an FO DS based on multifunctional Fe$_3$O$_4$ nanoparticles grafted with copolymer poly(sodium styrene-4-sulfonate)-co-poly(N-isopropylacrylamide). The resulting regenerable DS showed high osmotic pressure for seawater desalination. This was enabled by three essential functional components integrated within the nanostructure: (i) an Fe$_3$O$_4$ core that allows magnetic separation of the nanoparticles from the solvent, (ii) a thermoresponsive polymer, poly(N-isopropylacrylamide), that enables reversible clustering of the particles for further improved magnetic capturing at a temperature above its low critical solution temperature, and (iii) a polyelectrolyte, poly(sodium styrene-4-sulfonate), that provides an osmotic pressure that is well above that of seawater [33].

In the rapidly developing shale gas industry, managing produced water is a major challenge for maintaining the profitability of shale gas extraction while protecting public health and the environment. Shafer et al. [34] reviewed the current state of practice for produced water management across the USA and discussed the interrelated regulatory, infrastructure and economic drivers for produced water reuse. Within this framework, they examined the Marcellus shale play, a region in the eastern
USA where produced water is currently reused without desalination. In the Marcellus region, and in other shale plays worldwide with similar constraints, contraction of current reuse opportunities within the shale gas industry and growing restrictions on produced water disposal will provide strong incentives for produced water desalination for reuse outside the industry. The most challenging scenarios for the selection of desalination for reuse over other management strategies will be those involving high-salinity produced water, which must be desalinated with thermal separation processes. Shaffer et al. explore desalination technologies for treatment of high-salinity shale gas produced water, and critically review mechanical vapour compression, membrane distillation and FO as the technologies best suited for desalination of high-salinity produced water for reuse outside the shale gas industry. The advantages and challenges of applying mechanical vapour compression, membrane distillation and FO technologies to produced water desalination are discussed, and directions for future research and development are identified. They find that desalination for reuse of produced water is technically feasible and can be economically relevant. However, because produced water management is primarily an economic decision, expanding desalination for reuse is dependent on process and material improvements to reduce capital and operating costs.

14.6.2 Wastewater Treatment and Water Purification

Wastewater can be used as an alternative source of water and energy. FO shows promise and concern in wastewater treatment and reclamation. FO-wastewater technology has a long way to go before reaching full-scale potential. Lutchmiah et al. carried out research that was part of a sewer mining project aimed at developing a new technological concept by extracting water from sewage by means of FO. FO, in combination with a reconcentration system (e.g. RO), was used to recover high-quality water [35]. Furthermore, the subsequent concentrated sewage (containing an inherent energy content) can be converted into a renewable energy source (i.e. biogas). The effectiveness of FO membranes in the recovery of water from sewage was evaluated. Stable FO water flux values (>4.3 L m$^{-2}$ h$^{-1}$) were obtained with primary effluent (screened, not treated) used as the FS. Fouling of the membrane was also induced and further investigated. Accumulated fouling was found to be apparent, but not irreversible. Sewer mining could lead to a more economical and sustainable treatment of wastewater, facilitating the extraction of water and energy from sewage and changing the way it is perceived: not as waste, but as a resource. Research in the field of FO membrane technology has grown significantly over the last 10 years, but its application in the scope of wastewater treatment has been slower [36]. Drinking water is becoming an increasingly marginal resource. Substituting drinking water for alternate water sources, specifically for use in industrial processes, may alleviate the global water stress. FO has the potential to sustainably treat wastewater sources and produce high-quality water. FO relies on the osmotic pressure difference across the membrane to extract clean water from the feed; however, the FO step is still mostly perceived as a ‘pretreatment’ process. To prompt FO-wastewater feasibility, the focus lies with new membrane developments, DSs to enhance wastewater treatment and energy recovery, and operating conditions. Optimization of these parameters is essential to mitigate fouling, decrease concentration polarization and increase FO performance, issues that are all closely related to one another. Lutchmiah et al.’s review attempts to define the steps still required for FO to reach full-scale potential in wastewater treatment and water reclamation by discussing current novelties, bottlenecks and future perspectives of FO technology in the wastewater sector.

A microbial osmotic fuel cell (MOFC) has an FO membrane situated between the electrodes that enable desalinated water recovery along with power generation. Previous designs have required aerating the cathode chamber water, offsetting the benefits of power generation by power consumption for
aeration. An air-cathode MOFC design was developed by Werner et al. to improve energy recovery, and the performance of this new design was compared with conventional microbial fuel cells containing a cation or anion exchange membrane. Internal resistance of the MOFC was reduced with the FO membrane compared with the ion exchange membranes, resulting in a higher maximum power production (43 W m\(^{-3}\)) than that obtained with an anion exchange membrane (40 W m\(^{-3}\)) or cation exchange membrane (23 W m\(^{-3}\)). Acetate (carbon source) removal reached 90% in the MOFC; however, a small amount of acetate crossed the membrane to the catholyte. The initial water flux declined by 28% from cycle 1 to cycle 3 of operation but stabilized at 4.1 L m\(^{-2}\) h\(^{-1}\) over the final three batch cycles. This decline in water flux was due to membrane fouling. Overall desalination of the draw (synthetic seawater) solution was 35%. These results substantially improve the prospects for simultaneous wastewater treatment and seawater desalination in the same reactor [37].

Global water scarcity and substantial challenges associated with treatment of complex and impaired liquid streams have advanced the development of FO, which can successfully treat and recover water for beneficial reuse. Surging research and advancements in FO, a technology once unable to compete with conventional wastewater treatment processes, have identified its sweet spot: treatment and desalination of complex industrial streams, and especially oil and gas (O&G) exploration and production wastewaters. High salt concentrations, decentralized and transient operations, the presence of free and emulsified hydrocarbons, silts and clays leached from producing formations, and process additives common in O&G drilling wastewater and produced water render many common treatment technologies ineffective. Treatment and reuse of O&G wastewater, and other complex industrial streams, in a cost-effective and environmentally sound manner is critical for sustainable industrial development and to meet increasingly stringent regulations. Coday et al. [38] focused on the successful development and demonstration of FO membrane treatment systems, supported by a review of bench-scale, pilot and demonstration studies on treatment of O&G waste streams, landfill leachates, concentrate from anaerobic digesters, activated sludge in membrane bioreactors, and liquid foods and beverages.

Direct sewage filtration by FO was investigated with the aim of concentrating organic matters in sewage into a small volume of energy source [39]. The results showed that chemical oxidation demand in the feed sewage solution was concentrated by more than 300%. Although a gradual decline in membrane flux with filtration time occurred, a flux of 3–7.4 L m\(^{-2}\) h\(^{-1}\) was still produced satisfactorily. The membrane flux decline was caused by both membrane fouling and the decline of osmotic driving force due to the salinity change in both FS and DS. The membrane fouling analysis indicated that the fouling was mainly attributed to the formation of a cake layer on the membrane surface in both membrane orientations: the active layer facing the feed side (AL–FS) and the active layer facing the DS side (AL–DS). However, AL–FS outperformed AL–DS in terms of membrane flux and fouling. This study may offer new insight into the development of low-energy wastewater treatment processes and energy recovery.

Cooling water plays an important role in maintaining proper temperatures for many industrial processes [40]. To compensate for water loss and to maintain proper cooling water quality, fresh water must be added to the circulating system. Wang et al. evaluated the feasibility of FO using rainwater as the makeup water source for the cooling water. It was determined that the average water flux was 1.75 L m\(^{-2}\) h\(^{-1}\) at 23 °C and decreased gradually to 0.65 L m\(^{-2}\) h\(^{-1}\) after the DS was diluted four times. Although the changes in pH had a small direct effect on the water flux, the existence of sodium hydroxide would promote the dissolution of more carbon dioxide into the feed solution and thus inhibit the permeation process. However, the temperature showed a notable effect on the water flux. By increasing the temperature of the DS from 3 °C to 50 °C, the membrane flux increased approximately 10 times. During the extended operation, no decreases in flux were observed as a result of membrane fouling, even when 50 mg L\(^{-1}\) kaolin or 25 mg L\(^{-1}\) sodium alginate was added to the feed solution.
NASA’s water filtering system uses FO through a sugary solution injected into a semipermeable inner bag, which is nested inside an outer bag. The fluids that need to be filtered pass through the inner bag and its sugary solution, and then through the outer bag, thus getting cleaned. Four to six hours are needed to make a litre of water on Earth [41].

14.6.3 Pharmaceutical Applications

Rejection of four pharmaceutical compounds, carbamazepine, diclofenac, ibuprofen and naproxen, by FO membranes was investigated by Jin et al. [42]. For the first time, the rejection efficiency of the pharmaceutical compounds was compared between commercial CTA-based membranes and TFC polyamide-based membranes. The rejection behaviour was related to membrane interfacial properties, physicochemical characteristics of the pharmaceutical molecules and FS pH. TFC polyamide membranes exhibited excellent overall performance, with high water flux, excellent pH stability and great rejection of all pharmaceuticals investigated (>94%). For commercial CTA-based FO membranes, hydrophobic interaction between the compounds and membranes exhibited a strong influence on their rejection under acidic conditions. The pharmaceuticals rejection was well correlated to their hydrophobicity (log D). Under alkaline conditions, both electrostatic repulsion and size exclusion contributed to the removal of deprotonated molecules. The pharmaceuticals rejection by CTA-HW membrane at pH 8 followed the order diclofenac (99%) > carbamazepine (95%) > ibuprofen (93%) ≈ naproxen (93%). These results can be important for FO membrane synthesis, modification and their application in water purification.

The effects of FS pH and membrane orientation on water flux and the rejection of carbamazepine and sulfamethoxazole were investigated using a bench-scale FO system [43]. Water flux was pH dependent in both membrane orientations. In addition, water flux increased while the specific reverse salt flux and hydrogen ion flux decreased with increasing FS pH. Water flux was lower in the normal FO mode compared with that in the PRO mode because osmotic pressure differential was reduced due to the ICP phenomenon. The rejection of neutral carbamazepine was generally pH independent in both membrane orientations. The rejection of carbamazepine in the PRO mode was lower than that in the FO mode due to the higher concentration gradient caused by concentrative ICP in the porous supporting layer. Steric hindrance was probably the main separation mechanism for the neutral carbamazepine in the FO process. On the other hand, the rejection of sulfamethoxazole was significantly affected by the FS pH in both membrane orientations. Variation in the rejection of sulfamethoxazole could be attributed to the electrostatic repulsion between the negatively charged FO membrane surface and the varying effective charge of the sulfamethoxazole molecule.

14.6.4 Food Processing

Raspberries were processed into juice and concentrated to 45 °Brix by two processes: Osmotek’s cold, direct-osmotic concentration process and conventional evaporative technology. Compositional analyses included pH, titratable acidity, formal value, total anthocyanin pigment, polymeric colour, and nonvolatile acid, sugar and anthocyanin pigment profiles. Concentration by either process resulted in small anthocyanin pigment losses and formation of fumaric acid and small increases of polymerized pigment. The aroma and flavour of the experimental samples and nine commercial concentrates were evaluated in a raspberry drink formulation by a trained descriptive flavour panel. Principal component analysis revealed no significant flavour differences between the single-strength juice, the concentrates and three of the commercial samples [44].
A novel tubular module was used to investigate the direct osmosis concentration process in the case of tomato juice by Petrotos et al. [45]. This module was constructed, according to given specifications, by PCI UK and consisted of an external stainless steel shroud accommodating, internally, a set of two identical RO membrane tubes having no support lengthwise and properly sealed at their ends. The process performance was measured in terms of water permeation flux and its response to changes of the process parameters was experimentally assessed and established. The process parameters which were investigated in the course of this study were the kind of osmotic medium, the viscosity of osmotic medium, the osmotic medium concentration, the juice temperature, the juice flow rate, the juice concentration and the membrane thickness. Sodium chloride brine was found to be the best osmotic medium, among the six which were tried, and this was due to its very low viscosity. The above parameter appears to be of paramount importance regarding the effectiveness of an osmotic medium. Higher osmotic medium concentrations yielded to higher osmotic permeation rates. Increasing the juice temperature was found to markedly increase the permeation flux. However, only a slight enhancement of flux was observed by increasing the juice flow rate. Moreover, higher juice concentrations up to approximately 12 °Brix led to a lowering of the osmotic flux. Finally, as far as the membrane thickness was concerned, a strong trend was revealed for exponential increase of permeation by shifting towards lower membrane thicknesses. This trend, however, needed further investigation as an inadequate number of experimental points were obtained due to the lack of additional membranes.

A follow-up study was carried out by Petrotos et al. using a new tubular direct osmosis module, constructed by PCI UK and equipped with a novel AFC99 membrane 400 μm thick, to investigate the effect of clarifying tomato juice on the rate of direct osmotic concentration. Under virtually the same operating conditions, five respective clarifications of juice were tried, including full, unclarified, tomato juice. The process performance was calculated in terms of permeation flux. In all the experimental runs the osmotic medium was sodium chloride brine (initial concentration ~23% NaCl). A remarkable increase of permeation flux (over 100%) was observed shifting from unclarified to the clarified tomato juice. Clarification was carried out by passing the juice through 35 μm mesh and also by using membranes of molecular weight cut-off 200 000, 100 000 and 25 000 Da in order to obtain the juice ultrafiltrates. It is also worth mentioning that the flux value obtained with 25 000 Da ultrafiltrate appeared to be considerably higher than values reported in experiments carried out by other researchers, where unclarified juice was used, despite the disadvantage of a far thicker membrane being used by Petrotos et al. in their investigation. This specific finding discloses great potential in using a combined low temperature and pressure ultrafiltration and direct osmosis process to produce tomato concentrates [46].

Direct osmosis is a non-thermal membrane process employed for the concentration of fruit juices at ambient temperature and atmospheric pressure, thereby maintaining the organoleptic and nutritional properties of fruit juices. In a study by Babu et al., the concentration of pineapple juice by direct osmosis was explored. An aqueous solution of sucrose (0–40%, w/w)–sodium chloride (0–26%, w/w) combination was investigated as an alternative osmotic agent. The sucrose–sodium chloride combination can overcome the drawback of sucrose (low flux) and sodium chloride (salt migration) as osmotic agents during the direct osmosis process. The effect of the hydrodynamic conditions in the module and feed temperature (25–45 °C) on transmembrane flux was evaluated. For a range of hydrodynamic conditions studied, it was observed that transmembrane flux increases with Reynolds number. The increase in feed temperature resulted in an increase in transmembrane flux. The pineapple juice was concentrated up to a total soluble solids content of 60 Brix at ambient temperature. The effect of direct osmosis process on physico-chemical characteristics of pineapple juice was also studied. The ascorbic acid content was well preserved in the pineapple juice concentrate by direct osmosis process [47].
Concentrating sugar solutions is a common process used in the production of many food products for either dewatering a high-value product or concentrating waste streams prior to disposal. Thermal and pressure-driven dewatering methods are widely used, but they are prohibitively energy intensive, and hence expensive. Osmotically driven membrane processes, like FO, may be a viable and sustainable alternative to these current technologies. Using NaCl as a surrogate DS, Garcia-Castello et al.’s investigation shows that FO processes can lead to sucrose concentration factors that far exceed current pressure-driven membrane technologies, such as RO. For instance, a concentration factor of 5.7 was achieved by FO with a starting sucrose concentration of 0.29 M, compared with reported concentration factors of up to 2.5 with RO. Water fluxes were found to be lower than those commonly obtained in RO, which is a consequence of the significantly higher concentration factors in conjunction with ICP. The latter is a common problem in FO processes that utilize current-generation anisotropic polymeric membranes. Further advances in FO membrane technology would yield higher water fluxes and concentration factors [48].

An FO dewatering process was evaluated by Garcia-Castello and McCutcheon [49] as an alternative for dewatering orange peel press liquor. The press liquor is concentrated by removing water via osmosis into a concentrated ‘DS’ across a polymeric cellulose acetate membrane. For this investigation, the DS consisted of sodium chloride at two different concentrations (2 M and 4 M). These DSs were used to concentrate synthetic press liquor. Concentration factors up to 3.7 resulted when using a 4 M NaCl DS and the synthetic press liquor. Also during this investigation, fouling behaviour was observed and the mechanisms of fouling elucidated through a systematic approach. This approach identified the key components of the press liquor that were primarily responsible for fouling. Calcium, normally a critical component of organic fouling and ubiquitous to press liquor, was found to have little effect on fouling behaviour, likely due to complexation with citric acid also present in the liquor. Pectin was found to be the dominant component contributing to fouling, which was found to reduce permeate flux by as much as 50%. Removing pectin through a pretreatment process would enhance dewatering.

Fruit juices have been traditionally concentrated by multi-stage vacuum evaporation, resulting in a loss of fresh juice flavours, colour degradation and a ‘cooked’ taste due to the thermal effects. The promising alternative is RO concentration. However, it cannot reach concentrations larger than 25–30 °Brix with a single-stage RO system due to high osmotic pressure limitation, which is quite below the value of 45–65 °Brix for standard products obtained by evaporation. Technological advances related to the development of new membranes and improvements in process engineering have been proved to overcome this limitation. New membrane processes, including membrane distillation and osmotic distillation, and integrated membrane processes are still being identified and developed in concentrated fruit juice processing to improve product quality and reduce energy consumption. Recent advances and developments of the use of membrane processes for concentrating fruit juice are reviewed and discussed in the paper by Jiao et al., where major attention is focused on the application of new membrane processes and integrated membrane systems [50].

Vast amounts of liquid food are industrially concentrated in order to reduce storage, packaging, handling and transportation costs. Vacuum evaporation is the predominant method used by the food industry to produce liquid food concentrates, despite serious drawbacks (poor product quality, high energy demand). Petrotos and Lazarides [53] describe the research efforts to develop alternative techniques that could be applied on an industrial scale to overcome the disadvantages of currently used concentration methods. A major part of these attempts is focused on the application of osmotic membrane techniques, namely direct osmosis, membrane distillation and osmotic distillation.

The industrial thermal processing of foods may have a severe impact on the sensorial and nutritional properties of the final product. Membrane technologies have been extensively studied as alternative processes. FO is a promising membrane technology to be used in food industries. The only driving
force of the process is the osmotic pressure difference between the two solutions that flow in countercurrent mode on opposite sides of a permeable membrane. Thus, the main advantages of FO, compared with both thermal and conventional membrane processing, include low hydraulic pressure, low treatment temperature, low fouling tendency, high solids content processing capability and easy scale-up. A detailed, up-to-date summary of potential FO applications for concentrating liquid foods is presented in the review article by Sant’Anna et al. The effect of the main process parameters on the filtration performance and their impact on the sensorial and nutritional factors of the final product are described and discussed for a broad spectrum of foods [52].

The implementation of osmotic treatments of plant or animal materials in concentrated solutions (also called dehydration–impregnation by soaking process) presents a critical factor due to the management of concentrated sugar/salt solutions. In particular, some process steps must be evaluated in order to assess economic, environmental and technological impacts of the process itself. In the paper by Rosa and Giroux the critical points of the solution management have been criticized taking into account the items related to the solution changes during the process, the possibility to restore or reuse the solution itself and the relationship between the food ongoing to dehydration and the solution properties [53].

The patent of Herron et al. discloses an osmotic concentration cell wherein the flow chamber of the osmotic concentration cell has a continually changing flow path to provide a region of high turbulence to a semipermeable membrane defining the flow chamber. High turbulence at a first semipermeable membrane interface significantly reduces membrane fouling during osmotic concentration and allows for concentration of products with high suspended solids content. The inventive osmotic concentration cell can be used for a variety of purposes, including, for example, producing low-alcohol wine, concentrating a thin wine into a premium wine, concentrating a low-quality grape juice into a higher quality grape juice for fermenting a more premium wine, concentrating various fruit or vegetable juices, and concentrating various beverages, such as teas or coffee [54].

14.6.5 Power Generation

A model has been developed for obtaining the projected performance of membranes in PRO from direct osmosis and RO measurements. The model shows that concentration polarization within the porous substrate of the membrane markedly lowers the water flux under PRO conditions. The model has been used along with experimental data obtained with a variety of RO membranes to project PRO performance with several water–brine sources. Some literature data on PRO have been similarly examined. Based on these results and a simple economic analysis it was concluded that membranes with significantly improved performance will be needed if PRO is to become an economically feasible method for power generation using seawater–fresh water as the salinity gradient resource. However, the economics of a brine–fresh water system appear competitive with conventional power generation technologies.

In principle a very large quantity of electric power could be produced by the worldwide application of PRO to the osmotic pair river water–seawater. The study was limited to spiral modules (i.e. originally flat sheet membranes). Within some limitations in this process, the key parameters were found to be twofold. First was the $K$ term in PRO. This is the resistance to salt diffusion in the porous substructure and support fabric region of the membrane and must be as low as possible because an increase in $K$ decreases permeate flux virtually exponentially. Second was the size of the PRO plant, characterized by the flow rate of the river utilized. The larger the PRO plant, the more important the economy-of-scale factor becomes in minimizing the energy and power costs. A key assumption in the comparative plant cost calculations was that half of such costs would be independent of
changes in plant flux and the other half proportional to it. Based on previous PRO tests and some optimism, $K$ terms of 10 and 0 were considered. A ‘moderate’ river flow rate of $3 \times 10^6$ m$^3$ day$^{-1}$ was considered, as well as a ‘large’ river size flow rate of $1500 \times 10^6$ m$^3$ day$^{-1}$ for the Mississippi. The following was found. A ‘moderate’ flow rate PRO plant with an optimistically low $K$ term of 10 days$^{-1}$ (permeate flux 0.29 m$^3$ m$^{-2}$ day$^{-1}$) would give unacceptably high energy and power costs as would a moderate plant with $K = 0$ (flux 0.725 m$^3$ m$^{-2}$ day$^{-1}$). A Mississippi river plant with $K = 10$ would produce marginal energy and power costs (i.e. higher than expected from conventional existing power plants and perhaps acceptable under certain circumstances), but a $K$ value of zero would produce adequately low energy and power costs. If the specific plant capital cost estimate could be reduced from $1000$ to $500$ per daily cubic metre of permeate, as reported by some RO investigators, all PRO costs would be reduced by about half, thus rendering the moderate flow rate PRO plant with $K = 0$ marginally acceptable and both Mississippi PRO plants acceptable in terms of low energy and power cost [55].

The mixing of freshwater and seawater where a river flows into the salty ocean releases large amounts of energy. Can this energy be exploited for commercial large-scale power production? Aaberg described a technique that could harness significant amounts of energy in this context [56].

A novel method of converting thermal energy into mechanical work is presented, using semipermeable membranes to convert osmotic pressure into electrical power. This method, a closed-cycle PRO process known as an osmotic heat engine, uses a concentrated ammonia–carbon dioxide DS to create high osmotic pressures which generate water flux through a semipermeable membrane against a hydraulic pressure gradient. The depressurization of the increased DS volume in a turbine produces electrical power. The process is maintained in steady-state operation through the separation of the diluted DS into a reconcentrated DS and (nearly) deionized water working fluid, both for reuse in the engine. The use of deionized water working fluid has been shown to allow for high membrane water flux and efficient mass transport, as ICP effects are eliminated. Modelling of the engine indicates that membrane power density may exceed 200 W m$^{-2}$, given appropriate operating conditions. The thermal efficiency of the engine is predicted to approach a maximum of 16% of Carnot efficiency (maximum theoretical engine efficiency), with practical efficiencies most likely in the range of 5–10% of Carnot efficiency. The temperature of heat used for the engine may be very low (40 °C with a 20 °C ambient temperature), allowing for the production of potentially low-cost, carbon-neutral power from waste heat, low-temperature geothermal reservoirs, or other non-combustion thermal energy sources. This combination of a highly concentrated NH$_3$–CO$_2$ DS and a deionized working fluid may allow for highly effective power generation from osmotic pressure gradients [57].

Water has always been crucial to combustion and hydroelectric processes, but it could become the source of power in membrane-based systems that capture energy from natural and waste waters. Two processes are emerging as sustainable methods for capturing energy from seawater: PRO and reverse electrodialysis. These processes can also capture energy from waste heat by generating artificial salinity gradients using synthetic solutions, such as thermolytic salts. A further source of energy comes from organic matter in wastewaters, which can be harnessed using microbial fuel-cell technology, allowing both wastewater treatment and power production [58].

PRO is a novel membrane process to produce energy. PRO has the potential to convert the osmotic pressure difference between fresh water (i.e. river water) and seawater to electricity. Moreover, it can recover energy from highly concentrated brine in seawater desalination. Nevertheless, relatively little research has been undertaken for fundamental understanding of the PRO process. In this study, the characteristics of the PRO process were examined using a proof-of-concept device. FO, RO and nanofiltration membranes were compared in terms of flux rate and concentration polarization ratio. The results indicated that the theoretical energy production by PRO depends on the membrane type as
well as operating conditions (i.e. back pressure). The FO membrane had the highest energy efficiency, while the nanofiltration membrane had the lowest efficiency. However, the energy production rate was low due to high ICP in the PRO membrane. This finding suggests that the control of the ICP is essential for practical application of PRO for energy production [59].

14.7 Improvement of Forward Osmosis Membrane Performance

14.7.1 Improvement of Forward Osmosis Membrane

As described earlier, it is important to improve the support layer to bring about a reduction of the ICP to develop a high-efficiency FO membrane. As for the direction of current FO membrane development, this is aimed at high water flux by reduction of the ICP. The future direction should provide the most suitable FO membrane depending on the process to which it will be applied. This leads to miniaturization of the membrane module to raise water permeation performance per unit area by reducing ICP. However, ICP in the support layer reduces the efficiency of the water permeation performance that an active layer should originally show essentially. Therefore, one should not just pay attention to the improvement of the support layer, as development of the active layer with both high water and low salt permeability is important, like optimization of the structure of the support layer.

Yang et al. [60] demonstrated the prospect of dual-layer polybenzimidazole (PBI)–PES nanofiltration hollow-fibre membranes in the FO process for water production. The state of the art for dual-layer membrane fabrication via coextrusion technology could produce the resultant membrane consisting of an ultrathin selective skin, fully porous water channels underneath and a microporous sponge-like support structure. Together with its sharp pore size distribution and self-charged PBI selective membrane surface, the dual-layer hollow-fibre FO membrane can achieve a water flux as high as 33.8 L m$^{-2}$ h$^{-1}$ and a salt flux less than 1.0 g m$^{-2}$ h$^{-1}$ at a room temperature of 23°C using 5 M MgCl$_2$ as the DS. A comprehensive literature review of previous efforts on identifying suitable membranes and appropriate DSs in the FO process for water production and seawater desalination was also conducted. It shows that the water fluxes of the dual-layer hollow-fibre FO membrane developed in this work utilizing MgCl$_2$ as the DSs generally surpasses those FO processes utilizing RO membranes and is comparable to most FO processes using commercial FO membrane and employing other salts or sugar instead of MgCl$_2$ as the DSs.

Osmotically driven membrane processes have gained renewed interest in recent years and they might become a potential solution for the world’s most challenging problems of water and energy scarcity, note Klaysom et al. [61]. Though the concept of utilizing osmotic pressure difference between high- and low-salinity streams across semipermeable membranes has been explored for several decades, lack of optimal membranes and DSs has hindered competition between FO and PRO with existing water purification and power generation technologies respectively. Driven by growing global water scarcity and by energy cost and negative environmental impacts, novel membranes and DSs are being developed for osmotically driven membrane processes, mass and heat transfer in osmotic process are becoming better understood, and new applications of osmotically driven membrane processes are emerging. Therefore, osmotically driven membrane processes might become promising green technologies to provide clean water and clean energy from abundantly available renewable resources. Klaysom et al.’s review focuses primarily on new insights into osmotic membrane transport mechanisms and on novel membranes and DSs that are currently being developed. Furthermore, the effects of operating conditions on the overall performance of osmotic membranes are highlighted and future perspectives presented.
There has been a resurgence of interest in FO as a potential means of desalination, dewatering and in PRO, which Sidney Loeb was advocating over three decades ago. Chou et al. describe the characteristics and potential applications of a newly developed FO hollow-fibre membrane, which was fabricated by interfacial polymerization on the inner surface of a PES hollow fibre. This FO membrane presents excellent intrinsic separation properties, with a water flux of 42.6 L m$^{-2}$ h$^{-1}$ using 0.5 M NaCl as the DS and deionized water as the feed with the active layer facing the DS orientation at 23 °C. The corresponding ratio of salt flux to water flux was only 0.094 g L$^{-1}$, which is superior to all other FO membranes reported in the open literature. To evaluate different application scenarios, various NaCl solutions (500 ppm (8.6 mM), 1 wt% (0.17M) and 3.5 wt% (0.59M)) were used as the feed water to test the performance of the FO membrane. The membrane achieved a water flux of 12.4 L m$^{-2}$ h$^{-1}$ with 3.5 wt% NaCl solution as the feed and 2 M NaCl as the DS, suggesting it has good potential for seawater desalination [19].

In regard to capturing energy from natural and waste waters, the papers by Logan and Elimelech [58] and Kim et al. [59] discussed in Section 14.6.5 are also pertinent here.

Osmosis is a natural phenomenon and exists widely from the salinity gradient between seawater and fresh water. This green energy can be captured using PRO. A potential energy of 2.5 TW is available globally from rivers flowing into the sea. Membrane is the key component, and it has been the main limitation for this technique. The most challenging problem is the ICP, which reduces the water flux by up to 80%. Wang et al. review the most critical and recent publications on membrane fabrication (e.g. composite membrane, hollow-fibre membrane). A summary and perspectives are given in order to prepare high-performance membranes [62].

Valladares et al. [63] focused on the present status of FO niches in two main areas: seawater desalination and wastewater reuse. Specific applications for desalination and impaired-quality water treatment and reuse are described, as well as the benefits, advantages, challenges, costs and knowledge gaps on FO hybrid systems are discussed. FO can play a role as a bridge to integrate upstream and downstream water treatment processes, to reduce the energy consumption of the entire desalination or water recovery and reuse processes, thus achieving a sustainable solution for the water–energy nexus. FO hybrid membrane systems showed to have advantages over traditional membrane process like high-pressure RO and nanofiltration for desalination and wastewater treatment: (i) chemical storage and feed water systems may be reduced for capital, operational and maintenance cost, (ii) water quality is improved, (iii) reduced process piping costs, (iv) more flexible treatment units and (v) higher overall sustainability of the desalination and wastewater treatment process. Nevertheless, major challenges make FO systems not yet a commercially viable technology, the most critical being the development of a high-flux membrane, capable of maintaining an elevated salt rejection and a reduced ICP effect, and the availability of appropriate DSs (cost effective and nontoxic), which can be recirculated via an efficient recovery process. This review article highlights the features of hybrid FO systems and specifically provides the state-of-the-art applications in the water industry in a novel classification and based on the latest developments toward scaling up these systems.

An FO desalination pilot plant was built in Yale University in New Haven, Connecticut, and a novel desalination process investigated. This technology promised lower energy costs, higher recovery and less brine discharge than conventional desalination systems [64].

Zhong et al. [65] investigated a new approach to fabricate TFC hollow-fibre membranes via interfacial polymerization for FO applications. Different degrees of sulfonation of polyphenylenesulfone (PPSU) were adopted as membrane substrates to investigate their impact on water flux. It was established that the degree of sulfonation plays a role in both creating a macrovoid-free structure and inducing hydrophilicity to bring about higher water fluxes. The fabricated membranes exhibit extremely high water fluxes of 30.6 L m$^{-2}$ h$^{-1}$ and 82.0 L m$^{-2}$ h$^{-1}$ against a pure water feed using 2.0 M NaCl as the
DS tested under FO and PRO modes respectively, while maintaining low salt reverse fluxes below 12.7 g m$^{-2}$ h$^{-1}$. The structural parameter $S$ displayed remarkable decreases of up to 4.5 times as the membrane substrate was switched from a nonsulfonated one to a sulfonated one. In addition, the newly developed TFC-FO membranes containing 1.5 mol% sulfonated PPSU in the substrate achieved a water flux of 22 L m$^{-2}$ h$^{-1}$ in seawater desalination using a 3.5 wt% NaCl model solution and 2.0 M NaCl as the DS under the PRO mode. To the best of their knowledge, this value was the highest ever reported for seawater desalination using flat and hollow-fibre FO membranes. The use of sulfonated materials in the FO process opens up a frontier for sustainable and efficient production of potable water.

### 14.7.2 Improvement of Draw Solution

The requirements required for the DS are as follows: (1) high osmotic pressure to give high driving force, (2) low reproduction energy for dilute DS, (3) low permeability of solute in DS because the membrane performance is decreased by ICP when the solute in DS permeates through the FO membrane, (4) non-deterioration characteristics for the FO membrane, and (5) nontoxic in the drinking water generation by the FO method.

The FO process is constructed of an FO membrane, an FO module, a DS and a reproduction process of the DS. Therefore, improvement of the DS is one of the important points, and reproduction of the DS likewise. McGinnis and Elimelech examined the energy requirements of ammonia–carbon dioxide FO desalination as predicted by the use of chemical process modelling software (HYSYS). The FO process was modelled using single or multiple distillation columns to separate DS solutes from the product water for solute recycling within the FO system. Thermal and electrical energy requirements of the process were calculated, as well as a combined term for equivalent electrical work. The results of the simulations were compared with the energy requirements of current desalination technologies. Energy savings of FO compared with current technologies, on an equivalent work basis, were projected to range from 72% to 85%. FO desalination is in an early stage of its development, and several areas of future work promise opportunities to improve its energy utilization and cost [66].

The feasibility of bilayer polymer hydrogels as a draw agent in the FO process were investigated by Razmjou et al. [67]. The dual-functionality hydrogels consist of a water-absorptive layer (particles of a copolymer of sodium acrylate and N-isopropylacrylamide) to provide osmotic pressure, and a dewatering layer (particles of N-isopropylacrylamide) to allow the ready release of the water absorbed during the FO drawing process at lower critical solution temperature (32 °C). The use of solar concentrated energy as the source of heat resulted in a significant increase in the dewatering rate as the temperature of the dewatering layer increased to its lower critical solution temperature more rapidly. Dewatering flux rose from 10 to 25 L m$^{-2}$ h$^{-1}$ when the solar concentrator increased the input energy from 0.5 to 2 kW m$^{-2}$. Thermodynamic analysis was also performed to find out the minimum energy requirement of such a bilayer hydrogel-driven FO process. This study represented a significant step forward toward the commercial implementation of a hydrogel-driven FO system for continuous production of fresh water from saline water or wastewaters.

The effects of draw agent, feed concentration and membrane on the process performance were systematically examined by Li et al. [68]. Their results showed that the incorporation of carbon filler particles in polymer hydrogels led to enhanced swelling ratios of the draw agents and thus higher water fluxes in the FO process. The composite polymer hydrogel particles of sizes ranging from 100 to 200 μm as draw agents induced greater water fluxes in FO desalination compared with those with...
larger particle sizes (500–700 μm). Similar to other types of draw solutes, as the salt concentration in the feed increased, the water flux created by the polymer hydrogel draw agent decreased; the use of a CTA FO membrane resulted in higher water flux compared with the use of a polyamide composite RO membrane.

Cai et al. [69] reported a study exploring new materials and a new concept for temperature-driven quasi-continuous desalination using hydrogels as draw agents in FO. This concept was enabled by the design and preparation of thermally responsive hydrogels having a semi-interpenetrating network (semi-IPN) structure. Thermally responsive semi-IPN hydrogels were synthesized by polymerization of N-isopropylacrylamide (NIPAm) in the presence of poly(sodium acrylate) or poly(vinyl alcohol). Their functions as draw agents in FO were systematically studied and compared with hydrogels prepared from the poly-NIPAm homopolymer or the NIPAm–sodium acrylate copolymer. While the semi-IPN hydrogels displayed the desirable balanced thermally responsive swelling and dewatering behaviour, the NIPAm–sodium acrylate copolymer hydrogels were found to have poor dewatering behaviour, making them unsuitable for a continuous temperature-driven desalination process. At 40 °C, the semi-IPN hydrogels rapidly release nearly 100% of the water absorbed during the FO drawing process carried out at room temperature. Results clearly indicate the potential of semi-IPN hydrogels as semi-solid draw agents in the FO process, in which quasi-continuous desalination could be achieved by cyclic heating and cooling within a moderate temperature change.

Ge and Chung [70] reported a new class of draw solutes from hydroacid complexes, as shown in Figure 14.6. With hydroacid complexes as draw solutes in FO, superior performance is achieved in terms of high water fluxes and negligible reverse solute fluxes. The characteristics of expanded configurations, abundant hydrophilic groups and ionic species are essential for hydroacid complexes as competent draw solutes.

FO has emerged as one of potential technologies to mitigate clean water and energy shortage. It produces both clean water and energy by employing draw solutes to induce osmotic gradients across semipermeable membranes as the driving force for water production and power generation. Ideally, the semipermeable membrane performs as a barrier that allows only water to pass through but rejects all others. However, in reality, depending on the draw solute’s chemical properties and physical structure, the reverse flux of draw solutes may take place across FO membranes, which not only results in a lower effective osmotic driving force but also facilitates fouling. In addition, the asymmetric structure of FO membranes and the transport resistance of draw solutes within the FO membranes cause concentration polarization and lower the water flux. Furthermore, the regeneration of draw solutes from diluted DSs and the production of clean water might be energy intensive if inappropriate draw solutes and recycle processes are utilized. Therefore, in Ge et al. aimed to give a comprehensive review on the progress of DS for FO processes. An assessment on the advantages and limitations of the existing draw solutes was made. Various FO integrated processes for water production and draw solute regeneration are exemplified. They also highlight the challenges and future research directions for the molecular design of better draw solutes [71].

A new type of biocompatible draw solute, Na⁺-functionalized carbon quantum dots (Na_CQDs) with ultra-small size and rich ionic species, in FO was developed for seawater desalination by Guo et al. The aqueous dispersion of Na_CQDs demonstrates a high osmotic pressure, which allows high FO water flux and negligible reverse solute permeation [72].
Ge and co-workers proved the advantages of cupric and ferric hydroacid complexes as draw solutes in forward osmosis in terms of high water fluxes, negligible reverse solute fluxes and easy recovery [70,71]. They then explored cobaltous hydroacid complexes as draw solutes and compared them with a ferric hydroacid complex to study the factors influencing their FO performance [73]. The solutions of the cobaltous complexes produce high osmotic pressures due to the presence of abundant hydrophilic groups. These solutes are able to dissociate and form a multi-charged anion and Na⁺ cations in water. In addition, these complexes have expanded structures which lead to negligible reverse solute fluxes and provide relatively easy approaches in regeneration. These characteristics make the newly synthesized cobaltous complexes appropriate as draw solutes. The FO performance of the cobaltous and ferric–citric acid (Fe–CA) complexes were evaluated respectively through cellulose acetate membranes, thin-film composite membranes fabricated on PES supports (referred as TFC-PES), and PBI and PES dual-layer hollow-fibre membranes. Under the conditions of deionized water as the feed and facing the support layer of TFC-PES FO membranes (PRO mode), DSs at 2.0 M produced relatively high water fluxes of 39–48 L m⁻² h⁻¹ with negligible reverse solute fluxes. A water flux of 17.4 L m⁻² h⁻¹ was achieved when model seawater of 3.5 wt% NaCl replaced deionized water as the feed and 2.0 M Fe–CA as the DS under the same conditions. The performance of these hydroacid complexes surpasses those of the synthetic draw solutes developed in recent years. This observation, along with the relatively easy regeneration, makes these complexes very promising as a novel class of draw solutes.

Lower critical solution temperature phase transition of glycol ether (GE)–water mixtures induces an abrupt change in osmotic pressure driven by a mild temperature change. The temperature-controlled osmotic change was applied for the FO desalination by Nakayama et al. Among three GEs evaluated, di(ethylene glycol) n-hexyl ether (DEH) was selected as a potential FO draw solute. A DEH–water mixture with a high osmotic pressure could draw fresh water from a high-salt feed solution such as seawater through a semipermeable membrane at around 10 °C. The water-drawn DEH–water mixture was phase separated into a water-rich phase and a DEH-rich phase at around 30 °C. The water-rich phase with a much reduced osmotic pressure released water into a low-salt solution, and the DEH-rich phase was recovered into the initial DEH–water mixture. The phase separation behaviour, the residual GE concentration in the water-rich phase, the osmotic pressure of the DEH–water mixture, and the osmotic flux between the DEH–water mixture and salt solutions were carefully analysed for FO desalination. The liquid–liquid phase separation of the GE–water mixture driven by the mild temperature change between 10 and 30 °C is very attractive for the development of an ideal draw solute for future practical FO desalination [74].

14.7.3 Reproduction of Draw Solution

Membrane technology is one of the advance wastewater treatment processes with an aim for treated wastewater reuse. FO is the membrane process in which the transmembrane transport is driven by osmotic pressure of the DS. Ammonium bicarbonate is one of the chemicals that can be utilized as a DS because of its high solubility and osmotic pressure properties. A recovery concentration unit in the FO desalination system is necessary for DS reuse. In the Traisupachok et al. study, the thermal process was chosen for ammonium bicarbonate removal. Heated was provided to the synthetic DS with initial ammonium bicarbonate concentration between 0.05 and 0.5 M, and then the ammonium bicarbonate concentration was measured on an hourly basis. The result indicated that heat cannot completely remove ammonium bicarbonate. The addition of air bubbles can increase the removal efficiency to 40–70%. The optimal heating time is 5 h and the additional heating does not significantly affect the removal efficiency. Ammonium bicarbonate is removed as CO₂ and NH₃ gas, which can be recovered at 84.3% efficiency of removal [75].
14.8 Fouling in Forward Osmosis

The growing attention to FO membrane processes from various disciplines raises the demand for systematic research on FO membrane fouling. Mi and Elimelech [76,77] investigated the role of various physical and chemical interactions, such as intermolecular adhesion forces, calcium binding, initial permeate flux and membrane orientation, in organic fouling of FO membranes. Alginate, bovine serum albumin and Aldrich humic acid (AHA) were chosen as model organic foulants. Atomic force microscopy was used to quantify the intermolecular adhesion forces between the foulant and the clean or fouled membrane in order to better understand the fouling mechanisms. A strong correlation between organic fouling and intermolecular adhesion was observed, indicating that foulant–foulant interaction plays an important role in determining the rate and extent of organic fouling. The fouling data showed that FO fouling is governed by the coupled influence of chemical and hydrodynamic interactions. Calcium binding, permeation drag and hydrodynamic shear force are the major factors governing the development of a fouling layer on the membrane surface. However, the dominating factors controlling membrane fouling vary from foulant to foulant. With stronger intermolecular adhesion forces, hydrodynamic conditions for favourable foulant deposition leading to cake formation are more readily attained. Before a compact cake layer is formed, the fouling rate is affected by both the intermolecular adhesion forces and hydrodynamic conditions. However, once the cake layer forms, all three foulants have very similar flux decline rates, and further changes in hydrodynamic conditions do not influence fouling behaviour.

FO is a membrane process that uses the natural osmotic pressure of a concentrated DS to extract pure water from a feed stream. The attraction of the FO process is that it uses dense membranes, while operating at ambient pressure. This means that the FO process could potentially produce high-quality water with lower energy consumption, compared with the other desalination or reclamation processes. As FO does not entail the use of hydraulic pressure, FO has been hypothesized to have lower fouling propensity than pressure-driven membrane processes. Membrane fouling has a significant impact on the operational sustainability and economics of the process. Lay et al. examined the possible contributing factors to the slower flux decline observed in FO experiments based on a combined experimental and modelling approach. It was found that these factors could include low water fluxes, use of hydrophilic and smooth membranes, and the effect of ICP that is inherent to FO. It was also found that the transmission of draw solutes from the DS into the feed can have a significant effect on FO performance [78].

FO is a membrane separation technology that has been studied in recent years for application in water treatment and desalination. It can best be utilized as an advanced pretreatment for desalination processes such as RO and nanofiltration to protect the membranes from scaling and fouling. Hancock et al. investigated the rejection of trace organic compounds (TOrCs) such as pharmaceuticals, personal care products, plasticizers and flame-retardants by FO and a hybrid FO–RO system at both the bench and pilot scales. More than 30 compounds were analysed, of which 23 nonionic and ionic TOrCs were identified and quantified in the wastewater effluent studied. The results revealed that almost all TOrCs were highly rejected by the FO membrane at the pilot scale, while rejection at the bench scale was generally lower. Membrane fouling, especially under field conditions when wastewater effluent is the FO feed solution, plays a substantial role in increasing the rejection of TOrCs in FO. The hybrid FO–RO process demonstrated that the dual barrier treatment of impaired water could lead to more than 99% rejection of almost all TOrCs that were identified in reclaimed water [79].

As FO gains attention as an efficient technology to improve wastewater reclamation processes, it is fundamental to determine the influence of fouling in the rejection of emerging contaminants (micropollutants). The study by Valladares et al. focused on the rejection of 13 selected micropollutants,
spiked in a secondary wastewater effluent, by an FO membrane, using Red Sea water as the DS, differentiating the effects on the rejection caused by a clean and fouled membrane. The resulting effluent was then desalinated at low pressure with an RO membrane, to produce a high-quality permeate and determine the rejection with a coupled FO–low-pressure RO (FO–LPRO) system. When considering only FO with a clean membrane, the rejection of the hydrophilic neutral compounds was between 48.6 and 84.7%, for the hydrophobic neutrals the rejection ranged from 40.0 to 87.5%, and for the ionic compounds the rejections were between 92.9 and 96.5%. With a fouled membrane, the rejections were 44.6–95.2%, 48.7–91.5% and 96.9–98.6% respectively. These results suggest that, except for the hydrophilic neutral compounds, the rejection of the micropollutants is increased by the presence of a fouling layer, possibly due to the higher hydrophilicity of the FO fouled membrane compared with the clean one, the increased adsorption capacity of hydrophilic compounds and reduced mass transport capacity, membrane swelling, and the higher negative charge of the membrane surface, related to the foulants composition, mainly natural organic matter acids (carboxylic radicals) and polysaccharides or polysaccharide-like substances. However, when coupled with RO, the rejections in both cases increased above 96%. The coupled FO–LPRO system was an effective double barrier against the selected micropollutants [80].

Freshwater shortage is one of the most pressing global issues. FO desalination technology is emerging for freshwater production from saline water, which is potentially more energy efficient than the current RO process. However, the lack of a suitable draw solute is the major hurdle for commercial implementation of the FO desalination technology. Razmjou et al. explored magnetic-field-induced heating for the purpose of developing a more effective way to recover water from swollen hydrogel draw agents. The composite hydrogel particles were prepared by copolymerization of sodium acrylate and N-isopropylacrylamide in the presence of magnetic nanoparticles (γ-Fe₂O₃, <50 nm). The results indicate that the magnetic heating is an effective and rapid method for dewatering of hydrogels by generating the heat more uniformly throughout the draw agent particles, and thus a dense skin layer commonly formed via conventional heating from the outside of the particle is minimized. The FO dewatering performance is affected by the loading of magnetic nanoparticles and magnetic field intensity. Significantly enhanced liquid water recovery (53%) is achieved under magnetic heating, as opposed to only around 7% liquid water recovery obtained via convection heating. Their study shows that magnetic heating is an attractive alternative stimulus for the extraction of highly desirable liquid water from the draw agent in the polymer hydrogel-driven FO process [81].

FO indirect desalination systems integrate wastewater recovery with seawater desalination. Niche applications for FO systems have been reported, due to the demonstrated advantages compared with conventional high-pressure membrane processes such as nanofiltration and RO [82]. Among them, wastewater recovery has been identified to be particularly suitable for practical applications. However, biofouling in FO membranes has rarely been studied in applications involving wastewater effluents. Feed spacers separating the membrane sheets in crossflow systems play an important role in biofilm formation. The objective of Valladares et al.'s study was to determine the influence of feed spacer thickness (28, 31 and 46 mil) on biofouling development and membrane performance in an FO system, using identical cross-flow cells in parallel studies. Flux development, biomass accumulation, fouling localization and composition were determined and analysed. For all spacer thicknesses, operated at the same feed flow and the same run time, the same amount of biomass was found, while the flux reduction decreased with thicker spacers. These observations are in good agreement with biofouling studies for RO systems, considering the key differences between FO and RO. Their findings contradict previous crossflow studies on particulate/colloidal fouling, where higher crossflow velocities improved system performance. Thicker spacers reduced the impact of biofouling on FO membrane flux.
Fertilizer-drawn FO (FDFO) desalination was recently studied by Valladares et al. as one feasible application of FO for irrigation [83]. The potential of membrane scaling in the FDFO process was investigated during the desalination of brackish groundwater. While most fertilizers containing monovalent ions did not result in any scaling when used as an FO DS, diammonium phosphate (DAP) resulted in significant scaling, which contributed to severe flux decline. Membrane autopsy using scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray diffraction analysis indicated that the reverse diffusion of DAP from the DS to the FS was primarily responsible for scale formation during the FDFO process. Physical cleaning of the membrane with deionized water at varying crossflow velocities was employed to evaluate the reversibility of membrane scaling and the extent of flux recovery. For the membrane scaled using DAP as DS, 80–90% of the original flux was recovered when the crossflow velocity for physical cleaning was the same as the crossflow velocity during FDFO desalination. However, when a higher crossflow velocity or Reynolds number was used, the flux was recovered almost completely, irrespective of the DS concentration used. This study underscores the importance of selecting a suitable fertilizer for FDFO desalination of brackish groundwater to avoid membrane scaling and severe flux decline.

References


Pervaporation

15.1 Principle of Pervaporation

Pervaporation was coined as a word of the combination of ‘permeation’ of the permeate through the membrane and its ‘evaporation’ into the vapour phase based on the two basic steps of the process.

Pervaporation membranes are generally composite structures which consist of a dense layer (active or permselective layer) and a porous layer (support layer). Those membranes are effective for separation of organic liquid mixtures with high osmotic pressure, can be applied to the separation and concentration of azeotropic mixtures, close-boiling-point mixtures and structural isomers, and can be used for the removal of certain components in equilibrium reactions.

Figure 15.1 shows the principle of pervaporation. In this separation process, when a liquid mixture is fed to the upstream side of a membrane and the downstream side is evacuated, a component in the feed mixture can preferentially permeate through the membrane. In a pervaporation process, differences in the solubility of permeants into the membrane, the diffusivity of permeants in the membrane, and the relative volatility of permeants can influence the permeability and selectivity [1–4].

In general, pervaporation exhibits the following characteristics [5–8]:

1) Selective transport across a non-porous membrane is achieved by a three-step process consisting of solution, diffusion and evaporation, as shown in Figure 15.1.
2) Because the driving force for permeation is the vapour pressure for each component rather than total system pressure, this process is effective for separation of organic liquid mixtures with high osmotic pressure.
3) Pervaporation can be applied to the separation and concentration of mixtures that are difficult to separate by distillation. For example, it is useful for the separation of azeotropic mixtures, close-boiling-point mixtures and structural isomers.
4) Pervaporation can be used for the removal of certain components in equilibrium reactions.
5) Polymer membrane compaction, a frequent problem in high-pressure gas separations, is not encountered in pervaporation because the feed pressure is typically low.

This pervaporation process can be applied to the dehydration of organic liquids, concentration of alcohols, removal volatile organic compounds (VOCs) in aqueous solutions, separation of organic–organic mixtures, and facilitation of chemical reactions such as the esterification and analysis of liquid materials.
15.2 Fundamental Analysis of Pervaporation

15.2.1 Fundamental Permeation Equation

The permeation rate $Q_i$ of component $i$ is expressed by Fick's first law as follows [6,7]:

$$Q_i = -D(C_i) \frac{dC_i}{dx}$$  \hspace{1cm} (15.1)

where $D(C_i)$ is the diffusion coefficient, $C_i$ is the concentration of component $i$ in the membrane and $x$ is the distance from the membrane–feed-solution interface.

Fick's second law of diffusion is

$$\frac{dC_i}{dt} = D(C_i) \frac{d}{dx} \frac{dC_i}{dx} = D(C_i) \frac{d^2C_i}{dx^2}$$  \hspace{1cm} (15.2)

where $D(C_i)$ is given by

$$D(C_i) = D_0 \exp(\gamma C_i)$$  \hspace{1cm} (15.3)

Here, $D_0$ is the infinite dilution diffusion coefficient and $\gamma$ is a measure of membrane plasticization that is dependent on temperature.

At steady-state permeation, the boundary conditions are $dC_i/dt = 0$, $C_i = C_1$ at $x = 0$, $C_i = C_2$ at $x = l$. When Equation 15.3 is inserted in Equation 15.2 and is integrated, we obtain

$$Q_i = \frac{D_0}{\gamma l} (\exp \gamma C_1 - \exp \gamma C_2)$$  \hspace{1cm} (15.4)
The concentration distribution is expressed as follows:

\[ C_i = \frac{1}{\gamma} \ln \left[ \frac{\exp \gamma C_1 - \frac{x}{l(\exp \gamma C_1 - \exp \gamma C_2)}}{\exp \gamma C_1 - \exp \gamma C_2} \right] \]  

(15.5)

If the concentration at the boundary of the feed solution and the membrane is equilibrated thermodynamically, the following equations hold:

\[ C_1 = C^*(p^0) \]  

(15.6)

\[ C_2 = C^*(p_2) \]  

(15.7)

where \( C^* \) is a pressure-dependent function, \( p^0 \) is saturated vapour pressure and \( p_2 \) is the vapour pressure on the downstream side of the membrane.

Using these expressions, Equations 15.4 and 15.5 may be rewritten with \( p^0 \) and \( p_2 \). At the same time, the permeability \( P_i \) is derived as follows:

\[ P_i = \frac{Q_i l}{\Delta p} = \frac{D_0}{\gamma \Delta p} (\exp \gamma C_1 - \exp \gamma C_2) \]  

(15.8)

where \( \Delta p = p^0 - p_2 \). When Equations 15.6 and 15.7 obey Henry’s law, \( C^*(p) = SP \), and Equations 15.4, 15.5 and 15.8 are easily expressed as a function of \( p^0 \) and \( p_2 \):

\[ Q_i = \frac{D_0}{l} (\exp \gamma Sp^0 - \exp \gamma Sp_2) \]  

(15.9)

\[ C_i = \frac{1}{\gamma} \ln \left[ \frac{\exp \gamma Sp^0 - \frac{x}{l(\exp \gamma Sp^0 - \exp \gamma Sp_2)}}{\exp \gamma Sp^0 - \exp \gamma Sp_2} \right] \]  

(15.10)

\[ P_i = \frac{D_0}{\gamma \Delta p} (\exp \gamma Sp^0 - \exp \gamma Sp_2) \]  

(15.11)

### 15.2.2 Solution-Diffusion Model

When a similar treatment is applied to gas or vapour permeation, the following equations are obtained [1,9]:

\[ Q_i l = \int_{C_1}^{C_2} D(C_i) dC_i \]  

(15.12)

\[ Q_i = \frac{P_i (p_1 - p_2)}{l} \]  

(15.13)

where \( p_1 \) and \( p_2 \) are the vapour pressures on the high concentration side and low concentration sides of the membrane respectively.

Combining Equations 15.12 and 15.13 yields the following:

\[ P_i = \left[ \int_{C_1}^{C_2} D(C_i) dC_i \right] (p_1 - p_2) \]  

(15.14)

Rearrangement gives:

\[ Q_i l = R = P_i (p_1 - p_2) = \int_{C_1}^{C_2} D(C_i) dC_i \]  

(15.15)
where $R$ is the normalized permeation rate. When the concentration-averaged diffusion coefficient $D_i$ is defined as in Equation 15.16, $P_i$ and $R$ are expressed as in Equations 15.17 and 15.18 respectively:

$$D_i = \frac{\int_{C_1}^{C_2} D(C_i) dC_i}{C_1 - C_2} \quad (15.16)$$

$$P_i = \frac{D_i (C_1 - C_2)}{p_1 - p_2} \quad (15.17)$$

$$R = \frac{D_i (C_1 - C_2)}{C_1 - C_2} \quad (15.18)$$

If the diffusion coefficient is not dependent on permeant concentration then $D_i$ equals $D$. In pervaporation, the downstream pressure is much lower than the upstream pressure ($p_1 \gg p_2$). Hence, Equations 15.16, 15.17, and 15.18 can be represented as follows:

$$D_i = \frac{\int_{C_1}^{C_2} D(C_i) dC_i}{C_1} \quad (15.19)$$

$$P_i = \frac{D_i C_1}{p_1} \quad (15.20)$$

$$R = \frac{D_i C_1}{C_1} \quad (15.21)$$

where $C_1/p_1 = S_1$, which is the pseudo-solubility coefficient. Under these conditions $P_i$ may be expressed by

$$P_i = D_i S_1 \quad (15.22)$$

### 15.2.3 Separation Factor

The separation factor is represented by the ratio $\theta$ of the overall permeation rate for the mixed solution $Q^p$ and the sum of the permeation rate of each component in the mixture $Q^c$:

$$\theta = \frac{Q^p}{Q^c} \quad (15.23)$$

The permeation ratio in the A and B binary system $Q_i$ is defined as follows:

$$Q_A = \frac{q_A^p}{q_A^c} \ldots Q_B = \frac{q_B^p}{q_B^c} \quad (15.24)$$

$q_i^p$ and $q_i^c$ correspond to the components $Q^p$ and $Q^c$ respectively.

In an ideal system in which there is no interaction between the components in the mixed solution, $\theta$ is 0. In general, when $\theta > 1$, the permeation rate is larger than that in an ideal system; when $\theta < 1$, it is less than that in an ideal system.

### 15.2.4 Quantitative Treatment of Separation Factor

When the permeation rates for A and B components in the binary system are $q_A^p$ and $q_B^p$ respectively, the overall permeation rate $Q$ is

$$Q = q_A^p + q_B^p \quad (15.25)$$
In an ideal state in which there is no interaction between the components we have
\[
q_A^p = X_A q_c^A, \quad q_B^p = X_B q_c^B
\] (15.26)
where \(X_A\) and \(X_B\) are the weight fraction or mole fraction of components A and B in the upstream side respectively.

The overall permeation rate in an ideal system \(Q_c\) is
\[
Q_c = X q_c^A + (1 - X_A) q_c^B
\] (15.27)

From Equations 15.25, 15.26 and 15.27 when the weight fractions or mole fractions of A and B components in the downstream side in pervaporation are \(Y_A\) and \(Y_B\) respectively, we have
\[
\frac{q_B^p}{q_A^p} = \frac{Y_B}{Y_A}
\] (15.28)

The separation factor \(\alpha_{B/A}\) represented by the component fractions in the feed solution and permeate, is as follows:
\[
\alpha_{B/A} = \frac{Y_B}{Y_A} \frac{X_B}{X_A}
\] (15.29)

By using Equations 15.26, 15.27 and 15.28:
\[
\alpha_{B/A} = \frac{Y_B}{Y_A} \frac{X_B}{X_A} = \frac{Y_B(1 - X_B)}{X_B(1 - Y_B)} = \frac{q_B^p}{q_A^p} = \frac{(X_B q_c^B) X_A}{(X_A q_c^A) X_B} = \frac{q_c^B}{q_c^A}
\] (15.30)

The separation factors in the ternary component are as follows:
\[
\alpha_{B/A} = \frac{Y_B}{Y_A} \frac{X_B}{X_A}, \quad \alpha_{C/A} = \frac{Y_C}{Y_A} \frac{X_C}{X_A}, \quad \alpha_{C/B} = \frac{Y_C}{Y_B} \frac{X_C}{X_B}
\] (15.31)
\[
\alpha_{A/total} = \frac{Y_A / (Y_A + Y_B + Y_C)}{X_A / (X_A + X_B + X_C)} = \frac{Y_A / \sum Y_i}{X_A / \sum X_i}
\] (15.32)

In pervaporation, the separation factor \(\alpha_{B/A}\), a relative measure for the degree of separation, can be represented by the component mole fractions in the feed and permeate as follows:
\[
\alpha_{B/A} = \frac{Y_B}{Y_A} \frac{X_B}{X_A}
\] (15.33)

where \(X_A\) and \(X_B\) are the weight fraction or mole fraction of the A and B components in the upstream side respectively. \(Y_A\) and \(Y_B\) are the weight fraction or mole fraction of the A and B components in the downstream side respectively.

### 15.3 Membranes for Pervaporation

#### 15.3.1 Materials of Pervaporation Membrane

##### 15.3.1.1 Hydrophilic Membrane Materials

Typical hydrophilic pervaporation membrane materials fall into two categories: the polymer material and inorganic material. The former material is easier to prepare various module membranes and the
strength of produced membranes is higher. The latter one is also able to be designed in various shapes, with a range of average pore sizes and permeability, and excellent for high-temperature membrane operations [3].

**Hydrophilic Polymer Membrane Materials** Typical materials for hydrophilic polymer membrane are classified as non-charged and charged polymers. The former include poly(vinyl alcohol) (PVA), poly(acrylamide), poly(vinyl pyrrolidone) (PVP), poly(acrylonitrile) (PAN), poly(vinyl chloride) (PVC) and their copolymers, cellulose acetate and chitosan. The latter include poly(acrylic acid) (PAA), poly(methacrylic acid), poly(styrene sulfonic acid), carboxymethyl cellulose, carboxymethyl chitosan, quarternized chitosan, sodium alginate and their polyion complexes.

When those hydrophilic polymer membranes are applied to aqueous organic solvent solutions in pervaporation, they show water permselectivity. These water permselective membranes are effective when, for example, an aqueous ethanol solution is distilled in which an azeotropic mixture (96.5 wt% ethanol) is formed and cannot be concentrated more than this composition by a conventional distillation. In general, ethanol is concentrated by adding an entrainer such as benzene. If the water (3.4 wt%) in the azeotrope can be removed by a pervaporation membrane, this would save a lot of energy and be very effective.

The permeation and separation mechanism of the pervaporation method is insufficiently elucidated, but as mentioned earlier, it is the dissolution to a membrane of permeant, the diffusion of permeant in the membrane, and the evaporation of permeant from a membrane. Therefore, the separation in pervaporation is mainly influenced by differences in the solubility of each component in the feed into the membrane and the diffusivity of each component in the membrane. It is important that we know which of the differences of solubility and diffusivity influence separation predominantly on the structure design of the membrane. In the water permeative membranes in the pervaporation permeation experiments of water–ethanol mixture, there are two types: one is due to the difference of solubility and another is attributed to the difference of diffusivity. For example, in the PAN membrane shown in Figure 15.2, water concentration sorbed into the membrane is significantly dependent upon the water concentration in the permeate. The separation is governed by the difference of solubility [10].

On the other hand, in PVC membrane in Figure 15.3, ethanol is predominantly sorbed into the membrane but water is permeate selectively permeated in the permeate; consequently, the difference of diffusivity contributes to the separation [11]. The membranes which show water permselectivity predominated by the former solubility difference are cellophane [12], cellulose acetate [13], PVA [14,15], PAN [16] and chitosan membrane [17]. Those by the latter diffusivity are poly(styrene) [18], poly(sulfone) [10] and poly(tetrafluoroethylene) (PTFE)-graft membrane [9].

**Hydrophilic Inorganic Membrane Materials** Inorganic materials such as alumina, titania, zirconia oxides, recrystallized silicon carbide or some glassy materials are used for the preparation of ceramic membranes. Those membranes have a hydrophilic character due to the presence of the surface hydroxyl (–OH) groups, which can link very easily with water molecules [19,20].

### 15.3.1.2 Hydrophobic Membrane Materials

Hydrophobic pervaporation membrane materials are also classified into two categories: the polymer material and inorganic material. The former materials are Si-containing polymers, such as polydimethylsiloxane (PDMS). The strength of membranes produced is not high. Therefore, their strength is improved by copolymerization, blending, cross-linking, composite formation and hybridization
Hydrophobic Polymer Membrane Materials

Typical hydrophobic polymer membrane materials include the following: PDMS, poly(acetylene) such as poly[(1-trimethylsilyl)-1-propyne], poly(olefin) such as poly(ethylene), poly(propylene), PTFE, poly(vinylidene fluoride) (PVDF), poly(styrene), poly(alkyl methacrylate) such as poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate), poly(butyl methacrylate), and poly(styrene).

When these hydrophobic polymer membranes are applied to aqueous organic solvent solutions and organic mixtures in pervaporation, they show organic solvent permselectivity.

Hydrophobic Inorganic Membrane Materials

There are a very few hydrophobic inorganic materials compared with organic polymers, but hydrophobic zeolite prepared from zeolite is a typical material as a solid adsorbent for ethanol–water separation. Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminium, silicon and oxygen in their regular
framework. Since they have a pore size less than 1 nm, zeolites are able to separate components of a mixture on the basis of a difference in molecular size (i.e. molecular sieving effect). The zeolite pore size is mainly determined by its unique structure, but it can also be affected by zeolite composition. In addition to the molecular sieving effect, the hydrophilic/hydrophobic nature of zeolites is also a very important character in the membrane separation process. Those hydrophilic/hydrophobic properties depend mainly on the Al₂O₃/SiO₂ ratio; that is, the degree of hydrophilicity increases as the Al₂O₃ content in the zeolite framework increases and its degree of hydrophobicity increases with higher silica content [21]. Te Hennepe et al., [22] reported that silicone rubber membranes filled with particles of high-silica zeolite showed a high ethanol permselectivity. Afterwards, zeolites could be prepared as membranes, with both water- and ethanol-permselective membranes being fabricated. On the other hand, hydrophobic inorganic membranes are prepared by grafting hydrophobic silane compounds such as fluoroalkylsilane onto the surface of a hydrophilic inorganic membrane with —OH groups [23].

15.3.2 Membrane Structure

Typical membranes used in the pervaporation process are (1) symmetric type, (2) asymmetric type, (3) composite type and (4) hybrid type. The symmetric type has the same homogeneous structure on the surface and back side of the membrane; the asymmetric type consists of a thin homogeneous surface and porous support layer, the composite type contains an additive, such as nanotubes, which increase the selectivity; the hybrid type is composed of organic–inorganic hybridization.

15.3.2.1 Symmetric Membranes

Pervaporation membranes derived from seven homopolymers of poly(amide–sulfonamide) (PASA) were prepared by casting 10–17% polymer solutions of N,N-dimethylacetamide. The membranes were characterized by sorption experiments, scanning electron microscope, and wide-angle X-ray diffraction (XRD). During the pervaporation of 90 wt% aqueous solution of methanol, ethanol, 1-propanol and 2-propanol, all membranes were preferentially permeable to water, and their separation factors were mainly dependent on the molecular weight of the solvent. The exact structure of the PASAs had a profound effect on their pervaporation characteristics. Polymeric membrane based on N,N′-bis (4-aminophenylsulfonyl)-1,3-diaminopropane and isophthaloyl chloride exhibited the best selectivity factor of 1984 for a 10 : 90 (by weight) mixture of water/ethanol at 20 °C. However, the permeation rates of all materials for dehydration of 90 wt% ethanol were slow, in the range of 6.6–34.4 g m⁻² h⁻¹ [24].

The pervaporation performance and mechanism of water–ethanol mixtures through symmetric and asymmetric TPX – poly(4-methyl-1-pentene) – membranes were investigated. The results showed that TPX is a highly water permselective material, although it is strongly hydrophobic. It was found that, for a symmetric dense TPX membrane, the feed solution vaporizes first and then permeates through the membrane. The water selectivity stems from the huge difference in diffusivity between water and ethanol vapours. To improve the permeation flux, asymmetric TPX membranes were prepared by a wet inversion method. However, due to the swelling effect of ethanol on TPX, small pores occur when the dense skin contacts the feed solution, resulting in a loss of water selectivity. Stain experiments were carried out to verify this mechanism. In addition, it was found that a parallel model can describe the mechanism quite accurately. Good agreement between the theoretical calculation and experimental measurement was obtained. Furthermore, Wang et al. also found that the loss of selectivity can be avoided by turning the asymmetric membrane over; that is, letting the dense skin face the permeate [25].
15.3.2.2 Asymmetric Membranes

An asymmetric silica membrane supported on a porous alumina tube substrate was prepared by Jin et al. by dip-coating and then surface modification in a multistage assembly synthesis. The mesoporous silica membrane was repeatedly modified with hexamethyldisilazane after dip-coating in silica sol solution. The separation layer of the silica membrane had an average thickness of 2 μm, mean pore radius of 1.16 nm and BET surface area of 225 m² g⁻¹. In the presence of 1 wt% acetic acid, the membrane effectively removed ethanol and acetone from a 5 wt% organic–water binary system, or 5.0 wt% organic–94.0 wt% water ternary feeds by pervaporation (pervaporation) over a temperature range of 303–323 K. The separation factor α of ethanol at 303 K was about 8.7, while that of acetone was 28.4. The total permeate fluxes at 303 K were 0.92 kg m⁻² h⁻¹ and 1.15 kg m⁻² h⁻¹ for ethanol–water and acetone–water feed solution respectively [26].

Asymmetric polyamide-6 (PA-6) membrane was prepared using the wet-phase inversion technique from a casting dope containing 20 wt% of PA-6 in formic acid at 18 °C by Abdallaha et al. [27]. The membrane was then characterized by scanning electron microscopy (SEM) and further tested for the separation of methanol–methyl acetate solutions by pervaporation. The effects of feed methanol concentration, operating temperature and the feed liquid flow rate on the membrane performance were investigated. The permeation flux increased with increasing feed methanol concentration, feed temperature and feed flow rate. Some typical data of separation factor were as follows: at an operating temperature of 40 °C, a feed of 80% methanol–20% methyl acetate and feed liquid flow rates of 16.5 mL s⁻¹ and 20.6 mL s⁻¹ the separation factors were 50 and 83 respectively.

Koros and co-workers [28] reported the synthesis and organic–water separation properties of mesoporous silica membranes, supported on low-cost and scalable polymeric (polyamide-imide) hollow fibres, and modified by trimethylsilylation with hexamethyldisilazane. Thin (~1 μm) defect-free membranes were prepared, with high room-temperature gas permeances (e.g. 20 000 GPU for N₂). The membrane morphology was characterized by multiple techniques, including SEM, transmission electron microscopy (TEM), XRD, and Fourier transform attenuated total reflectance spectroscopy. Silylation led to capping of the surface silanol groups in the mesopores with trimethylsilyl groups, and did not affect the integrity of the mesoporous silica structure and the underlying hollow fibre. The silylated membranes were evaluated for pervaporative separation of ethanol, methylethyl ketone, ethyl acetate, isobutanol (i-BuOH) and n-butanol (n-BuOH) from their dilute (5 wt%) aqueous solutions. The membranes show separation factors in the range of 4–90 and high organic fluxes in the range of 0.18–2.15 kg m⁻² h⁻¹ at 303 K. The intrinsic selectivities (organic/water permeability ratios) of the silylated membranes at 303 K are 0.33 (ethanol/water), 0.5 (methylethyl ketone/water), 0.25 (ethyl acetate/water), 1.25 (i-BuOH/water), and 1.67 (n-BuOH/water), in comparison with 0.05, 0.015, 0.005, 0.08 and 0.14 respectively for the unmodified membranes. The silylated membranes allow upgradation of water/organics feeds to permeate streams with considerably higher organics content. The selective and high-flux separation is attributed to both the organophilic nature of the modified mesopores and the large effective pore size. Comparison with other organics–water separation membranes reveals that the Koros and co-workers’ membranes show promise due to high flux, use of scalable and low-cost supports, and good separation factors that can be further enhanced by tailoring the mesopore silylation chemistry.

Surface modification of polybenzoimidazole (PBI) membrane with chitosan chains was performed using 4-isocyanato-4’-(3,3’-dimethyl-2,4-dioxo-azetidino)diphenylmethane (IDD) as a coupling agent to build up chemical linkages between the PBI membrane surface and chitosan chains. Incorporation of chitosan chains to the PBI membrane surface increases its surface hydrophilicity and enhances its performance of pervaporation dehydration on isopropanol aqueous solutions. The surface chemical structure of the chitosan-modified PBI membrane (PBI-CS) was characterized with attenuated total
reflectance Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopies. The scanning electron micrographs of PBI-CS indicated the surface reaction between PBI and IDD might take place at the top surface of the PBI matrix in a thickness of about 2 μm as the PBI membrane is swollen with the solvent used. PBI-CS is effective for pervaporation dehydration on isopropanol aqueous solutions in a wide concentration range from 30 to 90 wt%. The chitosan layer increases the dissolution rate of water into the PBI-CS membrane so as to simultaneously increase the water permeability and selectivity of the membrane. PBI-CS shows high pervaporation separation indexes (PSIs) which are about 3.9-fold of the value measured with the neat PBI membrane [29].

15.3.2.3 Composite Membranes

Water Permselective Composite Membranes  
Chen et al. [30] prepared a novel zeolite (HY)-filled polymeric chitosan membrane. The membrane was characterized by wide-angle XRD and a swelling test. The pervaporation experiments were also performed for an ethanol–water system. The results showed that the crystalline structure of chitosan was damaged with increase in the zeolite content, indicating a strong interaction between the HY zeolite and chitosan. The separation factor of the ethanol–water mixture by pervaporation was improved by the filling zeolite. When the HY zeolite content in the membrane was 20 mass%, the separation factor reached the maximum and remained constant during the pervaporation process.

Patil et al. [31] reported the development of hybrid composite membranes of sodium alginate loaded with hydrophilic alumina-containing Mobile Composition Matter-41 (Al-MCM-41) in different compositions from 3 to 10 wt% that are used for pervaporation dehydration of 1,4-dioxane and tetrahydrofuran (THF) from aqueous mixtures in compositions of 10–40 wt% at 30 °C. The pervaporation performance of the hybrid composite membranes was much superior to that of plain NaAlg membrane in terms of selectivity and flux due to increased hydrophilicity of NaAlg membrane in the presence of Al-MCM-41 mesoporous zeolite particles that are also hydrophilic. Membranes cross-linked with glutaraldehyde were characterized by ion exchange capacity, Fourier transform spectroscopy and XRD. Morphology of the membranes was assessed by SEM. Sorption studies were performed to evaluate the extent of interaction and degree of swelling of the membranes with pure and mixed feed aqueous mixtures of 1,4-dioxane and THF. It was observed that flux and selectivity increased systematically with increasing amount of Al-MCM-41 particles in the NaAlg matrix. For a hybrid composite membrane containing 10 wt% Al-MCM-41, selectivity for water was infinity, which was attributed to the combined effects of molecular adhesion between particle surfaces and NaAlg matrix as well as higher selectivity of the composite membrane when compared with plain NaAlg membrane.

Shirazi and Mohammadi [32] studied the morphological and separation characteristics of PVA membranes incorporated with functionalized carbon nanotubes (CNTs). CNTs were extensively characterized using thermogravimetric analysis (TGA), field-emission SEM (FESEM) and TEM. The physicochemical properties of PVA–CNTs membranes were characterized using FESEM, tensile test, differential scanning calorimetry (DSC) and XRD. DSC measurements showed an increase in melting and glass transition temperature, implying enhancement of polymer chains compaction. XRD analysis confirmed the results of DSC and showed that CNTs can promote crystallinity of the PVA membranes. In addition, tensile measurements revealed that incorporating CNTs into the PVA membranes improves their mechanical properties. The synthesized nanocomposite membranes were then evaluated in pervaporation dehydration of isopropanol. The separation results showed that incorporating CNTs into the PVA membranes significantly increases water selectivity of the PVA membranes. This is attributed to the fact that incorporating CNTs compacts and rigidifies the PVA matrix and decreases its free volume. Furthermore, permeation of water molecules through
the nanocomposite membranes decreases as a result of polymer chains rigidification. Effects of feed composition and temperature on PVA–CNTs nanocomposite membranes were investigated. In addition, the effects of CNTs content on permeation properties and activation energies of PVA membranes were evaluated.

As an emerging technology, pervaporation has shown great promise in fresh water production from salty water. However, the low separation efficiencies of the present membranes hinder their practical applications. So Liang et al. fabricated thin graphene oxide (GO) films with two-dimensional nano-channels on PAN ultrafiltration membranes using a vacuum filtration-assisted assembly method. The GO–PAN composite membrane exhibited a high water flux of up to 65.1 L m$^{-2}$ h$^{-1}$ with high rejection (about 99.8%) for desalination by pervaporation at 90 °C. It is noteworthy that the composite membranes showed high performances in treating high-salinity water, even at salt concentrations of up to 100 000 ppm. This makes it possible to use GO-based membranes for seawater desalination, brackish water desalination and reverse osmosis concentrate treatment [33].

**Organic Permeselective Composite Membranes** A novel composite membrane using supramolecule calix [4]arene-filled PDMS as the top active layer and non-woven fabric as the support layer was developed for the pervaporative removal of benzene from water by Wu et al. [34]. Compared with unfilled PDMS homogeneous membrane, the composite membrane exhibited both higher separation factor and higher benzene flux by 1.8-fold and 3.2-fold respectively. Effects of pervaporation operating parameters such as feed Reynolds number, benzene concentration in feed, downstream pressure and operating temperature on the permeation flux and separation factor were investigated. The benzene permeation flux was proportional to both the benzene concentration in the feed and the downstream vacuum. From the temperature-dependent permeation flux values, Arrhenius activation energies for permeation of benzene and water were estimated.

New siloxane-imide block copolymers were designed and synthesized from 2,2’-bis[4-(4-amino- phenoxy)phenyl] hexafluoropropane, 4,4’-(hexafluoroisopropylidene) diphthalic anhydride and diamine-terminated PDMSs (SIDA; average molecular weight 900, 1680 and 4600) for application in organophilic pervaporation by Jiang et al. [35]. The chemical structure of the copolymer was confirmed by FTIR and $^1$H nuclear magnetic resonance spectra. In addition, its good thermal stability and micro-phase-separated amorphous structure were confirmed by TGA, DSC, wide-angle XRD and atomic force microscopy analyses. The content of siloxane blocks in the copolymer decreased, and thus the micro-phase separation became more serious with decreasing molecular weight of SIDA used for copolymerization. The siloxane-imide block copolymer membrane prepared from the lowest molecular weight of SIDA (900) was fragile. The siloxane blocks in the copolymer mainly contributed to the pervaporation properties of the copolymer membranes. Their increase made an improvement of the separation properties, including permeate flux and selectivity. But simultaneously, it would lead to a drop of mechanical strength of the corresponding copolymer membrane.

Sukitpaneenit and Chung [36] have demonstrated the design and engineering of PVDF–nanosilica dual-layer hollow fibres as novel pervaporation membranes for ethanol recovery. The newly developed dual-layer hollow-fibre membrane can exhibit a high separation factor of up to 29 with a sustainable high flux of 1.1 kg m$^{-2}$ h$^{-1}$, which is equivalent to the separation performance regime of inorganic membranes. Central to this performance achievement was the synergy of (1) desirable membrane morphology, nanopore size, and high surface porosity of a thin-PVDF–nanosilica composite on a fully porous substrate accomplished by the dual-layer coextrusion technology, and (2) optimal operating downstream pressure with the aid of controlled pervaporation transport. The membrane selectivity–downstream pressure dependence of PVDF–nanosilica hybrid membranes is comprehensible via a
modified pore-flow model. In this study, a new class of membranes for ethanol–water separation is represented.

**Organic–Organic Separation Composite Membranes**  Wang et al. [37] prepared a new pervaporation cellulose acetate membrane filled with metal oxide particles to intensify the separation of methyl tert-butyl ether (MTBE)–methanol mixtures. The SEM and Raman spectrometry revealed that the particles of metal oxide were evenly dispersed in the membrane matrix and made a denser membrane. When the content of Al₂O₃ and ZnO was 1.98 wt% and 4 wt% respectively, both the permeation flux and separation factor of blended cellulose acetate membrane were higher than those of pure cellulose acetate membrane. In comparison with the pure cellulose acetate membrane, the maximum flux of blended membrane filled with Al₂O₃ and ZnO improved 96.5% and 111.1% respectively; the maximum separation factor improved 48.0% and 37.8% respectively. In addition to the substantially improved permeation flux and selectivity, the cellulose acetate membrane filled with metal oxide was found to be easy to prepare and with low cost.

New polymer nanocomposites consisting of poly(phenylene isophthalamide) modified by CNTs were obtained by the solid-state interaction method to prepare dense membranes [38]. The investigation of the poly(phenylene isophthalamide)–CNT nanocomposites was made by Raman spectroscopy. The morphology of the dense membrane was analysed by SEM. The transport properties of the dense polyamide membranes modified by 2 and 5 wt% CNTs were studied in pervaporation of a methanol–MTBE mixture. It was shown that the selectivity with respect to methanol and permeability were the highest for membranes containing 2 wt% CNT as compared with membranes of pure poly(phenylene isophthalamide) and containing 5 wt% CNT. To analyse transport properties, sorption tests and contact-angle measurements were employed.

PDMS and hydrophobic nano-silica-filled PDMS membranes were prepared by Wang et al. [39] and employed in dimethylcarbonate (DMC) removal from the DMC–methanol mixture via pervaporation. The sorption and diffusion behaviour of the binary molecule were discussed separately to provide qualitative estimation of the pervaporation performance in both membranes. Compared with the PDMS membrane, hydrophobic nano-silica-filled PDMS membranes had a little lower sorption selectivity but higher diffusion selectivity. In both membranes, the sorption value was obtained by both experimentation and model prediction. The Flory–Huggins model was used to predict the solvent uptakes and the sorption concentrations based on the experimental results. The sorption behaviour of DMC was predictable, while the methanol solubility was a little higher than the experimental results. Moreover, the diffusion behaviour was studied by Fick’s law; the calculated diffusion coefficients of the permeates demonstrated a diffusion-coupling phenomenon, especially in hydrophobic nano-silica-filled PDMS membranes. Methanol molecules diffused faster than DMC, suggesting low diffusion selectivity. The pervaporation performance was affected by both sorption and diffusion. Sorption was demonstrated to be a decisive factor in this pervaporation process.

15.3.2.4 Hybrid Membranes

**Water Permeselective Hybrid Membranes**  To inhibit the swelling of PVA membranes in aqueous alcohol solutions, which leads to lowered water permselectivity during separation, organic–inorganic hybrid membranes composed of PVA and tetraethoxysilane (TEOS) were prepared by Uragami et al. [40]. When an aqueous solution of 85 wt% ethanol was permeated through the PVA–TEOS hybrid membranes during pervaporation, the separation factor for water permselectivity increased, but the permeation rate decreased, with increasing TEOS content. We concluded that the decreased permeation rate was caused by decreasing the degree of swelling of the membrane. Therefore, this
decrease in the degree of swelling and the increase in membrane density were due to the formation of hydrogen bonds between the silanol groups resulting from the hydrolysis of TEOS and the hydroxyl group of PVA. When the PVA and PVA–TEOS hybrid membranes were annealed, the separation factor of these membranes increased with increasing annealing temperature and time. The fact that annealing at higher temperatures promoted the dehydration–condensation reaction between PVA and TEOS in PVA–TEOS membranes was related to the enhanced permselectivity of the PVA–TEOS membranes.

To control swelling of quaternized chitosan (q-Chito) membranes, Uragami et al. prepared mixtures of q-Chito as an organic component and TEOS as an inorganic component using the sol–gel reaction to form novel q-Chito–TEOS hybrid membranes [41]. In the separation of an ethanol–water azeotrope by pervaporation, the effect of TEOS content on the water/ethanol selectivity of q-Chito–TEOS hybrid membranes was investigated. Hybrid membranes containing up to 45 mol% TEOS exhibited higher water/ethanol selectivity than the q-Chito membrane. This resulted from depressed swelling of the membranes by formation of a cross-linked structure. However, introduction of excess TEOS led to greater swelling of the hybrid membranes. Therefore, the water/ethanol selectivity of the hybrid membranes containing more than 45 mol% TEOS was lower than that of the q-Chito membrane. The relationship between the structure of q-Chito–TEOS hybrid membranes and their permeation and separation characteristics during pervaporation of an ethanol–water azeotrope was also discussed in detail.

To control the swelling of PVA membranes, Uragami et al. prepared mixtures of PVA and an inorganic oligosilane using sol–gel reactions to yield new PVA–oligosilane hybrid membranes [42]. In the separation of an ethanol–water azeotropic mixture during pervaporation, the effect of the oligosilane content on the water/ethanol selectivity of PVA–oligosilane hybrid membranes was investigated. The water/ethanol selectivity of PVA–oligosilane hybrid membranes was higher than that of PVA membranes, but the water/ethanol selectivity of hybrid membranes decreased with increasing oligosilane content. In order to increase the water/ethanol selectivity, PVA–oligosilane hybrid membranes were annealed. The water/ethanol selectivity of annealed PVA–oligosilane hybrid membranes was greater than unannealed hybrid membranes, and significantly governed by the oligosilane content, which could be attributed to both sorption and diffusion selectivities. The relationship between the structure of unannealed and annealed PVA–oligosilane hybrid membranes along with permeation and separation characteristics of an ethanol–water azeotropic mixture during pervaporation were discussed in detail.

Xie et al. prepared hybrid polymer–inorganic membranes by cross-linking PVA, maleic acid and silica via an aqueous sol–gel route [43]. Membrane characterization results revealed silica nanoparticles (<10 nm) were well dispersed in the polymer matrix and significantly reduced swelling of the membrane. The membranes were tested for pervaporation separation of aqueous salt solution with NaCl concentrations of 0.2–5.0 wt% at temperatures of 20–65 °C, feed flow rates of 30–150 mL min⁻¹ and permeate pressures of 2–40 Torr. The salt rejection remained high (up to 99.9%) under all operating conditions. A high water flux of 11.7 kg m⁻² h⁻¹ was achieved at a feed temperature of 65 °C and a vacuum of 6 Torr. The effect of operating conditions on water flux is discussed in relation to diffusion coefficients of water and fundamental transport mechanism through the membrane. The activation energy for water permeation was found to vary from 23.8 to 20.1 kJ kmol⁻¹ when the salt concentration in the feed was increased from 0.2 to 5.0 wt%.

Organic Permeactive Hybrid Membranes A membrane with selective permeability for ethanol was designed by Itoh et al. for the separation of ethanol from its aqueous solution by pervaporation on the basis of the difference in solubility between two components of the membrane. A liquid membrane
was introduced to extend this difference, and ethanol in the liquid membrane was isolated by the polymer membrane; that is, a liquid–polymer hybrid membrane was formed. Carbon tetrachloride was used as a liquid membrane, and 2-hydroxyethyl acrylate (branch)–acrylonitrile (backbone) graft copolymer membrane was used as a polymer membrane. The effect of the microphase separated structure of the graft copolymer membrane on permselectivity was studied. The microdomain of the acrylonitrile moiety displayed more dispersion and a smaller microdomain with decreasing chain length of the backbone polymer. It was found that the plasticizing effect was suppressed effectively by the microphase separated structure, and the permselectivity of the graft copolymer membrane for ethanol was higher. When pervaporation of the ethanol–water mixture was carried out using the liquid–polymer hybrid membrane, ethanol completely permeated the liquid–polymer hybrid membrane [44].

Supported liquid membrane pervaporation is a pervaporation process for separating VOCs from their dilute aqueous solution. It simultaneously integrates extraction of the VOCs from the aqueous solution with flash distillation of the VOCs from the organic phase. By using a liquid membrane consisting of reactive extractants, pervaporation of primarily acetic acid from its aqueous solutions was studied by Qin et al. Limited studies of butyric acid were also done. Among various extractants tested, trioctylamine and tridodecylamine demonstrated better performances. The supported liquid membrane is permselective for acetic acid and butyric acid. The acetic acid selectivity can be as high as 33 for a feed of 1 M at 60 °C, an order of magnitude higher than that obtained by any solid polymeric membrane reported in the literature. The simple supported liquid membrane system demonstrated long-term stability; for example, decreases of about 30% in both pervaporation flux and selectivity were observed over an operational period of 500 h. A new technique of continuous on-line regeneration of the liquid membrane during operation maintained completely stable operational performance [45].

Alcohol-permselective membranes may play an increasingly important role in bioalcohol production. Developments for this membrane mostly involve hybrid membranes. Obtaining high compatibility and nanodispersion of inorganic nanoparticles in the polymer matrix is the key to fabricating hybrid membranes with high pervaporation performance. Fan et al. studied a homogeneous, nanodisperse ZIF-8–PDMS membrane prepared by repeated immersion of a polysulfone supporting membrane in a dilute ZIF-8–PDMS suspension and subsequent removal of defects using a concentrated PDMS solution. To improve the nanoscale dispersion of ZIF-8, the nascent ZIF-8 suspension was directly dispersed in a PDMS solution without drying. This procedure avoids aggregation and redispersion of ZIF-8 nanoparticles after forming a powder. Analyses confirmed that the ZIF-8–PDMS dispersion effectively diminished aggregation between nanoparticles and led to the formation of a well-dispersed ZIF-8–PDMS membrane. A homogeneous and thin ZIF-8–PDMS permselective layer was obtained by adjusting the preparation conditions. The prepared ZIF-8–PDMS membrane exhibited a high separation factor (52.81) and high flux (2800.5 g m⁻² h⁻¹) in the separation of 5.0 wt% n-butanol–water solution at 80 °C. By comparing the powder-dispersed ZIF-8–PDMS hybrid membrane with the suspension-dispersed ZIF-8–PDMS membrane, Fan et al. found that the latter showed much higher performance in butanol separation. Therefore, the nanodisperse ZIF-8–PDMS membrane has great potential applications for in situ recovery of biobutanol [46].

Organic–Organic Separation Hybrid Membranes

Cross-linked organic–inorganic hybrid chitosan membranes were obtained from blending chitosan and γ-(glycidyloxypropyl)trimethoxysilane (GPTMS) in acetic acid aqueous solution [47]. The hydrophilicity of the modified membranes was not significantly decreased, so as to result in good permselectivity and high permeation flux in pervaporative dehydration on a 70 wt% isopropanol–water solution. A flux of 1730 g m⁻² h⁻¹ and a separation factor of 694
were found with the chitosan membrane containing 5 wt% GPTMS. Both of the cross-linked and organic–inorganic hybrid structures contributed to stabilize the membranes to maintain the performance of the membranes in a 140 days long-term operation.

Hybrid membranes composed of porous metal–organic molecule nanocages as fillers embedded in a hyperbranched polymer (Boltorn W3000) were fabricated that exhibit excellent pervaporation separation performances towards aromatic and aliphatic hydrocarbons. The unique nature of the molecule-based fillers and their good dispersion and compatibility in/with the polymer are responsible for the good membrane properties [48].

A series of pervaporation hybrid membranes were prepared by Zhao et al. from polyethylene glycol (PEG) and phenylaminomethyl trimethoxysilane (PAMTMS) based on the sol–gel process, in which PEG was used as an organic moiety to improve the affinity for organic alcohols and silicone of PAMTMS was used as inorganic moiety to increase the permeation flux of organic species. Their application to separate isopropanol–benzene mixtures was investigated. FTIR spectra confirmed the reaction products. DSC measurement revealed that the influence of PEG content on the $T_g$ and thermal behaviour of membranes A, B and C. FESEM images exhibited that phase-separated structure occurred when the PEG content was elevated to some extent. Pervaporation experiments showed that the permeation flux increased and the separation factor decreased with an increase in isopropanol content in feed at 30 °C. Meanwhile, the separation factor increased with an increase in feed temperature at 60 vol.% isopropanol content. Moreover, it was found that the permeation flux was independent of the feed temperature, suggesting that feed temperature has little impact on the thermal motion of polymer chains. The increasing cross-linking degree in hybrid matrix might be responsible for such a trend. Based on these findings, it was concluded that these pervaporation hybrid membranes have potential applications in the separation of isopropanol–benzene binary mixtures [49].

15.3.2.5 Inorganic Membranes

Because the separation performance improves the rate of transport in inorganic high flux pervaporation membranes, resistances in the boundary layer become the performance bottleneck in the dehydration of solvents. By operating the membranes at high temperature levels, permeate water fluxes of more than $10 \text{ kg m}^{-2} \text{ h}^{-1}$ can be obtained. Therefore, the design of efficient industrial-scale modules becomes significant. In Somme et al.‘s study, a set of generic rules for the construction of technical and economically feasible modules was derived and different design versions compared, including tubular, hollow-fibre, spiral-wound and multichannel monolith types. In particular, the performance efficiency and application limitations of the isothermal module concept Pervap® SMS (Silica Membrane System) from Sulzer Chemtech were evaluated. Steam condensation or a thermal liquid ensured the constant operation temperature for any permeate loading. For assessing the module efficiency the impact of concentration and temperature polarization was modelled with empirical correlations for the mass and heat transfer on the feed side. For these high-flux membranes the overall flux reduction by polarization effects in the technical module was around 30–50%. At lower permeate fluxes the losses in membrane performance were more the result of mass transfer limitations, whereas at higher permeation rates heat transfer became more significant. The pressure drop in the porous support was calculated by Knudsen diffusion, whereas the pressure loss in the permeate channel was determined with laminar flow according to Hagen–Poiseuille. At a permeate flux of 10 kg m$^{-2}$ h$^{-1}$ the friction loss in the support can reach up to 100 mbar, whereas the pressure drop in the permeate tube is negligible [50].

Tanaka et al. prepared microporous carbon membranes for pervaporation applications on a porous α-alumina support by a partial carbonization of a resorcinol–formaldehyde resin [51]. The stability
and dehydration performances of the carbon membranes were determined. The carbon membranes were used for the dehydration of several organic solvents (methanol, ethanol, isopropanol and acetic acid) containing water; it was found that water was selectively permeated through the membrane and the separation factor increased with the molecular diameter of the organic solvents. The high selectivity to water was explained by the hydrophilic nature of the pore surface and the molecular sieving effect. Furthermore, the membranes showed high durability in the pervaporation of water–alcohol mixtures. On the other hand, the membranes were unstable in a water–acetic acid mixture. However, the sulfonated carbon membranes were stable in pervaporation of a water–acetic acid mixture and maintained their separation properties.

Magalad et al. [52] prepared nanocomposite membranes of chitosan by incorporating Preysler-type heteropolyacid – namely, H$_{14}$[NaP$_5$W$_{30}$O$_{110}$] – nanoparticles by solution casting and the solvent evaporation method. The nanoparticles as well as the membranes were characterized by a variety of physicochemical techniques. The membranes were employed in pervaporation separation of water–ethanol mixtures at varying feedwater compositions and temperatures. The filler nanoparticles (58 nm size), also functioning as cross-linking agents, are responsible for increasing the thermal stability and mechanical strength of the nanocomposite membranes over that of the nascent chitosan membrane. Furthermore, a dramatic increase of separation factor of 35 991 for nanocomposite membranes from a base value of 96 for nascent chitosan membrane demonstrated the influence of filler nanoparticles in the matrix due to their favourable interactions with chitosan. Pervaporation performance of the nanocomposite membranes showed a decrease with increasing feedwater composition and temperature. Diffusion and permeability data of water and ethanol molecules were analysed by Fick’s equation, and temperature dependence was studied through the Arrhenius relationship. Pervaporation data were analysed on the basis of the sorption–diffusion model. Flory–Huggins theory was used to understand the sorption phenomenon and to estimate thermodynamic interaction parameters.

Sudhakar et al. [53] prepared novel polymeric composite membranes by the solution casting method by the incorporation of different amounts of 13X zeolite into sodium alginate. Membranes were cross-linked with glutaraldehyde and tested for pervaporation dehydration of isopropanol at 30 °C. The mixed matrix membranes were characterized by FTIR, XRD, TGA, DSC and SEM, with Sudhakar et al. finding that flux and selectivity increased systematically with increasing amount of zeolite in the sodium alginate matrix. The highest selectivity of 2300 was observed in the case of zeolite membrane containing 30 wt%, which was attributed to the combined effects of molecular adhesion between zeolites and sodium alginate matrix as well as enhanced hydrophilicity due to the zeolite.

### 15.4 Technologies


Pervaporation is effective for diluting solutions containing trace or minor amounts of the component to be removed. Based on this, hydrophilic membranes are used for dehydration of alcohols containing small amounts of water, and hydrophobic membranes are used for removal/recovery of trace amounts of organics from aqueous solutions.

Pervaporation is a very mild process, and hence very effective for separation of those mixtures that cannot survive the harsh conditions of distillation. Pervaporation processes are applied in many areas, such as: (1) dehydration of ethanol–water and isopropanol–water azeotropes; (2) continuous ethanol removal from yeast fermentors; (3) continuous water removal from condensation reactions, such as esterifications, to enhance conversion and rate of the reaction; (4) removing organic solvents from
industrial wastewaters; (5) combination of distillation and pervaporation/vapour permeation; (6) concentration of hydrophobic flavour compounds in aqueous solutions (using hydrophobic membranes). Also, a number of organophilic polymer materials have been developed and their pervaporation membranes are applied to the separation field of organic–organic mixtures, such as reduction of the aromatics content in refinery streams, breaking of azeotropes, purification of extraction media, purification of product stream after extraction and purification of organic solvents.

15.4.1 Dehydration

15.4.1.1 Water–Alcohol Dehydration

Water–alcohol selective membranes are effective for scenarios such as when an aqueous solution of dilute ethanol (about 10 wt%) produced by bio-fermentation is concentrated by distillation; since an aqueous solution of 96.5 wt% ethanol is an azeotropic mixture, ethanol cannot be concentrated any more by distillation, and consequently ethanol is concentrated by azeotropic distillation with the addition of benzene. If membranes that can preferentially permeate only water at 3.5 wt% in an azeotropic mixture of aqueous ethanol solution can be developed, significant energy savings would be achieved. The permeation and separation mechanisms in pervaporation, evapomeation, temperature-difference controlled evapomeation, and high-temperature and pressure evapomeation [54] through dense membranes consist of the dissolution of the permeants into the membrane, the diffusion of the permeants in the membrane and the evaporation of the permeants from the membrane. Therefore, the separation of permeants in these membrane separation techniques depends on the differences in the solubility and diffusivity of the permeants in the feed mixture. When the structure of water–alcohol and water–organic liquid selective membranes are dominically designed, hydrophilic materials can be recommended as membrane materials. Therefore, an increase in the solubility of water molecules into the membrane during the solution process can be expected. In order to raise the affinity of membranes for water molecules, membranes with dissociation groups introduced into their structure are used for dehydration from organic solvents.

Ihm and Ihm prepared various membranes that permeate water selectively from water–ethanol mixtures by the plasma graft-polymerization of styrene (g-PS) onto porous PVDF films by the sulfonation of the grafted membranes and by the ionization of the sulfonated (g-PSS Na+) membranes, respectively. The H$_2$O/ethanol selectivity increased with the ethanol concentration in the feed, and the grafted amount should be controlled for the optimum separation of water. The g-PSS Na$^+$ membrane with a grafted amount of polystyrene (PSt) of 0.14 mg cm$^{-2}$ was found to have a high permeation rate of 6.6 kg m$^{-2}$ h$^{-1}$, and a separation factor of 21 for pervaporation of aqueous 60 wt% ethanol solution at 50 °C [55].

The sorption and permeation characteristics of pure water and ethanol vapours and the permeation behaviour of their mixed vapour in PVC membranes were investigated at 40 °C [56]. Equilibrium sorption isotherms of pure water and ethanol vapours in the PVC membrane were well described by the dual-mode sorption model. All the dual-mode sorption parameters of ethanol vapour were higher than those of water vapour. Permeabilities for pure water and ethanol vapours of the PVC membrane decreased with increasing vapour pressure. This behaviour was analysed by the dual-transport model. It was found that the diffusion coefficient of water vapour in the PVC membrane was much higher than that of ethanol vapour. In the binary vapour mixture of water and ethanol, the permeability of water vapour was high and that of ethanol vapour was lower, compared with the expectation from the dual-transport model. The actual separation factor for water was much higher than the value presumed from the model.
$N$-Alkyl chitosans with different numbers of carbons and degrees of substitution of the $N$-alkyl group were prepared by Uragami et al. [57]. The water-permselectivity for aqueous ethanol solutions through the $N$-alkyl chitosan membranes in evaporation was studied. The permeation rate and separation factor for water-permselectivity were significantly influenced by the number of carbon atoms in the $N$-alkyl group; in particular, one $N$-alkyl chitosan membrane showed a maximum in the permeation rate and separation factor. The degree of substitution in the $N$-alkyl group affected the permeation rate little, but it significantly changed the separation factor. The characteristics of permeation and separation for an aqueous ethanol solution through the $N$-alkyl chitosan membranes with different $N$-alkyl groups and different degrees of substitution of the $N$-alkyl group were discussed from the viewpoints of physical and chemical structures of their membranes, such as density, crystallinity, surface free energy and degree of swelling of the membrane.

Homogeneous membranes based on sulfonated poly(ether ether ketone) of different sulfonation degrees were tested for sorption and pervaporation dehydration of water–isopropanol mixtures in a wide range of feed compositions. Coupled transport was observed in this pervaporation separation process, the permeation rate of isopropanol increased with increase in water feed composition. A new transport mechanism considering the coupled transport was proposed, which assumes that there are two types of environments in sulfonated poly(ether ether ketone) membranes: the hydrophilic environment A and hydrophobic environment B. Water can only dissolve in environment A, whereas isopropanol can dissolve in both environments. According to this model, the water percentage in permeate is mainly determined by the relative diffusivity and relative concentration of water to isopropanol in environment A. Some other separation characteristics of the membranes are also discussed based on this mechanism [58].

Composite hydrophilic pervaporation membranes were prepared from chitosan blended with hydroxyethylcellulose using cellulose acetate as a porous support by Huang and co-workers [59]. The membranes were tested for dehydration performance of ethanol–water mixtures of ethanol concentrations 70–95 wt% in the laminar flow region, at temperatures 50–70 °C and at permeate pressures of 3–30 mmHg. The composite membrane showed an improved dehydration performance compared with dense chitosan–hydroxyethylcellulose membrane developed earlier. The effects of operating conditions also revealed that pervaporation of low water content feed carried out at high feed flow rate and at low temperature and permeate pressure was an advantage.

Organic–inorganic hybrid membranes composed of PVA and TEOS were prepared as the dehydration membrane of an aqueous ethanol solution in pervaporation. The effect of the TEOS content in the PVA–TEOS hybrid membranes on the permeation rate and separation factor for the water permselectivity of an aqueous solution of 85 wt% ethanol during pervaporation is shown in Figure 15.4. As can be seen in this figure, the separation factor for water permselectivity increased with increasing TEOS content, but the permeation rate became constant after a decrease at low TEOS content [40].

To clarify the effects of TEOS on the permeation and separation characteristics of PVA–TEOS hybrid membranes, the degree of swelling of the membrane in an aqueous solution of 85 wt % ethanol and the membrane density were examined. Figure 15.5 shows that the degree of swelling of the PVA–TEOS hybrid membranes decreased remarkably, whereas the membrane density increased with increasing TEOS content. The results from this figure suggest that the decrease in permeation rate upon increasing TEOS content can be attributed to both a remarkable decrease in the degree of swelling of the membrane, and a significant increase in the membrane density. In particular, the change in the structure of the PVA–TEOS hybrid membranes with an increase in TEOS content caused a decrease in both solubility and diffusivity of the permeants. Consequently, the permeation rate decreased with increasing TEOS content. On the other hand, the increase in the total separation factor
for water permselectivity was due to an increase in the sorption and diffusion selectivity, based on the change in the PVA–TEOS hybrid membrane structure with an increase in the TEOS content.

Figure 15.4 Effects of the TEOS content in PVA on the permeation rate (○) and the separation factor for the water permselectivity (●) of an aqueous solution of 85 wt% ethanol through PVA–TEOS hybrid membranes by pervaporation at 40 °C.

Figure 15.5 Effects of the TEOS content in PVA on the degree of swelling (○) of the PVA–TEOS hybrid membranes in aqueous of 85 wt% ethanol and their density (●) at 40 °C.

Figure 15.6 shows the effects of TEOS content in the q-Chito–TEOS hybrid membranes on the normalized permeation rate and the ethanol concentration in the permeate for an azeotrope of ethanol–water during pervaporation. The TEOS content in mole per cent in the figure is for the pyranose ring in the q-Chito molecule. The permeate ethanol concentrations of all q-Chito–TEOS hybrid membranes were very low compared with that in the feed solution. These results suggest that the q-Chito–TEOS hybrid membranes showed high water/ethanol selectivity. High water/ethanol selectivity was observed in the q-Chito–TEOS hybrid membranes containing up to 45 mol% TEOS; however, selectivity decreased when the TEOS content was further increased. The best performance was observed for the q-Chito–TEOS hybrid membrane with 2 mol% TEOS content, where ethanol could not be detected in the permeate by gas chromatography. This result suggests that ethanol could be rejected almost perfectly by this q-Chito–TEOS hybrid membrane. The normalized permeation rate
gradually decreased by increasing the TEOS content up to 45 mol%, but it then increased at higher TEOS contents. These results can be attributed to both the formation of a cross-linked structure and a difference in the state of the cross-linked network [41].

Swelling of poly(vinyl alcohol-co-acrylic acid) (P(VA-co-AA)) membranes in aqueous alcohol solutions operated under pervaporation conditions leads to low water/ethanol selectivity. To reduce swelling, organic–inorganic hybrid membranes composed of P(VA-co-AA) and TEOS were prepared. However, when an aqueous ethanol solution was permeated through the P(VA-co-AA)–TEOS hybrid membranes by pervaporation, the permeation rate increased and the water/ethanol selectivity decreased with increasing TEOS content. The increase in the permeation rate and the decrease in the water/ethanol selectivity were caused by an increase in the degree of swelling of the membrane and a decrease in the membrane density with increasing TEOS content. These effects resulted from insufficient formation of hydrogen bonds between the silanol groups by hydrolysis of TEOS and the hydroxyl and carboxyl groups of P(VA-co-AA). When the P(VA-co-AA)–TEOS hybrid membranes were annealed, the water–ethanol separation factor increased with increasing annealing time and TEOS content. Longer annealing time promoted the dehydration–condensation reaction between P(VA-co-AA) and TEOS in P(VA-co-AA)–TEOS hybrid membranes, leading to enhanced water/ethanol selectivity of the hybrid membranes [60].

To control the swelling of sodium carboxymethylcellulose (CMCNa) membranes, mixtures of CMCNa and glutaraldehyde and mixtures of CMCNa as an organic component and TEOS as an inorganic component were prepared [61], and CMCNa–glutaraldehyde cross-linked membranes and CMCNa–TEOS hybrid membranes were formed. In the separation of an ethanol–water azeotrope by pervaporation, the effects of the glutaraldehyde or TEOS content on the water/ethanol selectivity and permeability of these CMCNa–glutaraldehyde cross-linked and CMCNa–TEOS hybrid membranes were investigated. Cross-linked and hybrid membranes containing up to 10 wt% glutaraldehyde or 10 wt% TEOS exhibited higher water/ethanol selectivity than CMCNa membrane without any cross-linker. This resulted from both increased density and depressed swelling of the membranes by the formation of a cross-linked structure. The relationship between the structure of the CMCNa–glutaraldehyde cross-linked membranes and CMCNa–TEOS hybrid membranes and their permeation and separation characteristics for an ethanol–water azeotrope during pervaporation was discussed in detail.

Figure 15.6 Effects of TEOS content on the normalized permeation rate (○) and the ethanol concentration in the permeate (●) during pervaporation of an azeotrope (96.5 wt%) of ethanol–water through q-Chito–TEOS hybrid membranes.
Trang et al. [62] prepared chitosan–cellulose composite membranes by cross-linking reaction with 3-methylglutaric anhydride. The cross-linked membranes with chitosan–cellulose were obtained at different chitosan contents in variations from 50 to 100 wt%, and these membranes were applied in the dehydration of ethanol–water mixtures. In particular, it was observed that a composite membrane containing 80% chitosan showed a performance with a separation factor of $\alpha = 17.1$ and a total permeation flux of $J = 326\text{gm}^{-2}\text{h}^{-1}$. It was observed that the total permeation flux decreased when the cross-linking increased and the increase in the ethanol content in the feed solution showed an increase in the separation factor. The composite membrane containing 80% chitosan showed excellent performance with good mechanical strength and dehydration performance in the ethanol–water mixture separation.

The permeation and separation characteristics of an ethanol–water azeotrope through chitosan membranes of different molecular weights and degrees of deacetylation during pervaporation were investigated [63]. The normalized permeation rate decreased with increasing molecular weight up to 90 kDa, but the rate increased at over 90 kDa. On the other hand, the water/ethanol selectivity increased with increasing molecular weight up to 90 kDa but decreased at over 90 kDa. With increasing degree of deacetylation, the water/ethanol permselectivity increased significantly, but the normalized permeation rate decreased. The characteristics of the chitosan membranes were discussed based on their chemical and physical structures, such as the contact angle, density, degree of swelling and glass transition temperature.

To obtain high dehydration membranes for an ethanol–water azeotrope, Uragami et al. prepared dried blend membranes from mixtures of sodium deoxyribonucleate (DNA-Na) and sodium alginate (Alg-Na) were cross-linked by immersing in a methanol solution of CaCl$_2$ or MgCl$_2$ [64]. In the dehydration of an ethanol–water azeotropic mixture by pervaporation, the effects of immersion time in methanol solution of CaCl$_2$ or MgCl$_2$ on the permeation rate and water/ethanol selectivity through DNA–Alg/Ca$^{2+}$ and DNA–Alg/Mg$^{2+}$ cross-linked membranes were investigated. DNA–Alg/Mg$^{2+}$ cross-linked membrane immersed for 12 h in methanol solution of MgCl$_2$ exhibited the highest water/ethanol selectivity. This results from depressed swelling of the membranes by formation of a cross-linked structure. However, excess immersion in solution containing cross-linker led to an increase in the hydrophobicity of cross-linked membrane. Therefore, the water/ethanol selectivity of DNA–Alg/Mg$^{2+}$ cross-linked membranes with an excess immersion in cross-linking solution was lowered. The relationship between the structure of DNA–Alg/Ca$^{2+}$ and DNA–Alg/Mg$^{2+}$ cross-linked membranes and their permeation and separation characteristics during pervaporation of an ethanol/water azeotropic mixture were discussed in detail.

15.4.1.2 Water–Organic Dehydration

Water–organic-selective membranes are effective for the dehydration of water–organic mixtures. The dehydrated organic solvents can be useful as industrial reaction solvents, washing solvents and analytical solvents. The permeation and separation characteristics of PVC and poly[(vinyl chloride)-co-(vinyl acetate)] (poly(VC-co-VAc)) membranes were investigated by Okuno et al. for aqueous organic acid solutions by pervaporation [65]. The PVC membrane preferentially incorporates organic acids and predominantly permeates water from aqueous organic acid solutions. Water permselectivities of these aqueous solutions through the PVC membrane are significantly dependent on high diffusivity of water across the membrane. It was found that the permeation rate increases and the separation factor for the water permselectivity decreases with increasing VAc content in the poly(VC-co-VAc) membrane. Preferential solubility of acetic acid into the poly(VC-co-VAc) membrane increases with the VAc content. This result was explained by a strong affinity between acetic acid and the VAc unit in the poly(VC-co-VAc) membrane.
Koops et al. prepared composite membranes consisting of a PVC top layer on either a dense PAN layer (bilayer membrane) or a porous PAN support layer (normal composite membrane) and studied them with respect to the dehydration of acetic acid. In particular, the influence of the surface porosity of the porous support layer on the selectivity and flux was studied and it was shown that the lower the surface porosity the higher the selectivity of the composite membrane, especially at high acetic acid concentrations in the feed. From the results it was concluded that the support material does contribute to the selectivity. Despite the low surface porosity, relatively high fluxes were obtained. Using a feed composition of 80/20 wt% acetic acid/water at 80 °C, selectivities of 182–274 and fluxes of 0.56–0.74 kg m⁻² h⁻¹ were obtained; and with a feed composition of 98/2, acetic acid–water selectivities of 206–318 and fluxes of 0.14–0.15 kg m⁻² h⁻¹ were obtained [66].

Pervaporative separation of acetone–water and isopropanol–water systems was studied by Burshe et al. in the water-lean range of composition of the feed mixtures. PVA membranes cross-linked with citric acid, adipic acid, maleic acid, glutaraldehyde and glyoxal were used for this purpose. The sorption characteristics of all the membranes indicated that these membranes had a good sorption selectivity for water in view of the hydrophilic nature of PVA. The type of cross-linker used for crosslinking was shown to have an important bearing on the permeation characteristics of the membranes. Thus, the trifunctional citric acid yielded the highest selectivity but lowest flux. A comparison of the productive capacities of the various membranes indicated that the glutaraldehyde cross-linked membrane had the maximum productive capacity for isopropanol dehydration, whereas maleic acid cross-linked membrane yielded the highest productive capacity for acetone dehydration [67].

Sodium alginate dense membranes demonstrated a good combination of selectivity and permeation flux for dehydrating organic solvents by pervaporation in the study by Shi et al. The pervaporation performances of alginate composite membranes were investigated to find out the best condition of membrane formation and the optimum operating conditions [68]. Some ultrafiltration membranes made of PVDF, PAN and hydrolysed PAN – either commercially available or prepared in their laboratories – were used as supports for the composite membranes. Sodium alginate dense membranes, modified through ion exchange of sodium with multivalent metal ions (such as Al³⁺, Cr³⁺, Fe³⁺, and Mg²⁺) were also prepared, and their permselectivities were tested for a water–ethanol mixture. An interesting stability of the modified membranes in long-term operation is expected.

A novel organic dehydration membrane consisting of aminated PAN microporous membrane as sublayer and alginate coating as top layer was prepared by Wang et al. and characterized by pervaporation experiment [69]. The influence of hydrolysis and amination of the microporous support layer on selectivity and flux was studied and it was shown that amination of the sublayer improved pervaporation performance of the composite membrane greatly. The counter cation of alginate coatings as dense separating layer also influenced separation properties of the membrane, which was better for K⁺ than for Na⁺. This novel composite membrane with K⁺ as counter ion had a high separation factor of 1116 and a good permeation rate of 350 g m⁻² h⁻¹ for pervaporation of 90 wt% ethanol aqueous solution at 70 °C, higher separation factors and fluxes for n-propanol–water, isopropanol–water, acetone–water and dioxane–water systems. The results showed that the separation factor and flux of this membrane increase with increased operating temperature. At the same time, SEM micrographs showed that the hydrolysis and amination of PAN microporous membrane change its pore structure. From the results it was concluded that pore structure of the sublayer in addition to its chemical structure also influence the separation properties of the composite membrane.

The pervaporation properties of two microporous three-layer stacked ceramic membranes that differ only with respect to the nature of the mesoporous interlayer were discussed by Sekulić et al. [70]. The adsorption–diffusion model and Maxwell–Stefan theory were applied to explain the influence of process parameters on the pervaporation of selected binary liquids. The temperature, feed
concentration and chemical nature of the permeating species were varied. The membrane system $\gamma$-Al$_2$O$_3$–$\gamma$-Al$_2$O$_3$–microporous SiO$_2$ was found to have the highest selectivity for dehydration of alcohols. This was due to a combination of small pores in the microporous silica layer and the hydrophilicity of this layer. When $\gamma$-Al$_2$O$_3$ was replaced by mesoporous anatase, lower separation factors were obtained. The hydrophilicity of the silica top layer appeared to be influenced by the nature of the underlying mesoporous supporting layer.

Zhou and Koros [71] adapted Matrimid® hollow fibres, originally developed for standard gas separation to dehydrate acetic acid and water mixtures. These fibres, with an integrally defect-free skin layer supported on an open porous substrate, exhibit intrinsic selectivity for gases such as N$_2$, O$_2$ and He. When applied to separate acetic acid and water mixtures, the separation factor and water flux of $\sim$15 kg m$^{-2}$ h$^{-1}$ and 2.5 kg m$^{-2}$ h$^{-1}$ respectively, were obtained for a regular 250 μm outer diameter and 20 cm long defect-free hollow fibre in a pervaporation process at 101.5 °C. A large bore pressure change along the axial direction of hollow fibres was shown to negatively impact separator performance. The separation factor and water flux were therefore increased by $\sim$150% using a similar fibre with a diameter twice as large as that of the regular gas separation fibre.

Novel hydrophilic polymer membranes based on cross-linked mixtures of poly(allylamine hydrochloride)–PVA were developed by Namboodiri et al. [72]. The high selectivity and flux characteristics of these membranes for the dehydration of organic solvents were evaluated using pervaporation technology and found to be very promising when compared with existing membranes.

Pervaporation is a membrane process used to separate liquid mixtures. In the dehydration application, water is removed from its mixtures with organic components by selective permeation through a dense hydrophilic membrane. The most relevant application of pervaporation is the separation of liquid azeotropes and close boiling point solvent–water mixtures. In the article by Urtiaga et al., the research work developed in the field of hydrophilic pervaporation by the Advanced Separation Processes group of the University of Cantabria (Spain) was reviewed. Special attention was devoted to the applications related to the recovery by dehydration of organic solvents employed in different industrial processes. A brief description of the theoretical background and design basis of hydrophilic pervaporation was followed by the presentation of a series of case studies: (i) valorization of an industrial ketonic waste; (ii) recovery of THF; (iii) isopropanol recovery from a pharmaceutical waste stream; and (iv) drying of cyclohexane in the chemical manufacturing of synthetic rubbers [73].

Conventional pervaporation (pervaporation) membranes usually have limited resistance to acetic acid, particularly in high-pressure and -temperature conditions, resulting in a cumbersome water–acetic acid separation. When acetic acid is to be recycled in process conditions in a hybrid pervaporation approach, the pervaporation membrane may experience these conditions of high temperatures and pressures. Jullok et al. [74] explored the potential of dehydrating acetic acid using pervaporation with novel polyphenylsulfone (PPSU) membranes. These membranes were tested for pervaporation dehydration of mixtures of acetic acid–water with 80 and 90 wt% acetic acid in the temperature range between 30 and 80 °C. In addition to that, an experimental study of membrane stability was performed at high concentration of acetic acid and high temperatures. It was found that a higher polymer concentration does not necessary yield a better separation factor: PPSU-based membranes with 27.5 wt% of the polymer (PPSU-27.5) were similar to 30 wt% (PPSU-30) in terms of overall performance, considering both flux and separation factor. Although the total flux of PPSU-27.5 (0.12–0.83 kg m$^{-2}$ h$^{-1}$) was lower than PPSU-25 (~0.24–1.48 kg m$^{-2}$ h$^{-1}$) the average separation factor can be higher than for the PPSU-30 membrane. For example, in 90 wt% acetic acid, the separation factor was 8.4 for PPSU-27.5 and 5.7 for PPSU-30. The swelling degree was found to decrease with feed temperature, while an increase of the selectivity and flux was observed. The activation energy of permeability $E_p$ showed that PPSU membranes have negative $E_p$ values. This indicates that the membrane partial
permeabilities decrease with increasing temperature. With the enrichment of acetic acid on the feed side of the membrane, the degree of swelling, flux and separation factor all increase. Regarding the membrane stability tests, the PPSU membranes showed promising results in the conditions tested.

15.4.2 Organic Separation from Water

Organic–water selective membranes are effective for the recovery of organic solvents from water and removal of organics in water. These membranes can contribute to the effective use of organic solvents and environmental problems.

15.4.2.1 Alcohol-Selective Concentration

Concentration of Bio-alcohols  Bioethanol as a clean and renewable fuel has gained increasing attention; however, greater energy inputs make for slow progress in industry. Membrane technology has potential in the bioethanol production process as a highly selective and energy-saving separation process. Wei et al.’s review presented membrane technologies applied in three aspects: (i) microalgae harvesting; (ii) sugar concentration and detoxification; (iii) bioethanol recovery. The performance of different membrane processes was summarized and compared. The advantages and limitations of membrane technologies for these applications were discussed, and it was thought that the hybrid process has great potential in improving membrane efficiency [75].

Graft copolymer membranes consisting of both ethanol- and water-permselective components for the separation of aqueous ethanol solutions were prepared by the copolymerization of an oligodimethylsiloxane (DMS) macromonomer with methyl methacrylate (MMA) [76,77]. As can be seen from Figure 15.7, the separation factor through the PMMA-g-PDMS membranes with a DMS content of less than 40 mol% was <1. This indicates that the water from an aqueous ethanol solution preferentially permeates the membrane by pervaporation. With increasing DMS content, however, the separation factor gradually increases until it becomes ~7. The fact that the separation factor >1 indicates

![Figure 15.7](image_url)

Figure 15.7  Effect of DMS content on separation factor (○) and normalized permeation rate (●) through PMMA-g-PDMS membranes by pervaporation. Feed solution: aqueous solution of 10 wt% ethanol (40 °C). Dashed line represents the feed composition.
that the PMMA-\textit{g}-PDMS membranes become ethanol permselective with an increase in DMS content. These results are attributable to an increase in both the hydrophobicity of the membrane and the diffusivity of the ethanol molecule as DMS content increases; since the DMS component is hydrophobic, it has a stronger affinity for ethanol molecules than for water molecules. Therefore, the DMS component preferentially incorporates more ethanol molecules than water molecules. Furthermore, the diffusivity of the ethanol molecule in the rubbery PDMS component may be similar to that of the water molecule due to considerably free rotation of the siloxane bond. As a result of both the higher solubility of ethanol and the diffusivity of ethanol comparable to water in the DMS component, the ethanol permselectivity of the PMMA-\textit{g}-PDMS membranes is enhanced with increased DMS content. Such changes in the permselectivity with copolymer composition are not common in the separation of aqueous alcohol solutions through polymer membranes by pervaporation. The DMS content with which the PMMA-\textit{g}-PDMS membrane changes from water to ethanol permselective corresponds to the content with which the normalized permeation rate increases sharply. These results have led us to speculate that the membrane structures change remarkably at a DMS content of about 40 mol\%. DSC measurement and TEM observation supported that PMMA-\textit{g}-PDMS membranes with a DMS content more than about 40 mol\% have a microphase-separated structure and the PDMS phase in a low DMS content membrane is a discontinuous layer but that in the membrane with higher DMS content forms a continuous layer structure. Also by image analysis processing it was confirmed that there is a phase transition in percolation with the DMS content. The change of ethanol permselectivity with the DMS content in Figure 15.7 can be easily understood by TEM observation and percolation transition. When the A and B components in a microphase-separated membrane form a continuous phase and discontinuous phase respectively, the Maxwell equation can be applied well to the permeation of such a membrane [78,79]. Figure 15.8 compares the permeation rate of PMMA-\textit{g}-PDMS membrane with the theoretical situation using the Maxwell equation. From a 34 mol\% DMS content the permeation rate shifts onto the DMS theoretical curve rather than following the MMA theoretical curve, and the existence of a percolation point is seen.

The permselectivity of block copolymer membranes consisting of ethanol-permselective PDMS plus water-permselective PMMA was compared by Miyata et al. with the permselectivity of graft copolymer membranes for the separation of an aqueous ethanol solution [80]. This paper focuses on the difference in molecular architecture between the block and graft copolymers and relates

Figure 15.8 Relationship between the DMS content and normalized permeation rate of an aqueous solution of 10 wt % ethanol through the PMMA-\textit{g}-PDMS membranes by pervaporation: (\ldots) theoretical normalized permeation rate calculated on the assumption that the DMS phase is continuous; (\ldots) assumption that the MMA phase is continuous, using Maxwell’s equation. The closed circles represent experimental normalized permeation rates.
microphase separation in these membranes to their permeability and permselectivity for an aqueous ethanol solution in pervaporation. With increasing DMS content, the block copolymer membranes changed from water- to ethanol-permselective at a DMS content of 55 mol%. As mentioned earlier, however, the graft copolymer membranes showed a dramatic change in the permselectivity at a DMS content of 34 mol%. Transmission electron micrography demonstrated that both membranes had distinct microphase separation consisting of PDMS and PMMA phases and that the morphology was quite different between the block and graft copolymer membranes. The morphological changes in these membranes were investigated by image processing of the micrographs and analysis using a combined model consisting of both parallel and series models. These investigations revealed that the percolation transition of the PDMS phase in the block and graft copolymer membranes takes place at a DMS content of about 55 mol% and 35 mol% respectively. This suggests that the continuity of the PDMS phase in the microphase separation strongly influences the ethanol permselectivity of these membranes for an aqueous ethanol solution. These results lead to the conclusion that the design of the molecular architecture in multicomponent polymer membranes is very important in controlling membrane characteristics which are governed by microphase separation.

The annealing effects of block and graft copolymer membranes consisting of ethanol-permselective PDMS plus water-permselective PMMA on their permselectivity for an aqueous ethanol solution in pervaporation were investigated in terms of their microphase separation [81]. The ethanol-permselectivity of the block copolymer membranes was strongly influenced by the annealing, but that of the graft copolymer membranes was not. The original block copolymer membranes changed from water- to ethanol-permselectivity at a DMS content of 55 mol%, but the annealed block copolymer membranes changed at a DMS content of 37 mol%. Transmission electron micrography demonstrated that the annealing of the block copolymer membranes with a DMS content between 37 and 55 mol% resulted in dramatic changes in the morphology of their microphase separation. However, the annealing of the graft copolymer membranes had very little effect on the morphology of their microphase separation, which was quite different from the morphology of the block copolymer membranes. The analysis using a combined model consisting of parallel and series models revealed that a continuous PDMS phase in the direction of the membrane thickness is readily formed by the annealing of the block copolymer membranes. As a result, the continuity of the PDMS phase in the microphase separation governed the ethanol permselectivity of these membranes for an aqueous ethanol solution. This report concludes that the morphological design of microphase-separated membranes, which can be achieved by membrane annealing, is very important in controlling their permeability and permselectivity.

When the membrane surface is modified by a hydrophobic graft copolymer poly(fluoroacrylate) (PFA)-g-PDMS shown in Scheme 2.1 (see Figure 5.15), the ethanol permselectivity is improved significantly [82]. In order to improve the surface properties of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membranes, surface-modified PTMSP membranes were prepared by adding a small amount of a polymer additive, which is a graft copolymer PFA-g-PDMS, consisting of PFA and PDMS, in a casting solution of PTMSP. Contact angles for water on air and glass plate sides in the preparation of surface-modified PTMSP membranes were significantly different and those on the air side were more hydrophobic, and the contact angles for water increased with increasing additional amount of PFA-g-PDMS. High hydrophobicity of the membrane surface on the air side and the increase in hydrophobicity with an increase of the additional amount of polymer additive were also confirmed by X-ray photoelectron spectroscopy. The permeation rate for an aqueous solution of 10 wt% ethanol in pervaporation of the surface-modified PTMSP membranes decreased slightly, but ethanol permselectivity increased considerably with the increase of the additional amount of PFA-g-PDMS.
Pure Silicalite™ membranes were prepared on porous supports of sintered stainless steel or alumina discs. The Silicalite layer was characterized by XRD, SEM and mercury porosimetry. Individual crystals were intergrown in three dimensions into the polycrystalline phase. The membranes were not disintegrated by thermal treatment in vacua or calcination for removing the organic amine occluded in the channels of Silicalite, indicating high thermomechanical stability of the membrane. The liquid separation potential of the membrane was investigated by pervaporation of an aqueous ethanol solution. The high ethanol permselectivity with a separation factor $\alpha_{\text{EtOH}/\text{H}_2\text{O}}$ of more than 60 was achieved for a 5 vol.% aqueous ethanol solution at 30 °C, indicating no cracks and pores between the Silicalite grains within the membrane. From adsorption experiments of ethanol and water on Silicalite, it was found that the high permselectivity is attributable to the selective sorption of ethanol into the Silicalite membrane [83].

The production of renewable ethanol biofuel from fermentation process as well as the investigation of energy-saving separation techniques was advanced by the energy crisis in the 1970s. As a rising membrane separation technology, pervaporation is especially attractive in the separation of azeotropic mixtures such as ethanol–water mixtures due to high separation efficiency, low energy consumption, integration of pervaporation with fermenter and synergy of performing pervaporation and other separation methods, and so on. Zhan et al. [84] reported a brief introduction of investigation background of ethanol permselective membrane by pervaporation. Theories used for the selection of ethanol permselective membrane materials were summarized and analysed. And the structure characteristics, modification methods and pervaporation performance of ethanol perm-selective membrane materials (such as silicon-containing polymers, fluorine-containing polymers, organic–inorganic composite membrane materials and other polymers, etc.) with separation priorities were presented in detail. The relationship between the structure characteristics of pervaporation membrane materials and their separation performance was discussed thoroughly.

Lignocellulosic biomass has potential as an alternative to corn as starting material for the production of non-fossil fuel energy sources. In this case, low concentration bioethanol is gained by yeast fermentation and it has to be efficiently recovered and concentrated. For this purpose, pervaporation separation of dilute alcohol–aqueous solutions was carried out using a poly(octylmethyl siloxane) membrane. The effect of different process parameters (feed composition, feed temperature, feed flow rate, permeate pressure) on pervaporation performance were investigated and discussed in terms of separation factor and total flux. The membrane studied was ethanol to water selective at ethanol feed concentrations lower than 2.5% w/w, while highest permeability was achieved at feed temperature of 95 °C [85].

**Concentration of Industrial Alcohols** To attain both high productivity and efficient recovery of ethanol from broth, a membrane bioreactor consisting of a jar fermenter and a pervaporation system was applied to the direct production of ethanol from uncooked starch with a thermophilic anaerobic bacterium, *Clostridium thermohydrolysulfuricum* [86]. From four types of ethanol-selective membranes tested, microporous PTFE membrane, the pores of which are impregnated with silicone rubber, was chosen for its large flux, high ethanol selectivity and high stability. During fed-batch fermentation with pervaporation in the membrane bioreactor, ethanol was continuously extracted and concentrated in two traps with concentrations at 5.6–6.2% (w/w) in trap 1 (20 °C) and 27–32% (w/w) in trap 2 (liquid N₂), while the ethanol concentration in the broth was maintained at 0.85–0.9% (w/w). Owing to the low ethanol concentration in the broth and the immobilization of bacterial cells by the membrane, the number of viable cells and, eventually, the ethanol productivity increased in the membrane bioreactor.
A supported liquid membrane system was developed for the extraction of ethanol during semicontinuous fermentation of *Saccharomyces bayanus*. It consisted of a porous Teflon sheet as support, soaked with isotridecanol. This assembly permitted combining biocompatibility, permeation efficiency and stability. The removal of ethanol from the cultures led to decreased inhibition and, thus, to a gain in conversion of 452 g L\(^{-1}\) glucose versus 293 g L\(^{-1}\) glucose without extraction. At the same time, the ethanol volumetric productivity was enhanced 2.5 times, due to an improvement of yeast viability, while the substrate conversion yield was maintained above 95% of its theoretical value. Besides these improvements in fermentation performances, the process resulted in ethanol purification, since the separation was selective towards microbial cells and carbon substrate, and likely selective to mineral ions present in the fermentation broth. For pervaporation, a concentration of ethanol four times greater was obtained in the collected permeate [87].

It is clear that biofuels have a positive impact in the social, environmental and economic aspects of our world. In Brazil, ethanol is produced from sugarcane and is mainly used as a biofuel for cars. However, much research is being done in order to reduce the price of ethanol. With this goal in mind, pervaporation is being studied as a recovery process for ethanol from wine from fermentation, and to simplify the distillation step in order to reduce its production costs. More specifically, the research project of Jaimes *et al.* studied ethanol separation by pervaporation from ethanol–water mixtures. The pervaporation was evaluated at 30 °C using a hydrophobic membrane of PDMS for ethanol recovery, using ethanol concentrations characteristic of sugarcane fermentation [88].

A hydrophobic polymeric PDMS membrane was used by Trinh *et al.* for the pervaporative separation of bioethanol produced from fermentation of lignocellulosic biomass (waste newspaper) and glucose [89]. As a preliminary study, the pervaporation permeation performance showed strong dependence on feed concentration and temperature. The pervaporation of bioethanol produced by the fermentation of waste newspaper by *Saccharomyces cerevisiae* decreased process performance. However, the process performance was restored reversibly by water cleaning. The pervaporative separation of bioethanol from the fermentation of waste newspaper was carried out without any significant decreasing process performance in the study.

A composite hollow-fibre membrane with a thin PDMS active layer on a polyetherimide macroporous support was used for pervaporative separation of ethanol produced by *Saccharomyces cerevisiae* from glucose fermentation broth. The pervaporation performance for ethanol–water binary mixtures was strongly dependent on the feed concentration and operating temperature for ethanol concentrations of 1–10%. The composite hollow-fibre membrane was stable over the long term (about 160 days) with an ethanol permeation flux of 60–62 g m\(^{-2}\) h\(^{-1}\) and a separation factor of 7–9. In comparison with published results for PDMS composite membranes, the PDMS–polyetherimide hollow-fibre composite membrane had relatively good pervaporation performance with a total flux of 231–252 g m\(^{-2}\) h\(^{-1}\) [90].

Dong *et al.* developed ceramic hollow-fibre-supported PDMS composite membranes by dip-coating the PDMS layer on the surface of the macroporous ceramic hollow-fibre support [91]. By controlling the properties of polymer solution and ceramic hollow fibre, high-quality ceramic hollow-fibre-supported PDMS composite membranes were fabricated for pervaporation recovery of bio-butanol. It was found that both the viscosity of the PDMS dip-coating solution and the pore size and structure of the ceramic support played critical roles in determining the microstructures, the mass transport and the pervaporation performance of PDMS composite membrane. The optimized composite membrane with defect-free PDMS layer and low transport resistance of support showed a total flux of 1282 g m\(^{-2}\) h\(^{-1}\) and separation factor of 42.9 for 1 wt% *n*-butanol–water mixtures at a temperature of 40 °C during 200 h continuous operation. In addition, the membrane pervaporation performance and stability in acetone–butanol–ethanol fermentation broth were investigated. The results showed the PDMS
composite membrane exhibited high and stable performance for butanol recovery from acetone–butanol–ethanol systems. Compared with the literature, Dong et al. demonstrated that the ceramic hollow-fibre-supported PDMS composite membrane could be a competitive pervaporation membrane for recovering organic compounds from fermentation broth to produce renewable biofuels. Table 15.1 compares the performances of the ethanol–water selective polymer membranes; as can be seen, the addition of PFA-g-PDMS to PTMSP membrane was very effective.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Feed (wt%)</th>
<th>Applied temperature (°C)</th>
<th>(\alpha_{\text{EtOH}/\text{H}_2\text{O}})</th>
<th>NPR(^a) (kg μm m(^{-2}) h(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>7</td>
<td>25</td>
<td>11.8</td>
<td>2.1</td>
<td>[92]</td>
</tr>
<tr>
<td>PTMSP</td>
<td>7</td>
<td>25</td>
<td>11.2</td>
<td>1.1</td>
<td>[93]</td>
</tr>
<tr>
<td>PTMSP</td>
<td>10</td>
<td>30</td>
<td>12.0</td>
<td>4.5</td>
<td>[94]</td>
</tr>
<tr>
<td>PFA-g-PDMS/PTMSP(^b)</td>
<td>10</td>
<td>40</td>
<td>20.0</td>
<td>24.1</td>
<td>[95,96]</td>
</tr>
<tr>
<td>PFA-g-PDMS</td>
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<td>30</td>
<td>22.5</td>
<td>5.5</td>
<td>[97]</td>
</tr>
<tr>
<td>PST-g-PhdFDA (87.6/12.4)</td>
<td>8</td>
<td>30</td>
<td>45.9</td>
<td>0.6</td>
<td>[98]</td>
</tr>
<tr>
<td>TFE/i-OcVE/C18VE Terpolymer (50/25/25)</td>
<td>15</td>
<td>50</td>
<td>7.13</td>
<td>5.0</td>
<td>[99]</td>
</tr>
<tr>
<td>Modified silicone</td>
<td>10</td>
<td>40</td>
<td>3.65</td>
<td>11.0</td>
<td>[100]</td>
</tr>
<tr>
<td>PDMS</td>
<td>10</td>
<td>40</td>
<td>7.44</td>
<td>6.4</td>
<td>[101,102]</td>
</tr>
<tr>
<td>PMMA-g-PDMS (34/66)</td>
<td>10</td>
<td>40</td>
<td>7.1</td>
<td>4.8</td>
<td>[89]</td>
</tr>
<tr>
<td>PMMA-g-PDMS (27/73)</td>
<td>10</td>
<td>40</td>
<td>8.0</td>
<td>5.1</td>
<td>[90]</td>
</tr>
<tr>
<td>PMMA-g-PDMS (38/62)(^c)</td>
<td>10</td>
<td>40</td>
<td>6.8</td>
<td>3.5</td>
<td>[91]</td>
</tr>
</tbody>
</table>

\(^a\) Normalized permeation rate.
\(^b\) PFA-g-PDMS is 0.2 wt.%.
\(^c\) Annealing is 120 °C, 2 h.

15.4.2.2 Organic Selective Removal

**Removal of Aromatic Hydrocarbons in Water**  Removal of VOCs such as benzene and chloroform in aqueous benzene and chloroform solutions through the PMMA-g-PDMS, poly(ethylmethacrylate)–PDMS (PEMA-g-PDMS) and poly(\(n\)-butylmethacrylate)–PDMS (PBMA-g-PDMS) graft copolymer membranes was investigated by pervaporation [101]. When aqueous solutions of dilute VOCs were permeated through the PMMA-g-PDMS and PEMA-g-PDMS membranes, these membranes showed a benzene and chloroform permselectivity. Permeation and separation characteristics of the PMMA-g-PDMS and PEMA-g-PDMS membranes changed drastically at a DMS content of about 40 mol% and 70 mol% respectively. Permeation rate and VOC permselectivity of the PBMA-g-PDMS membrane, however, increased gradually with increasing DMS content, unlike those of the PMMA-g-PDMS and PEMA-g-PDMS membranes. Furthermore, transmission electron microscope observations revealed that the PMMA-g-PDMS and PEMA-g-PDMS membranes had microphase separations consisting of a PDMS phase and a poly(alkylmethacrylate) phase, but the PBMA-g-PDMS membrane was homogeneous. The permeability and permselectivity for aqueous VOCs solutions through their
graft copolymer membranes in pervaporation are discussed in detail from the viewpoint of their membrane structure, and permselectivity was analysed by the solution-diffusion theory. Hydrophobically surface-modified membranes were prepared by adding a fluorine-containing graft copolymer into a microphase-separated membrane consisting of PDMS and PMMA. This study focuses on the effects of surface characteristics and microphase separation of the surface-modified membranes on their permselectivity for a dilute aqueous solution of benzene in pervaporation [102]. Contact-angle measurements and X-ray photoelectron spectroscopy revealed that the addition of a fluorine-containing copolymer produced a hydrophobic surface at the membrane air side due to its surface localization. It became apparent from TEM that adding a fluorine-containing copolymer of less than 1.2 wt% did not affect the morphology of the microphase-separated membrane, but adding the copolymer over 1.2 wt% resulted in a morphological change from a continuous PDMS phase to a discontinuous PDMS phase. The addition of a small amount of fluorine-containing copolymer into the microphase-separated membranes enhanced both the permeability and selectivity for a dilute aqueous solution of benzene in pervaporation because of their hydrophobic surfaces and microphase-separated structures. Specifically, the microphase-separated membrane containing 1.2 wt% of fluorine-containing copolymer concentrated from an aqueous solution of 0.05 wt% benzene to 70 wt% benzene and removed benzene in water very effectively. This paper of Miyata et al. also discussed the effect of the asymmetric surface structure of the hydrophobically surface-modified membranes on their permselectivity.

The structural characteristics of membranes used in the removal of benzene from a dilute aqueous solution of benzene by pervaporation were investigated [100]. PMMA-g-PDMS and PMMA-b-PDMS membranes containing tert-butylcalix[4]arene (CA), (CA–PMMA-g-PDMS and CA–PMMA-b-PDMS) were studied. When an aqueous solution of 0.05 wt% benzene was permeated through CA–PMMA-g-PDMS and CA–PMMA-b-PDMS membranes, these membranes showed strong benzene permselectivity. Both the permeability and the benzene permselectivity of CA–PMMA-g-PDMS and CA–PMMA-b-PDMS membranes were enhanced by increasing the CA content, due to the affinity of the CA for benzene. The permeability and the benzene permselectivity of CA–PMMA-b-PDMS membranes were much greater than those of CA–PMMA-g-PDMS membranes. TEM observations revealed that both the CA–PMMA-g-PDMS and CA–PMMA-b-PDMS membranes had a microphase-separated structure consisting of a PMMA phase and a PDMS phase containing CA. The microphase-separated structure of the latter membranes was much clearer than that of the former and was lamellar. The distribution of CA in the microphase-separated structure of the CA–PMMA-g-PDMS and CA–PMMA-b-PDMS membranes was analysed by DSC.

The effects of cross-linkers of the cross-linked PDMS membranes derived from PDMS dimethylmethacrylate macromonomer (PDMSDMMA) and divinyl compound on the pervaporation characteristics of the removal of benzene from an aqueous solution of dilute benzene were investigated [92]. When an aqueous solution of 0.05 wt% benzene was permeated through the cross-linked PDMSDMMA membranes, they showed high benzene permselectivity. Both the permeability and benzene permselectivity of the membranes were enhanced with increasing divinyl compound content as the cross-linker and were significantly influenced by the kind of divinyl compound. PDMSDMMA membranes cross-linked with divinylsiloxane (DVS) showed very high membrane performance during pervaporation. The best normalized permeation rate, separation factor for benzene permselectivity and PSI of a PDMSDMMA – DVS membrane were 1.96 × 10^{-5} m kg m^{-2} h^{-1}, 2886, and 5657 respectively. These pervaporation characteristics were discussed from the viewpoint of the chemical and physical structure of the cross-linked PDMSDMMA membranes.

The preparation of organic–inorganic hybrid membranes and their pervaporation permeation and separation characteristics for an aqueous solution of 0.05 wt% benzene were described by Uragami and
co-workers [93]. Organic–inorganic hybrid membranes were prepared by the sol–gel reaction of TEOS as an inorganic component with poly(MMA-co-vinyltriethoxysilane) (P(MMA-co-VTES)) and poly(butyl methacrylate-co-VTES) (P(BMA-co-VTES)) as organic components. When an aqueous solution of dilute benzene (0.05 wt%) was permeated through the P(MMA-co-VTES)–TEOS and P(BMA-co-VTES)–TEOS hybrid membranes, the benzene concentration in the permeate through all hybrid membranes was higher than that in the feed solution. This result demonstrates that these hybrid membranes are benzene selective for an aqueous solution containing dilute benzene. The benzene/water selectivity of the P(BMA-co-VTES)–TEOS hybrid membrane was about 20 times higher than that of the P(MMA-co-VTES)–TEOS hybrid membrane. Specifically, the P(BMA-co-VTES)–TEOS hybrid membrane with a TEOS content of 75 mol% showed the highest benzene/water selectivity. The benzene/water selectivity of the hybrid membranes depended significantly on the cross-linked structures formed by the sol–gel reaction of VTES and TEOS.

The effects of fluorine cross-linker of the cross-linked PDMS membranes from PDMSDMMA and divinyl perfluoro-n-hexane (DVF) on the pervaporation characteristics of the removal of benzene from an aqueous solution of dilute benzene were studied by Ohshima et al. [94]. When an aqueous solution of 0.05 wt% benzene was permeated through the cross-linked PDMSDMMA (PDMSDMMA–DVF) membranes they showed a high benzene permselectivity, and permeability of these membranes was enhanced with increasing DVF content significantly. The best normalized permeation rate, separation factor for benzene permselectivity and PSI of a PDMSDMMA–DVF membrane were 1.72 × 10^{-5} kg m^{-2} h^{-1}, 4316 and 7423 respectively. The best normalized permeation rate of a PDMSDMMA–DVF membrane was approximately the same as the PDMSDMMA membranes cross-linked with other divinyl compounds, but the separation factor and PSI of the former membrane were greater than those of the latter ones. These pervaporation characteristics were discussed from the viewpoint of chemical and physical structure of the cross-linked PDMSDMMA–DVF membranes in detail.

The permeation and separation characteristics of VOCs, such as chloroform, benzene and toluene, from water by pervaporation through cross-linked PDMS membranes prepared from PDMSDMMA and divinyl compounds, such as ethylene glycol dimethylmethacrylate (EGDM), divinylbenzene (DVB), DVS and DVF were investigated [95]. When aqueous solutions containing 0.05 wt% VOCs were permeated through cross-linked PDMSDMMA membranes, these membranes showed high VOC/water selectivity and permeability. Both VOC/water selectivity and permeability were affected significantly by the divinyl compound. Furthermore cross-linked PDMSDMMA membranes showed the highest chloroform/water selectivity. The VOC/water selectivity was mainly governed by the sorption selectivity rather than the diffusion selectivity. However, the difference in the selectivity between different types of VOCs depended on differences in the diffusivity of permeants. With increasing downstream pressure, the VOC/water selectivity of all cross-linked PDMSDMMA membranes increased, but the permeability decreased. A PDMSDMMA–DVF membrane exhibited a normalized permeation rate of 1.9 × 10^{-5} kg m^{-2} h^{-1} and a separation factor for chloroform–water of 4850, yielding a separation index of 9110. The pervaporation characteristics of the cross-linked PDMSDMMA membranes were discussed based on their chemical and physical structures as well as the chemical and physical properties of the permeants.

The pervaporation performance of optimized P(BMA-co-VTES)–TEOS hybrid membranes for the removal of benzene from water was investigated [96]. P(BMA-co-VTES)–TEOS hybrid membranes prepared by the sol–gel reaction were modified by annealing and trimethylsilylation to enhance the performance of these membranes. The annealing and trimethylmethoxysilane modifications of P(BMA-co-VTES)–TEOS hybrid membranes gave more hydrophobic membranes compared with untreated P(BMA-co-VTES)–TEOS hybrid membranes and, consequently, the amount of benzene
sorbed in the modified P(BMA-co-VTES)–TEOS hybrid membranes increased significantly. When an aqueous solution of dilute benzene was permeated by pervaporation through the annealed and trimethylmethoxysilane-modified P(BMA-co-VTES)–TEOS hybrid membranes, the annealing treatment enhanced the benzene/water selectivity significantly. This result was attributed to a decrease in residual silanol groups in the annealed hybrid membranes and the formation of an optimum cross-linked structure of the annealed P(BMA-co-VTES)–TEOS hybrid membranes.

Effects of the addition of CA to cross-linked PDMS membranes derived from PDMSDMMA and various divinyl cross-linker compounds, on the pervaporation characteristics for the removal of dilute benzene from an aqueous solution were investigated [97]. When an aqueous solution of 0.05 wt% benzene was permeated through the cross-linked PDMSDMMA membranes containing CA they showed high benzene/water selectivity and permeability. Both the benzene/water selectivity and permeability of the membranes were enhanced by increasing both the divinyl compound cross-linker content and the amount of CA, and were significantly influenced by the type of divinyl compound. Addition of CA to PDMSDMMA membranes cross-linked with DVF showed the best pervaporation performance. The normalized permeation rate, benzene/water separation factor, and PSI of these membranes were $1.86 \times 10^{-8}$ kg m$^{-2}$ h$^{-1}$, 5027 and 9350 respectively. The pervaporation characteristics of the cross-linked PDMSDMMA membranes containing CA were studied with respect to their chemical and physical structure. Furthermore, the mechanism of the selective permeation of benzene over water through these membranes was investigated.

The effects of the addition of fluorine-containing graft or block copolymer additives composed of 1H,1H,2H,2H-heptadecafluorodecyl acrylate (perfluoroalkyl acrylate, PFA) and PDMS macromonomer or PDMS macro-azo-initiator to a microphase-separated membrane consisting of PDMS and PMMA on the benzene/water selectivity for an aqueous dilute benzene solution during pervaporation and the surface characteristics and structures of the surface-modified PMMA–PDMS membranes were investigated [98]. The addition of the fluorine-containing copolymer additives, PFA-g-PDMS and PFA-b-PDMS, to a PMMA–g-PDMS membrane yielded hydrophobic surfaces at the air side of surface-modified membranes due to the localization of their additives on the air-side surface of these membranes. The addition of a small amount of the PFA-g-PDMS and PFA-b-PDMS enhanced both the benzene/water selectivity and the permeability for an aqueous dilute benzene solution during pervaporation because of the formation of their hydrophobic surfaces and the existence of the microphase-separated structures with a continuous PDMS phase inside these membranes. When larger amounts of the PFA-g-PDMS and PFA-b-PDMS were added to a PMMA–PDMS, the latter additive could keep the microphase-separated structures with a continuous PDMS phase, but the former did not. The relationship between the permeation and separation characteristics for the removal of benzene from an aqueous benzene solution and the structures of the PMMA-g-PDMS membranes surface modified with PFA-g-PDMS and PFA-b-PDMS as fluorine-containing polymer additives is discussed in detail.

The effects of the PSt content of PSt–PDMS interpenetrating network (IPN) polymer membranes, on the pervaporation characteristics during the removal of benzene from an aqueous solution of dilute benzene were studied [99]. When an aqueous solution of 0.05 wt% benzene was permeated through the PSt–PDMS IPN membranes, they showed high benzene/water selectivity. Both the permeability and the benzene/water selectivity of the membranes were enhanced with increasing PSt content in the PSt–PDMS IPN membrane. The physicochemical mechanism of permeation and separation through the PSt–PDMS IPN membranes during pervaporation was also discussed. The best normalized permeation rate, separation factor for benzene selectivity and PSI of the PSt–PDMS IPN membrane were $1.27 \times 10^{-6}$ kg m$^{-2}$ h$^{-1}$, 3293 and 41 821 respectively. These pervaporation characteristics were discussed from the viewpoint of the chemical and physical structure of the PSt–PDMS IPN membranes.
The effects of the addition of an ionic liquid, 1-allyl-3-butylimidazilium bis(trifluoromethane sulfonyl) imide (\([\text{ABIM}]\text{TFSI}\)), which has a high affinity for benzene, into PVC membrane on the pervaporation characteristics of the removal of benzene from aqueous solutions of dilute benzene were investigated. When aqueous solutions of 100–500 ppm benzene were permeated through the \([\text{ABIM}]\text{TFSI}–\text{PVC}\) membranes, they showed a high benzene/water selectivity, and permeability of these membranes was enhanced with increasing \([\text{ABIM}]\text{TFSI}\) content significantly. These pervaporation characteristics were discussed from the viewpoint of the chemical and physical structure of \([\text{ABIM}]\text{TFSI}–\text{PVC}\) membranes in detail. The mechanism of permeation and separation was analysed by the solution-diffusion model [103]. The removal of VOCs such as chloroform, benzene and toluene from aqueous solutions of dilute VOCs using the \([\text{ABIM}]\text{TFSI}–\text{PSt-b-PDMS}\) by pervaporation was also investigated [104]. When aqueous solutions of 0.05 wt% VOCs were permeated through \([\text{ABIM}]\text{TFSI}–\text{PSt-b-PDMS}\) membranes they showed strong VOC/water selectivity. Both the permeability and the VOC permselectivity of \([\text{ABIM}]\text{TFSI}–\text{PSt-b-PDMS}\) membranes were enhanced by increasing the \([\text{ABIM}]\text{TFSI}\) content, because the affinity of \([\text{ABIM}]\text{TFSI}–\text{PSt-b-PDMS}\) membranes for VOCs was increased by introducing \([\text{ABIM}]\text{TFSI}\) into the membranes. The \([\text{ABIM}]\text{TFSI}\) localized in the PSt-b-PDMS membrane plays an important role as an absorbent to selectively partition VOCs from the aqueous solution.

Table 15.2 compares the permeation and separation characteristics of various polymer membranes consisting of the PDMS components under the same pervaporation condition: feed solution, an aqueous solution of 0.05 wt% benzene; permeation temperature, 40 °C; pressure of permeation side, 1.33 Pa. As can be seen from Table 15.2, both the normalized permeation rate and the benzene–water selectivity of \(\text{CA–PDMSDMMA–DVB}\), \(\text{CA–PDMSDMMA–DVS}\) and \(\text{CA–PDMSDMMA–DVF}\) membrane were improved compared with \(\text{PDMSDMMA–DVB}\), \(\text{PDMSDMMA–DVS}\) and \(\text{PDMSDMMA–DVF}\) membrane respectively. Although, the separation factors of the \(\text{CA–PDMSDMMA–DVB}\), \(\text{CA–PDMSDMMA–DVS}\) membranes were lower than that of the \(\text{PFA-g-PDMS–PMMA-g-PDMS}\) membranes, the PSI of the former membranes was much greater than that of the latter one. In previous studies [104,105], the introduction of cross-linking structure into the membrane matrix using a suitable cross-linker with a high affinity for permeant was a very effective method to give both a high permeation rate and a high benzene/water selectivity. From Table 15.2, it can be seen that the addition of \(\text{CA}\) into the cross-linked PDMSDMMA membranes cross-linked with a suitable cross-linker is significantly effective in obtaining higher permeation and separation characteristics. A \(\text{CA–PDMSDMMA–DVF}\) membrane with DVF of 90 mol% and \(\text{CA}\) of 0.4 wt% showed the best membrane performance; that is, the normalized permeation rate, separation factor for benzene/water selectivity and PSI were \(1.86 \times 10^{-5}\) m kg m⁻² h⁻¹, 5027 and 9350 respectively. For the purpose of improvement of removal performance of VOCs from water, copolymer membranes from \(\text{PMMA}\) and PDMS, including the hydrophobic ionic liquid \([\text{ABIM}]\text{TFSI}, \text{were prepared. Permeation and separation characteristics for aqueous solutions of dilute VOCs through \([\text{ABIM}]\text{TFSI}–\text{PMMA-g-PDMS}\) membranes during pervaporation were investigated [106].}

Figure 15.9 shows the effects of the \([\text{ABIM}]\text{TFSI}\) content on the normalized permeation rate and the benzene concentration in the permeate for an aqueous solution of 0.05 wt% benzene through \([\text{ABIM}]\text{TFSI}/–\text{PMMA-g-PDMS}\) membrane during pervaporation. As can be seen from this figure, with increasing \([\text{ABIM}]\text{TFSI}\) content, both the normalized permeation rate and the benzene concentration in the permeate increased significantly. The permeation performance was significantly due to the increase in both the contact angle for water of the membrane and the benzene concentration in the membrane. The improvements in the permeation rate and the benzene/water selectivity by introducing \([\text{ABIM}]\text{TFSI}\) to \(\text{PMMA-g-PDMS}\) membrane are dependent upon both the enhancement of solubility of the benzene molecule into the \([\text{ABIM}]\text{TFSI}–\text{PMMA-g-PDMS}\) membrane and the
Table 15.2 Performance for benzene (Bz)–water (H₂O) of various membranes containing PDMS component in pervaporation.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>α_{sep.} Bz/H₂O</th>
<th>α_{sorp.} Bz/H₂O</th>
<th>α_{diff.} Bz/H₂O</th>
<th>NPR b)</th>
<th>PSI c)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>53</td>
<td>422</td>
<td>0.13</td>
<td>0.29</td>
<td>16</td>
<td>[101]</td>
</tr>
<tr>
<td>PMMA-g-PDMS d)</td>
<td>620</td>
<td>739</td>
<td>0.86</td>
<td>0.13</td>
<td>226</td>
<td>[105]</td>
</tr>
<tr>
<td>CA–PMMA-g-PDMS e)</td>
<td>1772</td>
<td>1267</td>
<td>1.40</td>
<td>0.71</td>
<td>1240</td>
<td>[105]</td>
</tr>
<tr>
<td>PFA-g-PDMS–PMMA-g-PDMS f)</td>
<td>4492</td>
<td>1270</td>
<td>0.61</td>
<td>2879</td>
<td></td>
<td>[102]</td>
</tr>
<tr>
<td>PDMSDMA–DVB g)</td>
<td>3171</td>
<td>1436</td>
<td>2.21</td>
<td>1.46</td>
<td>4629</td>
<td>[92]</td>
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<tr>
<td>PDMSDMA–DVSh)</td>
<td>2886</td>
<td>1270</td>
<td>2.46</td>
<td>1.96</td>
<td>5656</td>
<td>[92]</td>
</tr>
<tr>
<td>PDMSDMA–DV Fi)</td>
<td>4316</td>
<td>1804</td>
<td>2.49</td>
<td>1.7</td>
<td>7423</td>
<td>[92]</td>
</tr>
<tr>
<td>CA–PDMSDMA–DVB j)</td>
<td>4021</td>
<td>1689</td>
<td>2.18</td>
<td>1.75</td>
<td>7037</td>
<td>[97]</td>
</tr>
<tr>
<td>CA–PDMSDMA–DVSk)</td>
<td>3866</td>
<td>1620</td>
<td>2.39</td>
<td>1.97</td>
<td>7616</td>
<td>[97]</td>
</tr>
<tr>
<td>CA–PDMSDMA–DVFl)</td>
<td>5027</td>
<td>1998</td>
<td>2.52</td>
<td>1.86</td>
<td>9350</td>
<td>[97]</td>
</tr>
</tbody>
</table>

Source: [97].

a) Pervaporation experimental condition: feed solution, an aqueous solution of 0.05 wt% benzene; permeation temperature, 40 °C; pressure of permeation side, 1.33 Pa.

b) Normalized permeation rate \((10^{-5} \text{ m kg m}^{-2} \text{ h}^{-1})\)

c) PSI = NPR × α_{sep.} Bz/H₂O

d) PDMS content: 74 mol%.

e) PDMS content: 74 mol%. CA content: 40 mol%.

f) PDMS content: 74 mol%; PFA-g-PDMS content: 1.2 wt%.

g) DVB content: 80 mol%.

h) DVS content: 80 mol%.

i) DVF content: 80 mol%.

j) DVB content: 80 mol%; CA content: 0.5 wt%.

k) DVS content: 80 mol%; CA content: 0.5 wt%.

l) DVF content: 80 mol%; CA content: 0.5 wt%.

Figure 15.9 Effects of [ABIM]TFSI content on the benzene in the permeate (○) and the normalized permeation rate (●) for an aqueous solution of 0.05 wt% benzene through the [ABIM]TFSI–PMMA-g-PDMS membranes (DMS content: 58 mol%) during pervaporation at 40 °C.
diffusivity of the benzene molecule in the membrane. In this study, it was demonstrated that membranes with high benzene/water selectivity can be designed by addition of ionic liquid [ABIM]TFSI to the PMMA-g-PDMS membrane, and ionic liquid offers potential for selective separation of benzene–water. As already mentioned, the benzene removal performance of CA–PMMA-g-PDMS and CA–PMMA-b-PDMS membranes with CA were higher than those of membranes without CA. When CA is introduced to the [ABIM]TFSI–PMMA-g-PDMS membrane, the benzene removal performance of the CA–[ABIM]TFSI–PMMA-g-PDMS membrane was improved. It was confirmed that [ABIM]TFSI and CA in the microphase separated PMMA-g-PDMS membrane are localized in the PMMA and PDMS phase, respectively [107].

**Removal of Chlorinated Hydrocarbons in Water** Nakagawa and co-workers [108] tried to enhance the selectivity of a PDMS membrane for chlorinated hydrocarbons. The PDMS membranes were improved by graft polymerization of 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA), which has the effect of increasing the selectivity for chlorinated hydrocarbons. The PDMS membrane and HDFNMA were irradiated simultaneously by a 60Co source. The grafted membranes had a microphase-separated structure; that is, a separated structure of PDMS and grafted HDFNMA. In the grafted PDMS membrane, a great separation performance for a trichloroethylene (TCE)–water mixture was shown due to the introduction of the hydrophobic polymer, poly(HDFNMA). For the permeation of the grafted PDMS membrane, the permeability of molecules in the PDMS phase was significantly great, and that in the poly(HDFNMA) phase was too low to affect the whole permeation of the grafted PDMS membrane directly. However, the permeation of molecules at the interface of poly(HDFNMA) and PDMS played an important role because poly(HDFNMA) had a much stronger affinity for TCE than water. At a low feed concentration of the TCE solution, the diffusivity of TCE molecules must be much lower than that of water due to the larger molecular size of TCE. At a high concentration of TCE solution, TCE was sufficiently sorbed into the membrane so that the diffusion of water was prevented by TCE molecules; in turn, the permeselectivity of TCE was increased significantly.

1,1,1-Trichloroethane (TCA), a common chlorinated organic solvent and VOC, was removed from contaminated groundwater by using a bench-scale membrane pervaporation unit. The effects of TCA concentration, temperature and flow rate on permeation flux and selectivity of the process were evaluated. In general, a higher temperature led to higher VOC flux but lower selectivity, higher flow rate of TCA feed stream resulted in in higher VOC flux and selectivity (an indication of the effect of concentration polarization), and a higher TCA feed concentration produced higher TCA permeation; however, the selectivity was virtually unchanged [109].

The pervaporation performance of cross-linked PDMSDMMA membranes for an aqueous solution of various hydrocarbons was studied using sorption–diffusion theory. Three chlorinated hydrocarbons (chloroform, TCE and tetrachloromethane) and three aromatic hydrocarbons (benzene, chlorobenzene and toluene) were used as the permeants. When aqueous solutions of 0.05 wt% hydrocarbon were permeated through the crosslinked PDMSDMMA membranes, they showed high hydrocarbon/water selectivity and permeability during pervaporation. The hydrocarbon/water selectivity of the cross-linked PDMSDMMA membranes was significantly dependent upon the permeants; in particular, chloroform removed the hydrocarbons most efficiently in this study. The results of the temperature dependence of the pervaporation performance and hydrocarbon absorption into the membrane revealed that the difference in hydrocarbon/water selectivity for various aqueous solutions of hydrocarbons during pervaporation depended significantly on the molar volume and diameter of the hydrocarbons. The permeation and removal mechanism of hydrocarbons from water through cross-linked
PDMSDMMA membranes can be explained by a qualitative model based on the diffusion jump model [110].

Polymer membranes are potentially selective for separation of organic compounds from a mixture by pervaporation. A novel cross-linked hydroxy-terminated polybutadiene-based (HTPB) polyurethane urea (PUU)–PMMA IPN membrane was developed by Das et al. for the selective removal of chlorinated VOCs such as 1,1,2,2-tetrachloroethane, chloroform, carbon tetrachloride and TCE present in water in very low concentration by pervaporation [111]. IPNs of different PMMA content and also different cross-link density were used. Since the selective permeation and diffusion of the VOCs through the membrane are dependent on their interaction with the membrane material, their sorption and diffusion behaviours through the membrane were also investigated by swelling the membrane in pure VOCs. The sorption and diffusion behaviours were explained with the help of their solubility parameter data and calculated interaction parameter data of the membrane polymers with the VOCs. From the swelling kinetics data, diffusion coefficients of the VOCs through the membrane were calculated. Diffusion coefficients increased with the increase in cross-link density and PMMA content in the membrane. In the pervaporation experiment, concentrations of chlorinated organic compounds in feed were varied from 100 ppm (0.01%) to 1000 ppm (0.1%). All the three IPN membranes showed excellent separation performances of the chlorinated VOCs from water. One IPN containing 26% PMMA (PUU–PMMA-3) produced 88.7% TCE in permeate, 0.2 kg m$^{-2}$ h$^{-1}$ TCE flux and a separation factor of 7842 from a 0.1% aqueous feed after a pervaporation run of 3 h at 30 °C. All three IPN membranes of different compositions showed separation performances, with flux and separation factors for all the VOCs in the order 1,1,2,2-tetrachloroethane < carbon tetrachloride < chloroform < TCE.

15.4.3 Organic Mixture Separation

Organic–organic selective membranes are effectively used for purification and separation of industrial products and reuse of organic solvents based on separable recovery of organic mixtures.

15.4.3.1 Benzene–Cyclohexane Separation

2-Hydroxyethyl methacrylate (HEMA) (branch)–methyl acrylate (MA) (backbone) comb-type graft copolymers were synthesized by grafting an amino-semitelechelic oligo (HEMA) to an MA–glycidyl methacrylate random copolymer. From electron microscope observation, it was found that these graft polymeric membranes had microphase-separated structures. Pervaporation of a benzene–cyclohexane mixture through these membranes was carried out in order to study the effect of micro-phase-separated structures on selective permeability. Benzene was found to preferentially permeate through the membranes. Moreover, the pervaporation rate of benzene increased with increasing MA mole fraction in the graft copolymers. It was found that the continuous phases of poly(MA) domains functioned as permeating pathways for benzene and that the selectivity of the graft polymeric membranes occurred in the process of dissolution of the solvent into the membranes. The microphase separated structure was found to effectively enhance the selectivity as a result of its suppressing the plasticizing effect of benzene [112].

Side-chain liquid-crystalline polymer (LCP) was synthesized by the addition of mesogenic monomer to poly(methylsiloxane) with Pt catalyst. When the benzene–cyclohexane mixtures were permeated through the LCP membranes by pervaporation at various temperatures, the permeation rate increased with increasing benzene concentration in the feed solution and permeation temperature. Though the LCP membranes exhibited a benzene permselectivity, the mechanism of the permeation and separation for the benzene–cyclohexane mixtures was different in the glassy, liquid-crystalline and isotropic states of the LCP membranes. These results suggested that the permselectivity was fairly influenced by
the change of the LCP membrane structure; that is, a state transformation. It was found that a balance of the orientation of mesogenic groups and flexibility of siloxane chains is very important for the permeability and selectivity [113].

PMMA and PEMA, which have strong affinity for benzene, were selected as membrane materials and the characteristics of permeation and separation for the benzene–cyclohexane mixtures through these poly(alkyl methacrylate) cross-linked with EGDM membranes by pervaporation were investigated. The cross-linked poly(alkyl methacrylate) membranes exhibited a benzene permselectivity for the benzene–cyclohexane mixtures and the permeation rate increased with increasing benzene in the feed solution. The permselectivity of their membranes was strongly governed by the diffusion separation process depending on the difference of the molecular size between the benzene molecule and the cyclohexane molecule. The depression of swelling of those membranes with the increase of the cross-linker content in the benzene–cyclohexane mixtures enhanced the benzene permselectivity. This result was attributed to the increase of the selectivity in the sorption separation process with the depression of swelling of the membrane. Furthermore, the cross-linked copolymer (PMMA–PEMA–EGDM) membranes showed excellent benzene permselectivity. These results suggested that both the increase of affinity of the membrane for benzene and the depression of swelling of the membrane were very important in the separation of the benzene–cyclohexane mixtures [114].

When a benzene–cyclohexane mixture was permeated through poly(dimethyl acrylamide-random-MMA) (DMAA-r-MMA) and poly(DMMA)-graft-poly(MMA) (DMAA-g-MMA) membranes by pervaporation, the benzene permselectivity of the DMAA-r-MMA membrane changed from the diffusivity selectivity to the solubility selectivity with increasing DMAA content, but DMAA-g-MMA membranes with a high DMAA content had a higher apparent diffusivity selectivity than the apparent solubility selectivity. Furthermore, the apparent solubility selectivity for a benzene–cyclohexane mixture between the DMAA-r-MMA membrane and the DMAA-g-MMA membrane with a high DMAA content was remarkably different. These results were attributed to the difference in structure between the copolymers [115].

When a benzene–cyclohexane mixture of 10 wt% benzene was permeated through side-chain LCP membranes by pervaporation at various temperatures, the permeation rate increased with increasing permeation temperature. The LCP membranes also exhibited a benzene permselectivity. The permselectivity for the benzene–cyclohexane mixture through the LCP membrane was different in the glassy, liquid-crystalline and isotropic states. The LCP membrane had different apparent activation energies for permeation in each state. LCP membrane in the liquid-crystalline state had the highest apparent activation energy of the three states. The results suggest that the benzene permselectivity was influenced by changes in the LCP membrane structure (i.e. a state-transformation). It was found that a balance of the orientation of mesogenic groups and the flexibility of the siloxane chains was very important for benzene permselectivity [116].

A benzyolchitosan (BzChito) was synthesized as a membrane material for separation of benzene–cyclohexane mixtures. When the BzChito membrane was applied to the permeation and separation of benzene–cyclohexane mixtures in pervaporation, both the permeation rate and benzene concentration in the permeate increased with increasing benzene concentration in the feed, and thus this membrane showed benzene permselectivity. Characteristics of permeation and separation of benzene–cyclohexane mixtures through the BzChito membrane were analysed by the solution-diffusion model. It was found that the benzene permselectivity was dependent on both the sorption selectivity and diffusion selectivity but was significantly governed by the latter. Also, a tentative model for the benzene permselectivity was discussed [117].

BzChito membrane materials with a different degree of benzyolation were synthesized having a good durability for the separation of benzene–cyclohexane mixtures [118]. Characteristics of BzChito
membranes, such as contact angle, crystallinity and degree of swelling, were significantly influenced by the degree of benzoylation. The BzChito membranes showed a high benzene permselectivity for a benzene–cyclohexane mixture of 50 wt% benzene in pervaporation and the differences in the benzene permselectivity for the BzChito membranes with different degree of benzoylation corresponded to a difference in the physical structure of the membranes based on the characteristics of these membranes. When a benzene–cyclohexane mixture of 50 wt% benzene was permeated through the BzChito membranes, permeation rate increased and benzene permselectivity slightly decreased with increasing degree of benzoylation.

Chitosan and its derivatives have been used as membrane materials for a wide variety of pervaporation applications, including dehydration of ethanol–water mixtures. Uragami et al. synthesized BzChito with different degrees of benzoylation as a durable membrane material for the separation of benzene–cyclohexane mixtures. The characteristics of BzChito membranes, such as contact angle, crystallinity, and the degree of swelling, were significantly influenced by the degree of benzoylation. As shown in Figure 15.10, the BzChito membranes showed high benzene/cyclohexane selectivity for a mixture containing 50 wt% benzene during pervaporation. The difference in benzene/cyclohexane selectivity of the BzChito membranes with different degrees of benzoylation corresponded to differences in the physical structure of the membranes. When a benzene–cyclohexane mixture of 50 wt% benzene was permeated through the BzChito membranes, permeation rate increased and benzene/cyclohexane selectivity slightly decreased with an increasing degree of benzoylation [118,119].

When benzene–cyclohexane, toluene–cyclohexane and o-xylene–cyclohexane mixtures are subjected to pervaporation through a side-chain LCP membrane in the liquid-crystalline state, the permeation rate increases with increasing temperature and the LCP membrane exhibits permselectivity for the aromatic hydrocarbon. The permeation rate and permselectivity of the LCP membrane for each mixture decreases with increasing molecular size of the aromatic hydrocarbon in the binary feed mixture [120].

When benzene–cyclohexane mixtures were permeated through nematic and smectic side-chain LCP (n- and s-LCP) membranes under various conditions in pervaporation, the n- and s-LCP membranes exhibited a benzene permselectivity for the benzene–cyclohexane mixtures. The benzene permselectivity of the n-LCP membrane changed from the sorption selectivity to the diffusion selectivity by the state transformation of the membrane with an increase in the permeation temperature but
the benzene permselectivity of the s-LCP membrane was governed by the diffusion selectivity regardless of the state of the s-LCP membrane. At the low permeation temperature, the n-LCP membrane in the liquid-crystalline state exhibited a lower permeability and a higher permselectivity than the s-LCP membrane. However, at the high permeation temperature the relationship between the permeability and permselectivity of the n-LCP and s-LCP membranes in the liquid-crystalline state was vice versa. These results were led by the difference of the chemical and physical structure of the n-LCP and s-LCP membranes [120].

MMA–methacrylic acid (MMA–MAA) membranes ionically crosslinked with Fe$^{3+}$ and Co$^{2+}$ ions (MMA–MAA–Fe$^{3+}$ and –Co$^{2+}$) were prepared, and characteristics of permeation and separation for a benzene–cyclohexane mixture of 50 wt% benzene through these membranes in pervaporation were studied by Uragami and co-workers [121]. Although the introduction of the metal ions to the MMA–MAA membrane enhanced both benzene permselectivity and permeability for a benzene–cyclohexane mixture, the pervaporation characteristics between the MMA–MAA–Fe$^{3+}$ and –Co$^{2+}$ membranes were significantly different. The difference in the pervaporation characteristics between these membranes was strongly governed by the difference of these membrane structures based on the glass transition temperature, contact angle to methylene iodide, degree of swelling and mixture composition absorbed in the membrane, and so on.

Benzoylcellulose (BzCell) membranes with different degrees of benzoylation were synthesized for the separation of benzene–cyclohexane mixtures. A BzCell membrane with a degree benzoylation of 2 showed high benzene permselectivity for benzene–cyclohexane mixtures in pervaporation. The permeation rate of the BzCell membrane increases, but the benzene permselectivity decreases, with increasing benzene concentration in the feed mixture. This increase in the permeation rate is due to an increase in the swelling of the membrane, whereas the benzene permselectivity was attributed to a decrease in the sorption selectivity. With increasing benzoylation of the BzCells the permeation rate increases significantly, but the benzene permselectivity decreases slightly. These results were explained by the degree of swelling, the density and the contact angle of the BzCell membranes [122].

Tosylcelluloses (TosCells) with different degrees of tosylation were synthesized as membrane materials for the separation of benzene–cyclohexane mixtures. TosCell membranes showed a high benzene permselectivity for the benzene–cyclohexane mixtures in pervaporation. An increase in the benzene concentration in the feed mixtures increased permeation rate but decreased the benzene permselectivity of the TosCell membranes. The increase in the permeation rate was attributed to the increase of the degree of swelling of the TosCell membranes by the feed mixtures, and the decrease in the benzene permselectivity was mainly caused by the decrease of sorption selectivity. With low benzene concentrations in the benzene–cyclohexane mixtures, the permeation rate of a TosCell membrane with a higher degree of tosylation was greater than that with a lower degree of tosylation, but was vice versa with a high benzene concentration. The benzene permselectivity of the former TosCell membrane was higher than that of the latter membrane. Differences in the permeation rate and benzene permselectivity with changes in the benzene concentration in the feed mixture and degree of tosylation of the TosCell membrane were significantly influenced by the degree of swelling of the TosCell membrane and the benzene concentration sorbed into the TosCell membrane. The mechanism of separation for the benzene–cyclohexane mixtures through the TosCell membranes was discussed using the solution-diffusion model [123].

Butyrylcellulose (BuCell) with different degrees of butyrylation was synthesized as a membrane material for the separation of benzene–cyclohexane mixtures. A BuCell membrane with a degree of butyrylation of 2.3 showed high benzene/cyclohexane selectivity for benzene–cyclohexane mixtures by pervaporation. Both the permeation rate and the benzene/cyclohexane selectivity of the
BuCell membrane increased with increasing benzene concentration in the feed mixture. The increase in the permeation rate resulted from an increase in the swelling of the membrane, and the increase in the benzene/cyclohexane selectivity can be attributed to an increase in the diffusion selectivity. With increasing degree of butyrylation of BuCell, the permeation rate increased; on the other hand, the benzene/cyclohexane selectivity decreased slightly. This result was qualitatively explained by the degree of swelling, the density and the contact angle of the BuCell membranes. The permeation and separation mechanism of benzene–cyclohexane mixtures through BuCell membranes by pervaporation was discussed on the basis of the solution-diffusion model, which is typically applied for permeation through dense, nonporous membranes [124].

Cellulose alkyl esters such as ethyl, butyryl, pentyl and heptyl cellulose with different numbers of carbon atoms in the alkyl ester group were synthesized for the separation of a mixture of benzene/cyclohexane (5/95 w/w) with a low concentration of benzene. All of cellulose alkyl ester membranes showed high benzene/cyclohexane selectivity for a benzene–cyclohexane mixture in pervaporation. With increasing carbon number in the ester groups, the permeation rate increased but the benzene/cyclohexane selectivity decreased. The increase in the permeation rate was attributed to an increase in the swelling of the membrane due to the feed mixture, and the decrease in the benzene/cyclohexane selectivity was dependent on both the decrease in the solubility selectivity and the diffusion selectivity. These pervaporation characteristics were discussed from the viewpoints of chemical and physical structure of the cellulose alkyl ester membranes such as the degree of swelling, the contact angle, the density of the cellulose ester membranes and the solution composition absorbed into their membranes [125].

15.4.3.2 Organic–Organic Separation

 Preferential sorptions and pervaporation selectivities in PVC membrane for various binary liquid mixtures were investigated by Okuno et al. [126]. Methanol–n-propanol, benzene–n-hexane and ethanol–water mixtures were selected as binary liquid mixtures. In the methanol–n-propanol mixture, methanol was preferentially sorbed in the PVC membrane and predominantly permeated. In the benzene–n-hexane mixture, benzene was incorporated and permeated preferentially. In the ethanol–water mixture, ethanol was preferentially sorbed in the PVC membrane and water was preferentially permeated. The preferential sorptions were analysed according to Mulder’s model derived from Flory–Huggins thermodynamics. The pervaporation selectivity in these systems was discussed using sorption selectivity and diffusion selectivity.

The pervaporation separation and the swelling behaviour of chlorinated hydrocarbon–acetone mixtures were investigated using natural rubber and epoxidized natural rubber membrane with 25 mol% and 50 mol% epoxidation respectively. The swelling degree increased with increase in the epoxidation level. The flux and separation factor of the membranes were determined both as a function of mole per cent epoxidation and of the feed mixture composition. The membranes were found to be permselective to chlorinated hydrocarbons from acetone–chlorinated hydrocarbon mixtures. The flux decreased with increase in epoxidation level, whereas the separation factor increased. The permeation decreased and separation factor increased with increase in the acetone feed concentration. The availability of raw materials, low cost of implementation and easy processability of the system makes this method of separation highly applicable and recommendable [127].

A new kind of membrane was prepared by blending styrene–butadiene rubber and natural rubber in equal proportions [128]. These membranes were cross-linked by four different vulcanising systems; namely, conventional, efficient, dicumylperoxide and a mixture consisting of sulfur and peroxide. The properties of these membranes were evaluated by pervaporation separation of chlorinated hydrocarbon and acetone mixtures. The experimental results showed that the selectivity and the fluxes of these
membranes depended on the nature and distribution of cross-links between the macromolecular chains of the membrane. The effects of feed composition and the molecular size of the permeate on the permeation flux and selectivity were investigated.

Pervaporation separation and swelling experiments of methanol–MTBE mixtures were performed by using a flat-sheet, dense poly(2,6-dimethyl-1,4-phenylene oxide) membrane prepared from a chloroform casting solvent. The effect of the feed composition on the membrane performance was described by the permeability of the components, the separation factor and the sorption selectivity. The effect of the feed temperature on the separation was also studied, and the Arrhenius activation energy for permeability was determined over the whole range of feed composition. Pervaporation operations offered a maximum methanol selectivity of 5.4 and an overall normalized flux of 110 kg μm m⁻² h⁻¹. Pervaporation and sorption experiments were also conducted using ethanol, propanol, butanol and octanol to study the effect of the size of the alcohol molecule on the transport across the membrane [129].

Pervaporation separation of chlorinated hydrocarbon/acetone mixtures has been investigated using nanoclay modified poly(ethylene-co-vinyl acetate) films [130]. The results were compared with the unfilled poly(ethylene-co-vinyl acetate) films. The nanoclay modified membranes were characterized by XRD. The dispersion of layered silicates in the polymer matrix was analysed using TEM. The nanoclay showed excellent dispersion in the polymer matrix. The effect of free volume on the pervaporation performance was investigated by positron annihilation lifetime spectroscopy. Poly(ethylene-co-vinyl acetate) nanocomposite membrane showed high selectivity because of the platelet like morphology and high aspect ratio of layered silicates. The nanoclay content and the swelling effects on pervaporation performance of nanocomposite membranes were investigated in detail.

Highly hydrophobic titania, alumina and zirconia porous ceramic membranes were prepared by grafting of C₆F₁₃C₂H₄Si(OEt)₃ (C₆) and C₁₂F₂₅C₂H₄Si(OEt)₃ (C₁₂) molecules and subsequently applied in a pervaporation process for removal of VOCs (MTBE and ethyl acetate) from binary aqueous solutions. Transport of pure water through pristine and hydrophobized membranes were compared. The transport and separation properties in the pervaporation process of the hydrophobic membranes investigated were discussed. The influence of the membrane materials, pore size of the membranes and conditions of the grafting procedure (time and type of molecules) on the pervaporation properties was presented. All membranes investigated were selective toward organic compounds. The highest efficiency was found for the TiO₂ membranes, independently of the system utilized and grafting molecules applied. Better transport and selective properties were observed for membrane modified by C₆ molecules than by C₁₂ molecules. TiO₂ and ZrO₂ membranes modified by C₆ were characterized by high β separation factors of 84 (TiO₂) and 56 (ZrO₂). The least effective membrane was the alumina one. Additionally, the influence of contact of different solvents (water, ethyl acetate and MTBE) with the hydrophobic layer was discussed. It was found that in the presence of organic compounds in the aqueous solution the conformation of hydrophobic chains changed from a tangled to straight one [131].

### 15.4.3.3 Separation of Methyl tert-Butyl Ether–Methanol and Ethyl tert-Butyl Ether–Ethanol Mixtures

PVA–PAA and PVA–sulfo succinic acid (SSA) membrane performances were studied for the pervaporation separation of MTBE–methanol mixtures with varying operating temperatures, amount of cross-linking agents and feed compositions. Typically, the separation factor, about 4000, and the permeation rate, 10.1 g m⁻² h⁻¹, were obtained with 85/15 PVA/PAA membrane for 80/20 MTBE/methanol mixtures at 50 °C. For PVA–PAA membranes, it could be considered that the flux is affected by the structural changes of the membranes due to the cross-linking, and the free carboxylic acid group
also played an important role in the separation characteristics through the hydrogen bonding with PVA and the feed components leading to the increase of flux. The membrane containing 5% SSA showed the highest separation factor of 2095 with a flux of 12.79 g m\(^{-2}\) h\(^{-1}\) for 80/20 MTBE/methanol mixtures at 30 °C. In addition, swelling measurements were carried out for pure MTBE and methanol, and 90/10 and 80/20 MTBE/methanol mixtures using PVA–SSA membranes with varying SSA compositions. It has been recognized that there are two factors in the swelling measurements of PVA–SSA membranes: the membrane network and hydrogen bonding. These two factors act interdependently on the membrane swelling [132].

MTBE is now being extensively used as a lead-free octane enhancer for green fuel. A pervaporative separation process is used for separation of methanol–MTBE mixtures encountered during manufacturing of MTBE. Three different copolymers of acrylamide with increasing amount of HEMA (i.e. PAMHEMA-1, -2 and -3) were synthesized, and the cross-linked (gelled) copolymer membranes made from these sol copolymers were used for pervaporative separation of methanol from its mixtures with MTBE over the concentration range of 0–10 wt% methanol in the feed. These hydrophilic gel copolymer membranes were found to be highly methanol selective in both sorption and diffusion through the membranes. Methanol flux was found to decrease with increase in degree of cross-linking from PAMHEMA-1 to -3 copolymer membranes. Among the three membranes, PAMHEMA-3 membrane showed the highest selectivity and acceptable flux (511.7 and 9.9 g m\(^{-2}\) h\(^{-1}\) respectively for 0.53 wt% of methanol in the feed), while maximum flux with high selectivity was shown by PAMHEMA-1 membrane (18.48 g m\(^{-2}\) h\(^{-1}\) and 243 respectively for 0.53 wt% of methanol in the feed). MTBE was also found to have a negative coupling effect on methanol permeation. The membranes were found to show both sorption and diffusion selectivity for methanol [133].

Membranes based on polyarylethersulfone with cardo (PES–C) were prepared for pervaporation separation of methanol–MTBE mixtures [134]. The membranes were characterized using wide-angle XRD, SEM and contact-angle metering. The swelling and mechanical properties of the membranes in methanol–MTBE mixtures were studied. The degree of swelling was less than 7% originating from the good solvent proof and excellent mechanical properties of PES–C. N-Methyl pyrrolidone is found to be the optimum solvent for PES–C membrane preparation against N,N-dimethylformamide. The effect of annealing temperature and annealing time on the structure and pervaporation performance of the PES–C membranes was thoroughly discussed. The results showed that increasing annealing temperature or annealing time would enhance methanol permselectivity and reduce permeation flux. By varying feed methanol content from 5 to 40 wt%, permeation flux increased from 1.21 to 4.52 kg μm m\(^{-2}\) h\(^{-1}\), and methanol content in the permeate was almost constant. The permeation flux increased and methanol permselectivity decreased with increasing feed temperature.

The pervaporative separation of ethanol from ethanol–ethyl tert-butyl ether mixtures using the commercial membrane PERVAP 2256 was studied by Ortiz et al. [135]. Pervaporation flux was obtained and analysed as a function of feed composition in the range of ethanol concentration of 30–50 wt% and temperature in the range of 50–70 °C, whereas permeate pressure was kept constant in all the experiments and equal to 3 mmHg. Pervaporation fluxes showed an exponential dependence with both variables, which in the case of temperature fitted to an Arrhenius-type expression. Achievement of steady-state conditions with reference to the pervaporation flux needed long times that depended on the previous history of the membrane; thus, new membranes needed a long conditioning period before reaching steady state, which was considerably shortened in subsequent changes of the operation conditions.

A new kind of membrane was prepared by blending PAA with cellulose acetate propionate for the separation of ethyl tert-butyl ether and ethanol mixtures [136]. The properties of the membranes were evaluated by pervaporation separation of mixtures of ethyl tert-butyl ether–ethanol and sorption
experiments. The experimental results showed that the selectivity and the fluxes of this membrane depend on the blend composition and on that of processed feed mixtures. With respect to temperature, the ethanol fluxes obey the Arrhenius equation. The fluxes increase with increases in the PAA content in the blended membrane, the ethanol concentration in the feed and the experimental temperature. But the selectivity decreases as the PAA content and the experimental temperature are raised. When the feed composition is varied, this membrane shows the special characteristics at the azeotropic composition. In the vicinity of the azeotropic point, the minimum values of ethanol concentration in the permeate and in sorption solution are obtained. The swelling ratios increase with an increase in the temperature and the ethanol concentration. The ethanol concentration in the sorption solution was also influenced by the temperature and composition of the mixtures. When the temperature was increased, the sorption selectivity of the membrane decreased.

The pervaporation properties of poly lactic acid (PLA), a natural source polymer, were studied in a polar/nonpolar case study. PLA–PVP blend membranes were prepared containing different PVP contents and evaluated in ethanol–ethyl tert-butyl ether azeotropic separation [137]. The swelling and mechanical properties of the membranes were investigated. SEM cross-sectional images showed a porous structure at higher PVP concentrations. The degree of swelling as well as the permeation flux \((0.05–1.36 \text{ kg m}^{-2} \text{ h}^{-1})\) gradually increased when the PVP amount increased to 21 wt\%. On the other hand, the ethanol separation factor initially increased to 16 using 3 wt\% PVP and then decreased to 3 using 21 wt\% PVP. The continuously decreasing water contact angle from 74\(^\circ\) in PLA to 54\(^\circ\) confirmed higher hydrophilicity and ethanol affinity at higher PVP contents. However, the more porous morphology and the plasticization effect resulted in selectivity decrease. This was also in agreement with the observed mechanical behaviour of the blends. At higher ethanol concentrations and PVP contents, the elastic modulus of the membranes decreased, contrary to the membrane elongation.

15.4.3.4 Separation of Xylene Isomers
The separation of propanol and xylene isomer is very important for the separation of industrial chemical products and energy saving for the separation of those mixtures. The synthesis and preparation of polymeric membranes including Werner-type metal complexes, which are known to form selective clathrate compounds with specific xylene isomers, were investigated in order to study the feasibility of specific membranes that would separate xylene isomers. A porous PTFE membrane was radiation grafted with 4-vinylpyridine. The grafted membrane was combined with Werner-type metal complexes such as Ni(4-methylpyridine)\(_4\)(SCN)\(_2\), and Co(4-methylpyridine)\(_4\)(SCN)\(_2\) through the exchange of ligands between 4-methylpyridine of metal complex and the pyridyl group of the side chain. It was found that the membrane thus obtained is selective for \(p\)-xylene in the pervaporation process and the separation factor of \(p\)-xylene to \(m\)-xylene was 1.26 beginning with a feed containing equal weights of the three xylene isomers. Studies were also conducted on the effects of reaction time, concentration, continuous or intermittent procedure, grafting percentage and composition of ligand upon the uptake amount of metal complex in the graft membrane so as to find the best condition of membrane preparation [138].

MFI-type zeolitic membranes were prepared by a vapour-phase transport method on porous \(\alpha\)-alumina flat disks. Single- and mixed-gas permeation measurements of butane isomers were performed in the temperature range of 300–375 K. The separation factor was always greater than the ideal selectivity [139]. This result is explained by the preferential adsorption of \(n\)-butane on MFI in the binary system. The pervaporation tests for xylene isomers were performed at 303 K. \(p\)-Xylene was the most permeable component in the unary system. In the permeation measurements of a binary mixture of \(p\)-xylene–\(m\)-xylene and a ternary mixture of \(p\)-xylene–\(m\)-xylene–\(o\)-xylene, \(p\)-xylene predominantly permeated in the early stage, and then the flux of \(p\)-xylene decreased gradually and finally
became lower than that of the other xylene isomers. The adsorption of \( m \)-xylene in the pores of MFI seemed to block the permeation of \( p \)-xylene.

Molecular sieving MFI-type zeolite membranes were prepared by a secondary growth method without using an organic template [140]. Silicalite membranes with intercrystalline pores minimized or eliminated were obtained by this synthesis method which avoids the template removal step. The Silicalite membrane exhibits molecular sieving characteristics with a pervaporation separation factor for \( p \)-xylene to \( o \)-xylene or \( m \)-xylene of as high as about 70, the highest ever reported for a pervaporation membrane. They reported the results as shown in Table 15.3.

Silicalite-1 zeolite was modified with 3-aminopropyltriethoxysilane and then loaded into PAAS sodium (PAAS) to prepare PAAS–Silicalite-1 hybrid pervaporation membranes for the separation of xylene isomer mixtures by Qu et al. [141]. Characterization by FTIR and nuclear magnetic resonance spectroscopies confirmed that chemical modification on the zeolite surface had taken place. Based on sorption equilibrium experiments, the diffusion coefficients of permeates in the membrane were obtained, and the order of the diffusion coefficients of xylene isomers was found to be \( D_o < D_m < D_p \). An investigation of the effects of the original versus modified zeolite loading on the pervaporation performance was performed. With the original zeolite, the permeation flux of the binary xylene mixtures showed little change, whereas the selectivity of the hybrid membrane exhibited some enhancement. After modification of the zeolite surface, the selectivity of the hybrid membrane was clearly improved, the permeation flux of the membrane decreased slightly, and the maximum separation factors of the \( p \)-xylene–\( o \)-xylene and \( p \)-xylene–\( m \)-xylene mixtures were determined to be 2.62 and 2.68 respectively. The experimental results revealed that the modification promoted the compatibility of the PAAS and Silicalite-1 zeolite interface.

HTPB-based polyurethaneurea (HTPB–PU) membranes with and without cross-linkage were synthesized and first used as membrane material to separate \( p \)-xylene–\( o \)-xylene mixtures by pervaporation. Compared with HTPB–PU (without cross-linkage) membranes, HTPB–DVB–PU (cross-linked HTPB–PU with DVB) membranes demonstrated a lower degree of swelling in xylene isomer solutions and noticeable improved separation factor of \( p \)-xylene–\( o \)-xylene. On the other hand, the amount of \( p \)-xylene adsorbed in HTPB–DVB–PU membranes increased significantly rather than that of \( o \)-xylene. While the separation factor of \( p \)-xylene–\( o \)-xylene increased but the total flux decreased with increasing DVB content, which can be ascribed to the improved chemical structure and more homogeneous chain structures of the HTPB–DVB–PU membranes. The \( p \)-xylene normalized permeation rate and separation factor of \( p \)-xylene–\( o \)-xylene of HTPB–DVB–PU membrane reached 2.70 kg \( \mu \)\text{m}^{-2}\text{ h}^{-1} and 2.23 respectively at a feed concentration of 10 wt% \( p \)-xylene at 30 °C [142].

To evaluate the molecular recognition function of \( \beta \)-cyclodextrin (\( \beta \)-CD) to xylene isomers, \( \beta \)-CD polymer of branching chain extension was synthesized by cross-linking \( \beta \)-CD with ethylene glycol diglycidyl ether (EGDE) (\( \beta \)-CD–EGDE) [143]. The pervaporation blend membranes of \( \beta \)-CD–EGDE–PVA were prepared by casting an aqueous solution of PVA and \( \beta \)-CD polymer mixture,
and the membranes were used for separation of $p$-xylene–$m$-xylene and $p$-xylene–$o$-xylene mixtures. It was observed that the pristine PVA membrane almost had no selectivity for xylene isomer mixtures. The PVA membrane incorporating $\beta$-CD polymer had molecular recognition function, which selectively facilitated the transport of the xylene isomers. To ascertain pervaporation behaviour, the sorption and desorption processes of the membrane in xylenes were investigated. The sorption result showed that the complex formation constant between $\beta$-CDs and xylenes played a key role in swelling behaviour. There was a significant difference between diffusion coefficients $D$ and $D^0$, calculated from the sorption and desorption measurements respectively, indicating that the diffusivity selectivity in desorption stage may have a remarkable effect on the total selectivity during the pervaporation process.

### 15.4.3.5 Separation of Alcohol Isomers

PVA membranes containing cyclodextrin (CD–PVA) were prepared and characteristics of permeation and separation for propanol isomers through the CD–PVA membranes were investigated by pervaporation and evapomeation [144]. Evapomeation was more effective for the separation of propanol isomers through the CD–PVA membrane than was pervaporation. The CD–PVA membrane more preferentially permeated $n$-propanol than isopropanol from their mixtures. In particular, the mixture of 10 wt% $n$-propanol concentration was concentrated to about 45 wt% through the CD–PVA membrane. Both permeability and selectivity for $n$-propanol were improved with an increase of CD content in the membrane. The results were supported by the fact that the affinity of CD for $n$-propanol was stronger than that for isopropanol. The permeation mechanism of propanol isomers through the CD–PVA membrane was discussed based on the solution-diffusion theory.

The characteristics of permeation and separation for xylene isomers through CD–PVA membranes were investigated by pervaporation and evapomeation [145]. Evapomeation is more effective for the separation of xylene isomers through the CD–PVA membrane than pervaporation is. An increase in CD content gives rise to an increase in a $p$-xylene permselectivity through the CD–PVA membrane by evapomeation. This is attributed to the stronger affinity of CD for $p$-xylene as compared with $o$-xylene. In particular, the CD–PVA membrane at a CD content of 40 wt% showed a higher separation factor than had hitherto been reported. When the $p$-xylene concentration in the feed was lower, the $p$-xylene permselectivity was improved. The mechanism of permeation and separation for xylene isomers was discussed from the standpoint of solution-diffusion theory.

Mixed matrix membranes comprising polyamide–imide (PAI) and $\alpha$-, $\beta$- or $\gamma$-CD have been investigated experimentally and computationally for isomeric $n$-butanol–tert-butanol separation via pervaporation. Consistent with molecular simulation, experimental results showed that the CD inclusion ability and butanol discrimination ability are dependent on both CD cavity size and butanol molecular size. The PAI membrane incorporated with $\alpha$-CD has the smallest cavity and has the highest discrimination ability for the $n$-butanol–tert-butanol pair but with a low butanol flux. The mixed matrix membrane embedded with $\gamma$-CD has the lowest selectivity and the highest flux. The PAI–$\beta$-CD membrane has a comparable selectivity and flux, and exhibits preferential sorption and diffusion selectivity toward $n$-butanol. A maximum separation factor of 1.53 with a corresponding flux of 4.4 g m$^{-2}$ h$^{-1}$ were obtained at an optimal $\beta$-CD loading of 15 wt%. Further increments in the CD content eventually led to a decrease in separation performance because of CD agglomeration and severe phase separation. To better understand the influence of CD on the separation performance of mixed matrix membranes, SEM, FTIR and XRD were employed for membrane characterizations. The effect of $n$-butanol/tert-butanol ratio in the feed composition was also studied. It was found that both flux and separation factor decrease with increasing $n$-butanol content in the feed. The decline was attributed to the change in total vapour pressure at the upstream end and the mutual drag effect of isomeric butanol molecules [146].
A novel CD derivative, \( m \)-xylenediamine–\( \beta \)-CD (\( m \)-XDA–\( \beta \)-CD), was synthesized and used to graft \( \beta \)-CD on the membrane surface for the pervaporation separation of butanol isomers. The reaction mechanisms for the \( m \)-XDA–\( \beta \)-CD synthesis and the membrane surface grafting were confirmed by FTIR and TGA. The as-fabricated novel CD-grafted PAI membranes showed homogeneous morphology and significant improved separation performance as compared with the unmodified PAI membranes and PAI–CD mixed matrix membranes made of physical blends. The effects of chemical modification time and dope concentration on the asymmetric membrane were studied. The optimal separation performance was found with the CD-grafted PAI membrane cast from a 22 wt% dope concentration, which exhibited a total butanol flux of 15 g m\(^{-2}\) h\(^{-1}\) and a separation factor of 2.03. This newly developed membrane with surface-immobilized CD may open a new perspective for the development of next-generation high-performance pervaporation membranes for liquid separations [147].

15.4.3.6 Separation of Hydrocarbon Isomers

A pervaporation process was applied to the separation of different mixtures of aromatic \( C_8 \)-isomers using a dense homogeneous polyethylene membrane. The influence of feed temperature and downstream pressure on the flux of pure components was investigated. For mixtures, the effect of feed composition on permeation rates and separation characteristics was determined. Molar fluxes and separation factors depended on the feed composition. Coupled transport occurred, and the extent of coupling depended on the difference in the permeabilities of the pure components. The mass transport of pure components through the membrane was modelled for varying downstream pressures with diffusivities linearly dependent on the concentration of all the permeants in the membrane. On the basis of this model, molar fluxes of each component in the mixture of ethylbenzene and \( p \)-xylene were calculated and compared with the experimental data. The model and experimental data showed good agreement [148].

The pervaporation of binary mixtures through moderately swollen membranes was analysed as a ‘solution-diffusion’ process and on the assumption that the diffusivity of each permeant was an exponential function of both concentrations. A model was derived in which changes in selectivity and fluxes are related to major external conditions: the upstream mole fraction in the feed and the downstream total pressure of the pervaporate. In order to test the validity of this model, it was applied to a set of experimental data for the pervaporation of hydrocarbon binary mixtures through rubber membranes [149].

15.4.3.7 Separation of Organic–Organic Azeotropes

Dutta and Sikdar [150] reported that ionomeric membranes of perfluorosulfonic acid polymer allow selective pervaporation of polar organic compounds from their azeotropic mixtures with less polar compounds. A composite membrane of a thin perfluorosulfonic acid polymer film, cast on a porous Teflon support, provided desirable permeant fluxes with good selectivity. Model binary azeotropes, composed of alcohols and hydrocarbons, were separated with total pervaporation fluxes of up to 9.5 kg h\(^{-1}\) m\(^{-2}\) using a stirred membrane permeation cell, the product side of which was exposed to vacuum. Fluxes increased with increasing alcohol content of the feed and with temperature. But the selectivity of the more permeating component remained reasonably constant around the azeotropic point and also over the range of temperature used in the study (25–55 °C). Total pervaporation fluxes depended little on downstream pressure up to 6.66 kPa (50 Torr). These separation data were explained by a mathematical model based on a solution-diffusion mechanism.

The preparation and investigation of membranes based on a new IPN of vinyl-terminated PDMS and aromatic polyimide with respect to their thermal and pervaporation properties was investigated by Garg et al. [151]. The modified membranes were prepared using the simultaneous IPN technique.
by variation of polyimide loading of 5, 10 and 15 wt%. These membranes were characterized by different thermal, mechanical, morphological, spectroscopic and pervaporative techniques and compared with those of neat PDMS membranes. The IPN membranes exhibited synergistic improvement in the thermal stability in the range of 445–490 °C in air and 410–520 °C in inert atmosphere for 10% loss. Activation energies for the decomposition of polymers and their IPNs were calculated using the Coats and Redfern equation. Permeation properties of PDMS and IPN blends were evaluated by water diffusion, measured by the Fourier transform attenuated total reflectance method and moisture vapour transmission rate as per ASTM E 96. A 15 wt% polyimide content in PDMS membrane slows down the water diffusion and moisture vapour transmission rate significantly. All the IPNs form mechanically strong membrane with tensile strength up to 15.5 MPa and elongation at break up to 20%. The IPN membranes prepared in this work of Garg et al. were employed in pervaporation separation of azeotrope-forming toluene–methanol mixtures. The pervaporation properties could be tuned by adjusting the blend composition. All the blend membranes tested showed a decrease in flux with increasing polyimide content for methanol–toluene liquid mixtures. Toluene permeated preferentially through all blend membranes tested, and the selectivity increased with increasing polyimide content. The pervaporation characteristics of the blend membranes were also strongly influenced by the feed mixture composition. The flux increased exponentially with increasing toluene concentration in the feed mixtures, whereas the selectivities decreased for liquid mixtures. Their study demonstrates that polymer IPN blends is a simple way to modulate a membrane’s transport properties and can achieve higher performance than the pristine polymer materials.

Pervaporation separation of DMC–methanol azeotrope was investigated using composite membranes consisting of a PVA–PVP blend membrane as active layer and a PAN ultrafiltration membrane as substrate [152]. The active layer was physically blended and cross-linked with glutaraldehyde. The chemical and physical properties of the blend membranes with different proportions of PVA/PVP were characterized by FTIR spectroscopy, SEM, XRD, TGS and contact-angle measurement. The pervaporation properties of the membranes were investigated by the separation of azeotrope. The effects of PVP, glutaraldehyde content and operating temperature on pervaporation performances were investigated. Permeation flux increased with increasing PVP content and feed temperature, while separation factor decreased. However, the separation factor increased with increasing glutaraldehyde content, whereas the flux decreased. The results showed that the membrane containing 70 wt% PVP and 0.5 wt% glutaraldehyde exhibited excellent pervaporation properties with a flux of 955.77 g m⁻² h⁻¹ and separation factor of 68.00 at 50 °C.

15.4.4 Desalination by Pervaporation

A new desalination process consisting of air humidification by pervaporation through hydrophilic or microporous hydrophobic hollow fibres followed by dehumidification by cooling water was investigated by Korngold et al. In this system, hot water is passed through hollow fibres in a recycled air-sweep pervaporation process. The water is heated by waste heat or solar energy or by any other cheap source of energy. The flux of water through the hollow fibres is in the range of 1.5–3.0 L m⁻² h⁻¹, when water temperature is 45–65 °C. The energy requirement for recycling hot water depends on water temperature as well as on the diameter and length of the hollow fibres. The energy requirement for air recycling depends on the air temperature and on the pressure drop of the system. The calculated energy requirement for pumping air and water in a pilot plant unit with a capacity of 6.3 L h⁻¹ with 4 m⁻³ of anion-exchange hollow fibres was about 2 kWh m⁻³, when hot water temperature was 60 °C [153].

Hydrophobic dense PEBAX® membranes were prepared and their suitability for a water pervaporation process studied. The effects of the following parameters on the water flux were determined as
operating conditions: brine inlet temperature, 28–54 °C; NaCl concentration in the feed brine, 0–3.5 mol L\(^{-1}\). A water flux of 1.3–7 g m\(^{-2}\) h\(^{-1}\) was obtained using this type of membrane. It was found for this application that the optimal specifications for the membrane is a thickness of 100 mm and an operating temperature of 50 °C that allowed a water flux of 7 g m\(^{-2}\) h\(^{-1}\) in the permeate side. These data are required for the manufacturing of a novel desalination system based on these types of dense membranes [154].

Silicalite-1 and ZSM-5 membranes prepared by secondary growth on tubular ceramic supports were tested using a pervaporation set-up for the desalination of aqueous solutions containing NaCl in concentrations corresponding to brackish (0.3–1 wt%), sea (3.5 wt%) and brine (7.5–15 wt%) water. ZSM-5 membranes delivered higher water fluxes when compared with Silicalite-1 membranes due to enhanced hydrophilicity of the Al-rich zeolite structure leading to fluxes as high as 11.5 kg m\(^{-2}\) h\(^{-1}\) for 0.3 wt% NaCl feed solutions at 75 °C. At higher salt concentration the water flux decreased alongside with the salt rejection rate; however, the hydrophilic ZMS-5 membrane became more susceptible to performance loss, particularly at high temperatures. Detailed stability experiments carried out for up to 560 h showed the dissolution of both Silicalite-1 and ZSM-5 top layers. This was attributed to the combined effects of ion exchange and water dissolution mechanisms. Interestingly though, the MFI structure zeolite was still observed on the XRD patterns, whilst the energy-dispersive X-ray (EDX) depth profile showed the presence of silica up to 30 μm depth into the support. These results suggest the formation/infiltration of a compact amorphous phase in the substrate, derived from the aggregation of the dissolved silicate species and possibly together with the arrangement of MFI nano-slabs during the desalination tests. Despite generating lower water fluxes, the Silicalite-1 membrane exhibited relatively high robustness under the long-term testing conditions, which included temperature cycling, delivering salt rejections from initial >99% to <80% at the end of the testing period (560 h) [155].

Elma et al. [156] reviewed a global overview of microporous silica-based membranes for desalination via pervaporation with a focus on membrane synthesis and processing, transport mechanisms and current state-of-the-art membrane performance. Most importantly, the recent development and novel concepts for improving the hydro-stability and separating performance of silica membranes for desalination were critically examined. Research into silica-based membranes for desalination has focused on three primary methods for improving the hydro-stability. These include incorporating carbon templates into the microporous silica both as surfactants and hybrid organic–inorganic structures and incorporation of metal oxide nanoparticles into the silica matrix. The literature examined identified that only metal oxide silica membranes have demonstrated high salt rejections under a variety of feed concentrations, reasonable fluxes and unaltered performance over long-term operation. As this is an embryonic field of research, several target areas for researchers were discussed, including further improvement of the membrane materials, but also regarding the necessity of integrating waste or solar heat sources into the final process design to ensure cost competitiveness with conventional reverse osmosis processes.

Natural zeolite membranes, directly sectioned from mineral deposits, have been previously reported to show molecular sieve characteristics in selective separation of water and hydrated cations. Although a high removal of cations was observed, the low water flux was a limitation for any potential industrial applications. In the study by An et al., novel clinoptilolite-based phosphate composite membranes were prepared by dry pressing of mixed powder materials followed by high-temperature autoclave steaming and characterized by XRD and SEM-EDX. Their performance for pervaporative water desalination was examined using different levels of salinity in a temperature range of 25–95 °C and feed side pressure of 1 atm. At 1400 ppm Na feed salinity and 95 °C, a water flux of 15 kg m\(^{-2}\) h\(^{-1}\) and over 95% removal of Na\(^+\) were obtained. The water flux achieved was about 10 times higher than the flux obtained using natural zeolite rock membranes. Introducing phosphate into the composite
membranes appears to provide not only mechanical strength, through the possible chemical bonding between zeolite particles and the in-situ phosphate cement, but also to create a chemically favourable interface between zeolite crystals. Such an interface might facilitate the desalination process bypassing the technical difficulties of ion leakage/diffusion through the intercrystal spaces commonly associated with synthetic zeolite membranes [157].

References


Evapomeation

16.1 Principle of Evapomeation

Presently, pervaporation is applied as the chosen membrane separation technique for the separation of water–organic, organic–water, and organic–organic mixtures. However, it seems that conventional pervaporation is not the most efficient membrane separation process for the treatment of some liquid mixtures for the following reasons. Because the polymer membranes used in pervaporation are directly in contact with the liquid feed solutions (as shown in Figure 16.1), specifically designed chemical and physical membrane properties are often impaired by swelling or shrinking of the membrane due to sorption of the feed components. Swelling or shrinking of the polymer membranes is disadvantageous for the membrane performance with respect to the separation of mixtures.

A novel membrane separation technique known as ‘evapomeation’ [1–19] makes use of the advantages of pervaporation, but reduces the negative effects of swelling on membrane performance. In this technique, the feed solution is fed to the membrane without directly contacting the polymer membrane. This is accomplished by vaporizing the liquid feed so that only vapour is supplied to the polymer membrane, as shown in Figure 16.2. Therefore, swelling or shrinking of the polymer membranes due to contact with the feed solutions is minimized. Evapomeation was coined from the combination of the words evaporation (of the feed liquid) and permeation (of the permeant through the membrane and its evaporation into the vapour phase based on the former parts, such as feed solution and feed vapour, in the three basic steps of the process) [1,2].

The advantages of evapomeation compared with pervaporation are as follows:

1) In the evapomeation process, membranes are not in direct contact with liquid feed mixtures as only vapours are supplied to the membranes. Accordingly, any swelling or shrinking of the membrane due to the feed mixtures is minimized, and consequently an improvement in membrane performance may be expected.

2) Because the organic liquid mixtures are vaporized, interactions between component molecules are significantly weakened, and consequently the separation performance is remarkably improved.

3) In evapomeation, the problem of fouling of the membrane by contaminants in a liquid feed mixture, such as macromolecular solutes, is avoided.

4) During evapomeation, the temperature of both the feed solution and the membrane surroundings can be controlled; hence, an improvement in the permeation and separation characteristics of the membrane can be achieved.

Li et al. [20] and Bernardo et al. [21] interestingly introduce the characteristics of evapomeation, and interesting experimental results in various fields using the evapomeation method are reported by many membrane scientists [22–39].

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16.2 Membranes of Evapomeation

Typical hydrophilic and hydrophobic membranes used in evapomeation are as follows: chitin [40], alginic acid [2], poly(styrene) [41,42], poly(vinyl chloride) (PVC) [43], poly(dimethyl siloxane) (PDMS) [44,45], chitosan acetate [46], cross-linked chitosan [46], modified silicon [47], poly(vinyl p-tert-butyl benzoate) (PVBB) [48], block copolymer of poly(ethylene glycol methacrylate) as hydrophilic monomer and benzyl methacrylate as hydrophobic monomer [49], copolymer of benzyl methacrylate and poly(ethylene glycol dimethacrylate) [50], poly[(vinyl chloride)-co-(vinyl acetate)] [51], chitosan [1,52], chitosan acetate (Chito A) (I) [53].
and carboxymethyl chitosan acetate (CM–ChitoA) (II) [53], chitosans cross-linked with glutaraldehyde (GA) and modified with n-alkyl aldehyde [52], poly(vinyl alcohol) (PVA) and PVA containing cyclodextrin (CD) [54,55], poly[(bis(2,2,2-trifluoroethoxy) phosphazene] [56], N-alkyl-chitosans [57], poly[(1-trimethylsilyl)-1-propyne] [58,59], chitosans with different degree of quaternization and degree of cross-linking with diethylene glycol diglycidyl ether (DEDGE) (Scheme 16.1) [60], cross-linked quaternized chitosan (q-Chito) on porous support.

Scheme 16.1 Crosslinking of q-Chito with DEDGE.
[61], polion complex (PIC) between $q$-Chito and sodium poly(ethylene oxydiglycolic acid) (sodium PEO acid) (Scheme 16.2) [62], $q$-Chito hybridized with tetraethoxysilane (TEOS) (Scheme 16.3) [63], Nylon-4-deposited poly(vinyl acetate) [22], PVA-g-Nylon 4 [23], poly(vinyl alcohol-g-itaconic acid) [24], PVA–malic acid [25], alginate [26], PVA–poly(acrylic acid) alloy [27], poly(vinyl alcohol-g-4-vinyl pyridine) [64], sodium alginate-g-n-vinyl-2-pyrrolidone [28], sodium alginate–PVA alloy [29], sodium alginate–poly(vinyl pyrrolidone) cross-linked with calcium chloride [30,31].

Scheme 16.2 PIC between $q$-Chito and sodium PEO acid.
16.3 Technology of Evapomeation

16.3.1 Comparison of Membrane Performance in Pervaporation and Evapomeation

Figure 16.3 shows diagrams of the pervaporation and evapomeation apparatus.

16.3.1.1 Water Permselectivity

Table 16.1 compares the permeation and separation characteristics for various aqueous ethanol solutions through a chitosan membrane by evapomeation and pervaporation [1]. The permeation rates for both evapomeation and pervaporation decreased with increasing ethanol concentration in the feed. These results suggest that the chitosan membrane becomes dense as the ethanol content in the feed increases. The permeation rates for evapomeation were smaller by one order of magnitude compared with those for pervaporation. This supports the assumption that the chitosan membrane can almost fully maintain its pre-test dense structure during evapomeation, and that, consequently, the diffusivity
Figure 16.3 Diagrams of (a) pervaporation and (b) evapomeation: (1) permeation cell, (2) membrane, (3) U-tube, (4) vacuum pump, (5) cold trap, (6) Pirani gauge, (7) magnetic stirrer, (8) thermostat.

Table 16.1 Characteristics of permeation and separation for aqueous ethanol solution in pervaporation and evapomeation.a)

<table>
<thead>
<tr>
<th>Ethanol in feed (wt%)</th>
<th>Pervaporation</th>
<th>Evapomeation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Permeation rate ($10^{-2}$ kg m$^{-2}$ h$^{-1}$)</td>
<td>Separation factor $\alpha$</td>
</tr>
<tr>
<td>0</td>
<td>186.0</td>
<td>0.7</td>
</tr>
<tr>
<td>10 (43.9)</td>
<td>150.0</td>
<td>2</td>
</tr>
<tr>
<td>30 (60.4)</td>
<td>136.0</td>
<td>13</td>
</tr>
<tr>
<td>50 (67.7)</td>
<td>67.1</td>
<td>50</td>
</tr>
<tr>
<td>70 (77.3)</td>
<td>34.6</td>
<td></td>
</tr>
<tr>
<td>90 (90.8)</td>
<td>12.3</td>
<td>31</td>
</tr>
<tr>
<td>96.5$^b)$</td>
<td>6.5</td>
<td>17</td>
</tr>
<tr>
<td>100</td>
<td>2.9</td>
<td></td>
</tr>
</tbody>
</table>

a) Values in parentheses are for vapour compositions.

b) Azeotrope.
of the permeating species during the diffusion process is lowered. As can be seen in Table 16.1, water was predominantly permeated through the chitosan membrane both in pervaporation and evapomeation. An azeotropic composition – 95.6 wt% ethanol in the feed solution – was not observed for both methods, and water permselectivities for evapomeation were greater than those for pervaporation. These results depend on the fact that swelling of the chitosan membrane is much more inhibited during evapomeation than during pervaporation.

In order to explain the separation mechanism for aqueous ethanol solution through the hydrophilic polymer membranes by the pervaporation and evapomeation, the membrane models shown in Figure 16.4a and b are proposed for the pervaporation and evapomeation process. In pervaporation, the membrane consists of three layers: swelling layer in the side that faces the feed liquid, boundary layer and dry layer in the permeate side under reduced pressure.

The existence of these three layers could not be experimentally observed. However, the assumption of three layers helps in understanding the separation mechanism. The dissolution of permeating molecules into the swelling layer, the diffusion of these molecules through the swelling layer and the separation through the dry layer can be explained by the experimental results of the adsorption of permeating molecules into the membrane, the permeation under pressure and the evaporation respectively. Also, the evaporation of permeating molecules occurs in the boundary layer between the swelling layer and the dry layer, and the separation in this boundary layer is due to the specific volatility of the permeating molecules. If this membrane model is used, the separation mechanism for higher ethanol content in the feed through the hydrophilic membrane by the pervaporation method, which could not be explained previously, can be easily understood. That is, the water molecules are selectively adsorbed into the swelling layer, and the adsorbed molecules are diffused without separation through the swelling layer. Then the permeating molecules are evaporated into the boundary layer, and the evaporated molecules are permeated through the dry layer.

On the other hand, in evapomeation, since there is no change of the membrane structure by the feed vapour, the membrane consists of only one layer. In the membrane model in evapomeation,
the vapour molecules are dissolved into the dry layer, diffused through the dry layer and evaporated in the permeate side.

The permeation and separation characteristics of aqueous ethanol solutions through a hydrophilic chitosan membrane with the same thickness in pervaporation and evapomeation are shown in Figure 16.5 [42]. From this figure it is found that the permeation rates in pervaporation are higher than those in evapomeation, but water permselectivities in the former are considerably lower compared with those in the latter. These results can be easily understood by the membrane models in pervaporation and evapomeation shown in Figure 16.4; namely, the thickness of the dry layer in pervaporation and evapomeation significantly influences the permeation rate and permselectivity. The chitosan membranes with a thinner dry layer in pervaporation give higher permeation rates and those with a thicker dry layer in evapomeation bring higher water permselectivity.

Permeation rate and separation factor for aqueous dimethyl sulfoxide solutions through a chitosan membrane in pervaporation and evapomeation as a function of the dimethyl sulfoxide concentration.

**Figure 16.5** Permeation and separation characteristics for aqueous ethanol solution through a chitosan membrane by pervaporation (○) and evapomeation (●). -- -- : liquid–vapour equilibrium curve.
in the feed solution or feed vapour are shown in Figure 16.6 [65], in which the separation factor $\alpha_{\text{H}_2\text{O}/\text{DMSO}}$ is expressed as

$$\alpha_{\text{H}_2\text{O}/\text{DMSO}} = \frac{Y_{\text{H}_2\text{O}}}{Y_{\text{DMSO}}} \frac{X_{\text{H}_2\text{O}}}{X_{\text{DMSO}}} \tag{16.1}$$

where $X_{\text{H}_2\text{O}}, X_{\text{DMSO}}$ and $Y_{\text{H}_2\text{O}}, Y_{\text{DMSO}}$ are the weight fractions of water and dimethyl sulfoxide in the feed solution and permeate respectively in pervaporation or are the weight fractions of water and dimethyl sulfoxide vapours from the feed solution and in the permeate respectively in evapomeation.

From these results, it is found that the chitosan membrane predominantly permeated water from aqueous dimethyl sulfoxide solutions, and that the separation factor in both pervaporation and evapomeation increased with increasing dimethyl sulfoxide concentration in the feed solution and feed vapour. Also, the total permeation rate in pervaporation was greater than that in evapomeation, but the permselectivity for water in evapomeation was higher than that in pervaporation. In order to interpret the permeation and separation characteristics in Figure 16.6, the composition of the solution sorbed into the chitosan membrane and the degree of swelling of the chitosan membrane for aqueous dimethyl sulfoxide solutions were measured. The chitosan membrane sorbed water preferentially from aqueous dimethyl sulfoxide solutions. The lowering of the dimethyl sulfoxide concentration in the permeate (i.e. the increase of the permselectivity for water through the chitosan membrane in Figure 16.6) is attributed to both the high solubility of water in the chitosan membrane and the high diffusivity of water, which has a smaller molecular size, in the chitosan membrane. That is, both solubility selectivity and diffusivity selectivity governed the water permselectivity through the chitosan membrane significantly. On the other hand, the degree of swelling of the chitosan membrane decreased with increasing dimethyl sulfoxide concentration in the feed solution. That is, since chitosan is hydrophilic, the chitosan membrane is more swollen in a feed with high water content. The decrease of the total permeation rate is dependent on both the decrease in the degree of swelling of the chitosan membrane and the increase in the dimethyl sulfoxide concentration in the feed.

As shown in Figure 16.6, the dimethyl sulfoxide concentration in the permeate slightly increased with increasing dimethyl sulfoxide concentration in the feed solution and feed vapour. If the selectivity is represented by the separation factor defined in Equation 16.1, however, both the separation factors in pervaporation and evapomeation increased with increasing dimethyl sulfoxide concentration in the feed. That is, it is implied that the water permselectivity for aqueous dimethyl sulfoxide solutions through the chitosan membrane increases as the dimethyl sulfoxide concentration in the feed increases. The increase of the separation factor with an increase of the dimethyl sulfoxide
concentration in the feed can be understood by the degree of the swelling of the membrane mentioned earlier (i.e. the decrease of the degree of swelling causes an increase of the separation factor).

In order to confirm the discussion for the dehydration from aqueous dimethyl sulfoxide solution and vapour in pervaporation and evapomeation through a hydrophilic chitosan membrane, similar experiments were carried out for aqueous acetic acid solution and vapour. Figure 16.7 shows the effects of the acetic acid concentrations in the feed solution and vapour on the permeation rates, separation factors through hydrophobic PVC membrane in pervaporation and evapomeation, and the degree of swelling of the PVC membrane in pervaporation [51]. The degree of swelling of the PVC membrane increases with increasing acetic acid concentration in the feed solution. In general, the permeation rate increases with an increasing degree of swelling of the membrane. The permeation rates in both pervaporation and evapomeation in Figure 16.7, however, decrease with increasing degree of swelling of the membrane. In the PVC–aqueous acetic acid solution system, the degree of swelling of the PVC membrane is very low, so that the swelling of membrane does not affect so much the permeation rate. The decrease of the permeation rates is closely related to the water concentration in the feed. The PVC membrane is a highly water-selective one [42,51]. The permeation rate of the water-permselective PVC membrane is significantly dependent on the quantity of water incorporated into the PVC membrane. Therefore, a decrease of the water concentration in the feed brought about the decrease of the permeation rate. A similar phenomenon was also observed in a PVC–aqueous alcohol solution system [42].

The separation factor in evapomeation was higher than that in pervaporation. As described earlier, the interaction between water and acetic acid molecules in evapomeation is weaker than that in pervaporation. This weak interaction results in the high water permselectivity; that is, high separation factor. The separation factor is a parameter that represents a separation efficiency for binary liquid mixtures. The separation factors in both pervaporation and evapomeation in Figure 16.7 increase with increasing acetic acid concentration in the feed solution and vapour. In particular, a very high separation factor (>200 in evapomeation, >100 in pervaporation) was observed in the range of high acetic acid concentration in the feed solution and vapour. This shows that the separation of an aqueous acetic acid solution through a PVC membrane is efficient for an acetic acid containing a trace amount of water. The PVC membrane is the water-permselective membrane as described above, so that the removing of water from acetic acid containing a trace amount of water is advantageous in view of the energy consumption.
Pervaporation and evapomeation separations of water–alcohol mixtures through a modified Nylon 4 membrane coated with plasma-deposited, hydrolysed vinyl acetate (VAc) (PVAc-p-N4), were investigated by Lai and co-workers [22,23]. Compared with pervaporation, evapomeation effectively increased the separation factor for the water–alcohol mixtures, while the permeation rate decreased. The permeation and separation characteristics of acetic acid–water mixtures through IA-g-PVA membranes – grafted itaconic acid (IA) onto PVA – were applied to the pervaporation and evapomeation processes [27]. The permeation rates in evapomeation were lower than those in pervaporation, whereas the separation factors in evapomeation were higher.

Solak and Şanlı [26] also investigated the permeation and separation characteristics of dimethyl formamide–water mixtures through alginate membranes by pervaporation and vapour permeation, which corresponds to evapomeation that is proposed by Uragami and co-workers [1,2,15]. The relation for the permeation characteristics between pervaporation and evapomeation using alginate membranes was similar to that in IA-g-PVA membranes.

### 16.3.1.2 Organic Permselectivity

The effect of permeation temperature on the permeation separation characteristics of 10 wt% ethanol aqueous solution through a modified silicone rubber membrane in pervaporation and evapomeation is shown in Figure 16.8 [47]. The permeation rates in both pervaporation and evapomeation increase with increasing permeation temperature. The increase in those permeation rates is attributed to the fact that motions of polymer chains constituting the modified silicone rubber membrane and permeating molecules are activated with a rise of the permeation temperature. The modified silicone rubber membrane showed ethanol permselectivity in both pervaporation and evapomeation. The ethanol permselectivity in pervaporation was constant regardless of the permeation temperature, but that in evapomeation significantly increased with increasing permeation temperature. The permeation rates in pervaporation are higher than those in evapomeation, but the ethanol permselectivity in evapomeation is much greater. This result suggests that the application of hydrophobic membranes with a high affinity to ethanol for the concentration of ethanol in the permeate is much better.

The effect of ethanol concentration in the feed solution on the permeation rate and the ethanol concentration in the permeate through a modified silicone rubber membrane by pervaporation and evapomeation is shown in Figure 16.9, in which the temperatures of both the feed solution and the membrane surroundings were kept at 40 °C.

The permeation rate in pervaporation increased remarkably, but that in evapomeation only slightly, with increasing ethanol concentration in the feed. Also, the permeation rates in pervaporation were larger than those in evapomeation. These results can be easily understood in view of the degree of swelling of the membrane, which increased with the ethanol concentration in the feed or feed vapour.
Further, the degree of swelling in evapomeation was smaller than that in pervaporation.

The closed circles in Figure 16.9b imply that in evapomeation based on feed vapour composition water is selectively permeated through a modified silicone rubber membrane. However, if the ethanol concentrations in the permeate in evapomeation are represented as a function of the feed solution composition, which are shown as triangle plots, it is evident that the ethanol permeates predominantly, as those in the case of pervaporation shown as open circle plots. However, in the latter case the ethanol concentrations in the permeate are lower. Thus, the permselectivity for ethanol in evapomeation is greater than that in pervaporation.

Figure 16.10 shows the relationship between the ethanol concentrations in the membrane and in the feed solution or feed vapour. When the ethanol concentrations in the permeate Figure 16.9b and in the membrane Figure 16.10a are compared, in pervaporation the ethanol concentration in the permeate is higher than that in the membrane, but in evapomeation this relation is the reverse. It is presumed from these results that the permeation and separation characteristics in pervaporation are related to the solution of the permeant into the membrane, diffusion of the permeant through the membrane and the volatility of the permeant from the membrane, which in evapomeation are mainly governed by the diffusion of the permeant through the membrane. This discussion can be supported by the membrane models in pervaporation and evapomeation in Figure 16.4.

The permeation rates and separation factors for various alcohol solutions through a PDMS membrane by pervaporation and evapomeation are summarized in Table 16.2, in which the separation factors in parentheses are for the feed vapour in evapomeation [45].

In both pervaporation and evapomeation, the permeation rate for all aqueous alcoholic solutions increased and the separation factors decreased as the alcohol concentration in the feed was increased. The results obtained for aqueous methanol and 1-propanol solutions were similar to those for an aqueous ethanol solution. Namely, alcohol predominantly permeated from aqueous alcoholic solutions. In spite of that, the molecular size increases in order of methanol < ethanol < 1-propanol. The permeation rates and separation factors for aqueous alcoholic solutions through the PDMS membrane in both pervaporation and evapomeation increased with the molecular size. These permeation and separation characteristics suggest that both the solubility of the permeating molecule in the membrane and the diffusivity of the permeating molecule through the membrane are very significant. Table 16.3 lists the solubility parameter \( \delta \) of the permeating molecule [66] and the difference between the \( \delta \) values of the PDMS and permeating molecules. The difference in the \( \delta \) value between the PDMS and alcohol is in order of \( (\delta_{\text{PDMS}} - \delta_{\text{MeOH}}) > (\delta_{\text{PDMS}} - \delta_{\text{EtOH}}) > (\delta_{\text{PDMS}} - \delta_{\text{1-PrOH}}) \). This implies that the
PDMS membrane has the strongest affinity for 1-propanol among these alcohols. Namely, 1-propanol is the easiest to dissolve in the PDMS membrane. On the other hand, since the PDMS membrane is rubbery, the PDMS chain is very flexible. Therefore, the permeating molecule can easily diffuse through the PDMS membrane. Consequently, 1-propanol, which has a high solubility, can be easily permeated through the PDMS membrane, and a high permselectivity for 1-propanol is shown.

Poly[(1-trimethylsilyl)-1-propyne] (PTMSP) membrane was applied to pervaporation and evapomeation, and permeation and separation characteristics for an aqueous solution of 10 wt% ethanol through membrane were investigated [15]. Table 16.4 compares their characteristics. As can be seen from Table 16.4, the permeation rate in evapomeation is slightly lower than that in pervaporation but the ethanol concentration in the permeate and the separation factor in evapomeation are higher than those in pervaporation. These results are considered as follows. Since the PTMSP membrane has a high affinity to ethanol, this membrane is easily swollen by ethanol in pervaporation. Consequently, the permeation rate in pervaporation is higher but the separation factor for the ethanol permselectivity becomes lower.

16.3.1.3 Permselectivity of Isomers

The relationship between \( n \)-propanol concentrations in the feed (\( n \)-propanol–isopropanol mixture) and in the permeate through a CD–PVA membrane by pervaporation and evapomeation is shown in Figure 16.11, in which the CD content was 40 wt% [54]. The \( n \)-propanol concentration in the permeate through the CD–PVA membrane by pervaporation was approximately same as that in the feed solution, namely, the propanol isomers could hardly be separated through the CD–PVA membrane by pervaporation.

On the other hand, the \( n \)-propanol concentration in the permeate by evapomeation was higher than that in the feed solution. This result implies that the CD–PVA membrane in evapomeation permeates \( n \)-propanol in preference to isopropanol. This result can be explained by the tentative illustration shown in Figure 16.12. In pervaporation, it is difficult for each propanol to interact specifically with the CD–PVA membrane, because the propanol isomers associate in the feed solution. In evapomeation, however, \( n \)-propanol can be preferentially sorbed into the CD–PVA membrane, because each propanol is isolated in the feed vapour. These results support the thesis that evapomeation is more effective for the separation of the propanol isomers through a CD–PVA membrane than is pervaporation.

Therefore, mainly, the permeation and separation phenomena of propanol isomers by evapomeation is discussed in detail in Section 16.3.2.
Table 16.2 Effect of feed composition of aqueous alcoholic solution on the permeation and separation characteristics through a PDMS membrane by pervaporation and evapomeation.

<table>
<thead>
<tr>
<th>Method</th>
<th>Alcohol</th>
<th>Aqueous solution of 10 wt% alcohol</th>
<th>Aqueous solution of 30 wt% alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Permeation rate × 10² (kg m⁻² h⁻¹)</td>
<td>Separation factor α_{alcohol/H₂O}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Separation factor α_{alcohol/H₂O}</td>
<td></td>
</tr>
<tr>
<td>Pervaporation</td>
<td>MeOH</td>
<td>4.03</td>
<td>6.03</td>
</tr>
<tr>
<td></td>
<td>EtOH</td>
<td>5.33</td>
<td>7.44</td>
</tr>
<tr>
<td></td>
<td>1-PrOH</td>
<td>8.04</td>
<td>16.24</td>
</tr>
<tr>
<td>Evapomeation</td>
<td>MeOH</td>
<td>2.29</td>
<td>9.96 (1.32)</td>
</tr>
<tr>
<td></td>
<td>EtOH</td>
<td>4.01</td>
<td>14.36 (2.04)</td>
</tr>
<tr>
<td></td>
<td>1-PrOH</td>
<td>6.73</td>
<td>30.70 (6.59)</td>
</tr>
</tbody>
</table>

MeOH: methanol; EtOH: ethanol; PrOH: propanol.

Table 16.3 Difference between the solubility parameters of permeation molecules and PDMS.¹)

<table>
<thead>
<tr>
<th>Permeating molecule</th>
<th>δ_p b)</th>
<th>(δ_p - δ_{PDMS}) b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>47.9</td>
<td>45.5</td>
</tr>
<tr>
<td>MeOH</td>
<td>29.7</td>
<td>27.3</td>
</tr>
<tr>
<td>EtOH</td>
<td>26.0</td>
<td>23.6</td>
</tr>
<tr>
<td>1-PrOH</td>
<td>25.8</td>
<td>23.4</td>
</tr>
</tbody>
</table>

¹) Solubility parameter of PDMS δ_{PDMS} was 2.4 J¹/² m⁻³/² × 10⁻³.
²) J¹/² m⁻³/² × 10⁻³.

Table 16.4 Permeation and separation characteristics for an aqueous solution of 10 wt% ethanol through a PTMSP membrane in pervaporation and evapomeation.

<table>
<thead>
<tr>
<th>Membrane process</th>
<th>Evapomeation</th>
<th>Pervaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeation temperature (°C)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Permeation rate (kg m⁻² h⁻¹)</td>
<td>0.53</td>
<td>0.59</td>
</tr>
<tr>
<td>EtOH in permeate (wt%)</td>
<td>62.4</td>
<td>58.8</td>
</tr>
<tr>
<td>Separation factor α_{EtOH/H₂O}</td>
<td>14.9</td>
<td>12.8</td>
</tr>
</tbody>
</table>

α_{EtOH/H₂O} = [Y_{EtOH}/(1 - Y_{EtOH})]/[X_{EtOH}/(1 - X_{EtOH})], where X_{EtOH} is the weight fraction of ethanol in the feed and Y_{EtOH} is the weight fraction of ethanol in the permeate.
Figure 16.13 shows the influence of the feed composition on the \( p\)-xylene concentration in the permeate through a CD–PVA membrane containing 40 wt% CD by pervaporation and evapomeation [55].

The \( p\)-xylene concentration in the permeate through the CD–PVA membrane by pervaporation is approximately the same as that in the feed solution. This means that the CD–PVA membrane could
hardly separate xylene isomers by pervaporation. Lee [67] tried the separation of xylene isomers through a hydroxypropylmethylcellulose membrane containing CD by pervaporation, but obtained a very low separation factor. Our result through the CD–PVA membrane by pervaporation supports the results of Lee [67]. Evapomeation, however, displayed higher \( p \)-xylene concentration in the permeate than in the feed solution. The \( p \)-xylene concentration in the permeate by evapomeation was higher than that by pervaporation. These facts indicate that the CD–PVA membrane can separate xylene isomers by evapomeation and is \( p \)-xylene permselective. This leads us to the conclusion that evapomeation is more effective for the separation of xylene isomers through a CD–PVA membrane than pervaporation. This conclusion is supported by the previous result that evapomeation is superior to pervaporation in the separation of propanol isomers through the CD–PVA membrane [52]. The effectiveness of evapomeation is attributed to the unique permeation system being different from pervaporation, as shown in Figure 16.13. In pervaporation, since the CD–PVA membrane is in contact with the feed solution in which xylene isomers associate, the specific interaction between CD in the membrane and xylene isomers occurs with difficulty. The difficult distinction between \( p \)-xylene and \( o \)-xylene in the feed solution results in a low separation of xylene isomers through the CD–PVA membrane by pervaporation. On the other hand, in evapomeation, xylene isomers are fed to the CD–PVA membrane in the state of their vapours in which molecules of xylene isomers are isolated. In evapomeation, consequently, CD in the membrane can recognize the difference between \( p \)-xylene and \( o \)-xylene and interact with them specifically. Such molecular recognition of CD in evapomeation enables the CD–PVA membrane to separate xylene isomers effectively. Since evapomeation is more effective for the separation of xylene isomers through a CD–PVA membrane than pervaporation, the permeation and separation phenomena of xylene isomers in evapomeation are also discussed in Section 16.3.2.

16.3.2 Effect of Cyclodextrin Content on Permeation and Separation Characteristics of Xylene Isomers

The effect of the CD content on the \( p \)-xylene concentration in the permeate and normalized permeation rate through CD–PVA membranes by evapomeation is shown in Figure 16.14, in which the concentration of \( p \)-xylene incorporated in the membrane is also shown. The normalized permeation
rate is the product of the permeation rate and the membrane thickness. The composition of the p-xylene/o-xylene mixture as a feed solution was 10/90 weight ratio. Xylene isomers could hardly be separated through the PVA membrane and the CD–PVA membrane containing 20 wt% CD. With increasing CD content to more than 30 wt%, however, the p-xylene concentration in the permeate through the CD–PVA membranes increased gradually. This indicates that CD in the membrane plays an important role in the separation of xylene isomers. The addition of CD to the membrane also led to an increase in the normalized permeation rate. As the improvement of selectivity of the membrane is often attended by a drop in the permeability, it is difficult to improve both permeability and selectivity of the membrane. The addition of CD in the membrane, however, can give rise to increases in both the p-xylene concentration in the permeate and the normalized permeation rate; that is, to improvements of both the permeability and selectivity. The p-xylene concentration in the membrane can explain the characteristics of permeation and separation for xylene isomers through the CD–PVA membrane.

The concentration of p-xylene incorporated in the membrane increased with an increase in the CD content. The increasing p-xylene concentration in the membrane by the addition of CD causes the increase in both the p-xylene in the permeate and the normalized permeation rate through the CD–PVA membrane. However, since p-xylene was no more significantly incorporated in the CD–PVA membrane compared with o-xylene, the p-xylene concentration in the membrane cannot clarify why a CD–PVA membrane shows p-xylene permselectivity.

Figure 16.14 Effects of cyclodextrin content on the concentration of p-xylene sorbed in the CD-PVA membrane, the p-xylene concentration in the permeate, and the normalized permeation rate through the membrane by evapomeation. Feed: p-xylene/o-xylene=10/90 (w/w).
The solubility of xylene isomers in the membrane can be discussed by the sorption selectivity \( \alpha_{\text{sorp}} \), which is determined from the concentration of \( p \)-xylene incorporated in the membrane using

\[
\alpha_{\text{sorp}} = \frac{M_{p-\text{xylene}}}{M_{o-\text{xylene}}} \quad \frac{F_{p-\text{xylene}}}{F_{o-\text{xylene}}} \tag{16.2}
\]

where \( F \) and \( M \) are the composition of one component in the feed and the membrane respectively. Furthermore, the diffusion selectivity of the membrane \( \alpha_{\text{diff}} \) can be calculated from the separation factor obtained by Equation 16.3 and the sorption and selectivity as shown in Equation 16.4:

\[
\alpha_{\text{sep}} = \frac{M_{p-\text{xylene}}}{M_{o-\text{xylene}}} \quad \frac{F_{p-\text{xylene}}}{F_{o-\text{xylene}}} \tag{16.3}
\]

\[
\alpha_{\text{diff}} = \frac{\alpha_{\text{sep}}}{\alpha_{\text{sorp}}} \tag{16.4}
\]

Such a division of the separation factor into its sorption and diffusion selectivities enables us closely to discuss the permeation mechanism of the xylene isomers through a CD–PVA membrane by evaporation.

Table 16.5 lists the separation factors, their sorption and diffusion selectivities of the CD–PVA membranes containing various amounts of CD. The feed solution composition was a 10/90 (w/w) \( p \)-xylene/o-xylene mixture. The separation factors of the PVA membrane and the CD–PVA membrane containing 20 wt% CD were <2. The separation factor of the CD–PVA membrane increased gradually with increasing CD content above 20 wt%. In particular, the CD–PVA membrane at a CD content of 40 wt% showed a high separation factor, the value of which was ~4. In the separation of xylene isomers through polymer membranes, this separation factor is higher than that reported previously [69–72]. The high separation factor is attributed to both the addition of CD in the membrane and evaporation. The fact that the sorption selectivity of a PVA membrane is about 0.5 means that o-xylene is more predominantly incorporated in the PVA membrane than \( p \)-xylene is. The solubility parameters of \( p \)-xylene and o-xylene are 8.75 cal\(^{1/2}\) cm\(^{-3/2}\) and 9.0 cal\(^{1/2}\) cm\(^{-3/2}\) respectively [73]. This indicates that o-xylene is slightly less hydrophobic than \( p \)-xylene. Therefore, the hydrophilic PVA membrane has a little stronger affinity for o-xylene than for \( p \)-xylene. This is why o-xylene is predominantly incorporated in the PVA membrane. By the addition of CD, however, the sorption selectivity increases slightly. It is well known that CD more predominantly forms a complex with the para derivative than with the ortho derivative owing to the steric effect [74]. The slight increase in the sorption selectivity must be due to the stronger affinity of CD for \( p \)-xylene compared with

<table>
<thead>
<tr>
<th>CD content (wt%)</th>
<th>( \alpha_{\text{sep}} )</th>
<th>( \alpha_{\text{sorp}} )</th>
<th>( \alpha_{\text{diff}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.72</td>
<td>0.53</td>
<td>3.27</td>
</tr>
<tr>
<td>20</td>
<td>1.19</td>
<td>0.94</td>
<td>1.27</td>
</tr>
<tr>
<td>30</td>
<td>2.93</td>
<td>1.08</td>
<td>2.71</td>
</tr>
<tr>
<td>40</td>
<td>3.93</td>
<td>0.78</td>
<td>5.04</td>
</tr>
</tbody>
</table>

\(^a\)\( p \)-xylene/o-xylene; 10/90 (w/w).
The CD–PVA membrane with a CD content of 40 wt% had a diffusion selectivity of ~5. The high diffusion selectivity means that the addition of CD in the membrane induces the differences in the diffusivity between \( p \)-xylene and \( o \)-xylene. CD may act as a carrier in the membrane and facilitate the transport of \( p \)-xylene by an interaction between them. Since the high diffusion selectivity for \( p \)-xylene exceeds the low sorption selectivity – that is, the \( p \)-xylene selectivity in the diffusion becomes more dominant than the \( o \)-xylene selectivity in the sorption – the separation factor becomes >1 totally. This led to the conclusion that the separation of xylene isomers through the CD–PVA membrane by evapomeation is mainly governed not by the solubility but by the diffusivity of the permeants in the membrane. However, the permeation mechanism of xylene isomers through the CD–PVA membrane cannot be sufficiently revealed.

### 16.3.3 Dehydration of Organic Liquid in Evapomeation

The permeation rates and separation factors for the chitosan derivative membranes in evapomeation are summarized in Table 16.6 [46]. When the ethanol concentration in the feed is less than 70 wt%, the separation factor for the chitosan acetate salt (CAS) membrane is not appreciable. This is attributed to an important increase of the degree of swelling of the CAS membrane for feed compositions rich in the water vapour, because the CAS membrane is soluble in water. As the ethanol content in the feed becomes higher than 90 wt%, the CAS membrane is not swollen, and instead shrinks and consequently becomes denser. The separation factors for 90 wt% and 95.6 wt% of feed composition are 1002 and 2556 respectively. These values are about 10 times greater than the separation factors at the same feed compositions for the chitosan membrane.

In addition, there are no large differences between the permeation rates of the CAS and chitosan membranes. In the GA cross-linked (GAC) chitosan membranes, when the ethanol concentrations in the feed are 30–70 wt%, the separation factors are infinite. This means that the GAC membrane permeates only water from the feed mixtures with 30–70 wt% of ethanol concentration. The fact that

<table>
<thead>
<tr>
<th>Ethanol in feed (vapour) (wt%)</th>
<th>CAS membrane</th>
<th>GAC membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \alpha_{\text{H}_2\text{O}/\text{EtOH}} \times 10^3 )</td>
<td>( \alpha_{\text{H}_2\text{O}/\text{EtOH}} \times 10^3 )</td>
</tr>
<tr>
<td>0</td>
<td>176</td>
<td>237</td>
</tr>
<tr>
<td>10 (43.9)</td>
<td>148</td>
<td>204</td>
</tr>
<tr>
<td>30 (60.4)</td>
<td>126</td>
<td>149</td>
</tr>
<tr>
<td>50 (67.7)</td>
<td>96</td>
<td>106</td>
</tr>
<tr>
<td>70 (77.3)</td>
<td>39</td>
<td>55</td>
</tr>
<tr>
<td>90 (90.8)</td>
<td>18</td>
<td>25</td>
</tr>
<tr>
<td>95.6 (95.6)</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>100</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>

CAS: chitosan acetate salt membrane; GAC: glutaraldehyde cross-linked chitosan membrane.
the GAC membrane has such a high separation factor was supported by the experimental result of the composition of vapour adsorbed inside the membrane. The GAC membrane predominantly adsorbed water in all feed compositions. This result is attributed to the higher hydrophilicity of the GAC membrane. The fact that water molecules are selectively dissolved into the GAC membrane and also that these molecules with smaller molecular size can easily diffuse through the GAC membrane significantly influences the high permeation rate and separation factor.

Table 16.6 also shows that the permeation rates for these feed compositions are greater than those for the chitosan membrane. The separation factors for 90 wt% and 95.6 wt% feed compositions are about 20 and 10 times greater respectively than those for the chitosan membrane. Higher permeation rates and separation factors of the GAC membrane can be considered to be very interesting features of membrane performance.

Table 16.7 summarizes the permeation and separation characteristics for aqueous ethanol solution through water-selective polymer membranes in evapomeation. The separation factors for these derivative membranes are greater than those in pervaporation, but it is desired to improve the permeation rate further. In future, if ultrathin membranes can be prepared from those chitosan derivatives, the appearance of chitosan derivative membranes with both high permeation rate and high separation characteristics can be expected.

The effects of the composition of the feed vapours from aqueous methanol, ethanol and 1-propanol solutions on the permeation rates and separation factors through a PVBB membrane in evapomeation were investigated [29]. The results obtained for aqueous methanol and 1-propanol solutions were similar to that for the aqueous ethanol solution. Namely, water permeated preferentially from aqueous alcohol solutions. The permeation rate for a water–1-propanol mixture is the lowest and the separation factor is the highest among the three mixtures. In other words, the water–alcohol system containing an alcohol that has a stronger affinity for the PVBB membrane gives lower permeability and higher selectivity. This is due to the fact that the interaction between the higher alcohol and the PVBB membrane is stronger and the molecular size of the higher alcohol is larger. It is interesting that the permeability of the penetrant having a stronger affinity for the PVBB membrane is lower. The PVBB membrane seems to play a role as an adsorbent. Similar results have also been observed in hydrophobic, dense polymer membranes such as PVC [43] and polystyrene [44], and have never been

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Feed (wt%)</th>
<th>Permeation rate (kg cm(^{-2}) h(^{-1})) (\times 10^3)</th>
<th>Separation factor (\alpha_{\text{H}_2\text{O}/\text{EtOH}})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>95.6</td>
<td>2.1</td>
<td>203</td>
<td>[25]</td>
</tr>
<tr>
<td>Poly(styrene)</td>
<td>95.6</td>
<td>3.4</td>
<td>1516</td>
<td>[26]</td>
</tr>
<tr>
<td>PVBB</td>
<td>95.6</td>
<td>2.8</td>
<td>120</td>
<td>[29]</td>
</tr>
<tr>
<td>Alginic acid</td>
<td>95.6</td>
<td>7.3</td>
<td>1940</td>
<td>[2]</td>
</tr>
<tr>
<td>Chitosan</td>
<td>95.6</td>
<td>7.5</td>
<td>202</td>
<td>[27]</td>
</tr>
<tr>
<td>CAS</td>
<td>95.6</td>
<td>2.7</td>
<td>2556</td>
<td>[27]</td>
</tr>
<tr>
<td>GAC</td>
<td>70</td>
<td>55</td>
<td>(\infty)</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>95.6</td>
<td>4.3</td>
<td>2208</td>
<td>[27]</td>
</tr>
</tbody>
</table>
recognized in hydrophilic polymer membranes. It is well known that water preferentially permeates through a hydrophilic polymer membrane from an aqueous alcohol solution. This is attributed to the strong affinity between the water molecules with small molecular size and the hydrophilic polymer membrane.

From the previous discussion, it is found that the mechanism is different for the permselectivity of water from aqueous alcohol solutions through hydrophobic and hydrophilic polymer membranes. That is, in the case of the hydrophilic polymer membrane, water is predominantly adsorbed by the membrane and is selectively diffused through the membrane. In a hydrophobic dense polymer membrane, however, alcohol is predominantly incorporated into the membrane and strongly absorbed in the membrane, and water is selectively diffused in the membrane. This phenomenon is due to a stronger interaction between the hydrophobic membrane and the permeant.

From the analysis of data in permeation and separation experiments for aqueous solutions of acetic acid through a PVC membrane in evapomeation, the diffusion of the permeant in the PVC membrane was found to be an important process for the separation of aqueous acetic acid solutions [51]. In general, the diffusivity of permeants is influenced by their molecular size and shape. It is expected that the diffusivity difference based on the molecular size and shape of the permeant significantly affects the permselectivity through the polymer membrane. In order to reveal such factors, the permselectivities of the PVC membrane for aqueous solutions of other organic acids, such as formic acid and propionic acid, were also investigated by evapomeation. Table 16.8 summarizes the evapomeation properties of the aqueous solutions of formic acid, acetic acid and propionic acid. It is found that water is predominantly permeated from these aqueous solutions through the PVC membrane. Formic acid and propionic acid were preferentially incorporated into the PVC membrane. The mechanism of the separation for these aqueous solutions can be explained by that for aqueous acetic acid solutions.

The concentration of propionic acid in the PVC membrane is higher than that of formic acid. The acetic acid concentration in the PVC membrane is situated between propionic acid and formic acid.

<table>
<thead>
<tr>
<th>Organic acid (wt%)</th>
<th>Organic acid in feed solution a) (wt%)</th>
<th>Organic acid in membrane (wt%)</th>
<th>Organic acid in permeation (wt%)</th>
<th>Separation factor b) $\alpha_{\text{water/organic acid}}$</th>
<th>Permeation rate $\times 10^3$ (kg m$^{-2}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>10 (6.2)</td>
<td>15</td>
<td>1.3</td>
<td>5.0</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>50 (44)</td>
<td>55</td>
<td>1.1</td>
<td>67</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>90 (94)</td>
<td>93</td>
<td>7.9</td>
<td>156</td>
<td>2.2</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>10 (7.6)</td>
<td>18</td>
<td>0.36</td>
<td>23</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>50 (36)</td>
<td>72</td>
<td>0.90</td>
<td>62</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>90 (82)</td>
<td>95</td>
<td>1.86</td>
<td>248</td>
<td>3.2</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>10 (12)</td>
<td>20</td>
<td>0.54</td>
<td>24</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>50 (31)</td>
<td>75</td>
<td>0.36</td>
<td>784</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>90 (67)</td>
<td>95</td>
<td>0.25</td>
<td>125</td>
<td>3.5</td>
</tr>
</tbody>
</table>

a) The values in parentheses are the feed vapour composition.
b) Separation factors were calculated by the feed vapour composition.
That is, the solubility of the organic acids into the PVC membrane from their aqueous solutions is in the order of formic acid < acetic acid < propionic acid. This order of solubility can be explained using solubility parameters of PVC and each organic acid. The solubility parameters [75] of formic acid, acetic acid and propionic acid, and the difference of the solubility parameters between PVC and organic acids are summarized in Table 16.9. The $\delta_{\text{propionic acid}} - \delta_{\text{PVC}}$ value is the smallest one. Such a strong affinity between the PVC membrane and the propionic acid results in a more preferential solubility of propionic acid into the PVC membrane.

As can be seen in Table 16.8, the separation factors for the aqueous organic acid solutions through the PVC membrane increase in the reverse order of the preferential solubility. Propionic acid has the largest molecular size in these organic acids, so that its diffusivity in the PVC membrane is predicted to be the lowest, in spite of it having the highest solubility. As described earlier, the separation of these aqueous solutions through the PVC membrane is mainly governed by the diffusion process in the membrane. A large difference in the diffusivities between water and organic acids leads to high selectivity through the PVC membrane.

Table 16.10 summarizes the permeation and separation characteristics in evapomeation of feed vapours from aqueous solutions of methanol, ethanol, and 1-propanol through the GA–CM–ChitoA (II) membrane which was prepared from the casting solution containing 6.0 wt% of GA. In spite of

<table>
<thead>
<tr>
<th>Methanol</th>
<th>Feed vapour (wt%)</th>
<th>Permeation rate (g m$^{-2}$ h$^{-1}$)</th>
<th>Separation factor $\alpha_{\text{H}_2\text{O}/\text{MeOH}}$</th>
<th>Feed vapour (wt%)</th>
<th>Permeation rate (g m$^{-2}$ h$^{-1}$)</th>
<th>Separation factor $\alpha_{\text{H}_2\text{O}/\text{EtOH}}$</th>
<th>Feed vapour (wt%)</th>
<th>Permeation rate (g m$^{-2}$ h$^{-1}$)</th>
<th>Separation factor $\alpha_{\text{H}_2\text{O}/\text{1-ProOH}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>141</td>
<td></td>
<td></td>
<td>0</td>
<td>141</td>
<td></td>
<td>0</td>
<td>141</td>
<td></td>
</tr>
<tr>
<td>43.2</td>
<td>44.1</td>
<td>165</td>
<td>0.91</td>
<td>46.1</td>
<td>51.3</td>
<td>0.95</td>
<td>49.9</td>
<td>44.2</td>
<td>0.94</td>
</tr>
<tr>
<td>70.4</td>
<td>48.5</td>
<td>105</td>
<td>1.17</td>
<td>68.6</td>
<td>47.8</td>
<td>1.33</td>
<td>67.4</td>
<td>44.2</td>
<td>1.32</td>
</tr>
<tr>
<td>80.9</td>
<td>48.7</td>
<td>58</td>
<td>1.61</td>
<td>75.9</td>
<td>42.6</td>
<td>1.95</td>
<td>69.7</td>
<td>52.6</td>
<td>1.96</td>
</tr>
<tr>
<td>88.3</td>
<td>31.8</td>
<td>20</td>
<td>2.63</td>
<td>81.7</td>
<td>33.3</td>
<td>2.63</td>
<td>71.3</td>
<td>43.6</td>
<td>2.62</td>
</tr>
<tr>
<td>95.9</td>
<td>28.9</td>
<td>14</td>
<td>3.59</td>
<td>91.2</td>
<td>11.1</td>
<td>3.59</td>
<td>82.1</td>
<td>12.1</td>
<td>3.59</td>
</tr>
<tr>
<td>100</td>
<td>95.2</td>
<td>4.97</td>
<td>100</td>
<td>100</td>
<td>3.26</td>
<td>100</td>
<td>100</td>
<td>3.26</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 16.9 Solubility parameters of organic acid and differences of solubility parameters between the organic acid and PVC.

<table>
<thead>
<tr>
<th></th>
<th>Formic acid</th>
<th>Acetic acid</th>
<th>Propionic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{\text{organic acid}}$ (MPa$^{0.5}$)</td>
<td>24.8</td>
<td>20.7</td>
<td>20.3</td>
</tr>
<tr>
<td>$\delta_{\text{organic acid}} - \delta_{\text{PVC}}$ (MPa$^{0.5}$)</td>
<td>5.0</td>
<td>0.9</td>
<td>0.5</td>
</tr>
</tbody>
</table>

a) $\delta_{\text{PVC}}$: 19.8 MPa$^{0.5}$.  

Table 16.10 Permeation and separation characteristics in evapomeation for the feed vapours from aqueous alcoholic solutions through a GA–CM–ChitoA membrane.
the fact that the separation factor for the feed vapour from aqueous ethanol solutions increased with increasing ethanol concentration in the feed vapour, that from aqueous methanol solutions decreased with an increase of methanol concentration in the vapour. This result is mainly attributed to the fact that the molecular size of methanol is smaller than that of ethanol and the relative volatility of methanol is higher than that of ethanol. The permeation and separation characteristics for the feed vapour from aqueous 1-propanol solutions were similar to those for ethanol, but the separation factors for 1-propanol were greater than those for ethanol. This result is due to the fact that the molecular size of 1-propanol is larger than that of ethanol and the relative volatility of 1-propanol is lower than that of ethanol. The permeation and separation characteristics for the feed vapours from aqueous alcoholic solutions are summarized as follows. The permeation rate is in the order of methanol > ethanol > 1-propanol, and the separation factor is in the order of methanol < ethanol < 1-propanol. It seems that these characteristics are significantly influenced by the molecular size and relative volatility of alcohols.

The permeation and separation characteristics for the feed vapour compositions of aqueous ethanol solution through the GA–Chito and GA–CM–ChitoA (II) membranes in evapomeation are compared in Figure 16.15. The separation factor of the GA–CM–ChitoA (II) membrane was smaller than that in the GA–Chito membrane, but the former showed a considerably high separation performance. The GA–CM–ChitoA (II) membrane is more hydrophilic than the GA–Chito membrane, because it carries carboxymethyl groups and, furthermore, it is an acetate salt. The GA–ChitoA membrane also was more hydrophilic than the GA–Chito membrane. The separation performance was not good, as shown in Table 16.10 and Figure 16.15. The difference in the separation performance between the GA–ChitoA and the GA–CM–ChitoA (II) membranes is explained as follows. A high hydrophilicity of the GA–CM–ChitoA (II) membrane increases the solubility of the water molecules in the membrane and the introduction of bulky carboxymethyl groups disturbs the diffusivity of ethanol molecules having larger molecular size. These factors significantly influence the separation performance of the GA–CM–ChitoA (II) membrane. From these results, it is found that a control in both chemical and physical structure is very important in the permeation and separation through the membranes.

Figure 16.16 shows the effect of the feed vapour composition of the aqueous ethanol solutions on the permeation rate, the ethanol concentration in the permeate through the chitosan and GAC membranes in evapomeation, and the degree of swelling of the membrane [52].

**Figure 16.15** Effects of feed vapour composition of aqueous ethanol solution on the permeation rate and separation factor in evapomeation through the GA–Chito (○, △) and GA–CM–ChitoA (●, ▲) membranes. The GA content in the casting solution is 3.6 wt% for the GA–Chito membranes and 6.0 wt% for the GA–CM–ChitoA.
GAC membrane had a content of 0.5% GA (3.2% GA in the casting solution). Both the chitosan and GAC membranes had a low ethanol concentration in the permeate and showed a high water/ethanol selectivity. Also, there are significant differences between the compositions in the permeate of the chitosan, and the GAC membrane was higher than that of the chitosan membrane in spite of the fact that the permeation rate of the GAC membrane was greater than that of the chitosan membrane. Furthermore, the degree of swelling of the GAC membrane was higher than that of the chitosan membrane, and this tendency increased with a decreasing ethanol concentration in the feed mixture. When polymer membranes are cross-linked, in general, the permselectivity is improved but the permeation rate is decreased because the degree of swelling of the membrane is lowered. In this case, however, the permeation rate, the water/ethanol selectivity and the degree of swelling of the GAC membrane are higher than those of the chitosan membrane.

In order to clarify the results in Figure 16.16, the density and the crystallinity of chitosan and the GAC membranes were determined by the flotation method and wide-angle X-ray diffraction, respectively. The density and the correlation crystallinity index decreased with an increasing GA content in the casting solution. These results imply that the increase in the cross-linking of the chitosan membrane decreases the density and the crystallinity of the membrane. From these results, a model structure, as shown in Scheme 16.4, is assumed for the chitosan and GAC membranes.

The chitosan membrane has many intermolecular hydrogen bonds between hydroxyl and amino groups. A few of these hydrogen bonds in the GAC membrane are broken by cross-linking with GA and free hydrophilic groups such as hydroxyl, and amino groups are formed. These hydrophilic groups have a strong affinity to water molecules; that is, the solubility of water molecules into the GAC membrane is increased. On the other hand, since the size of the water molecule sorbed into the GAC membrane is

---

**Figure 16.16** Effects of ethanol concentration in the feed vapour on the permeation and separation characteristics and degree of swelling of the chitosan (●) and GAC (○) membranes by evaporation.
smaller than that of the ethanol molecule, the water molecule can more easily diffuse in the GAC membrane than the ethanol molecule can. Consequently, the GAC membranes are moderately swollen by water molecules and simultaneously increase the water/ethanol selectivity. The increase of the water/ethanol selectivity in the GAC membrane is due to both the increase in the solubility of water molecules into the GAC membrane and the increase in the diffusivity of water molecules in the GAC membrane. From this discussion, both the increase in the permeation rate and the separation factor with increasing GA content cross-linked in the chitosan membrane can be understood.

If a deformation of the hydrogen bonds in the chitosan membrane, as shown in Scheme 16.4, gives a high permeation rate and high water/ethanol selectivity, it can be assumed that cross-links are not necessarily needed. So a chemical modification of the chitosan membrane was tried using N-alkyl aldehyde as a monofunctional aldehyde, and these N-alkyl chitosan membranes were applied to the permeation and the separation for aqueous ethanol solutions in evapomeation [57]. If the balance between an increase of the hydrophilicity of the N-alkyl chitosan membranes based on the deformation of the hydrogen bonds in the chitosan membrane and an increase of the hydrophobicity of the membranes due to the N-alkylation of the amino groups in the chitosan membrane is suitable, both the permeation rate and the water/ethanol selectivity are improved by the alkylation of the chitosan membrane.

The effect of number of carbons in the N-alkyl group of the chitosan molecule on the permeation rate and the separation factor for an aqueous solution of 10 wt% ethanol through N-alkyl chitosan membranes in evapomeation is shown in Figure 16.17. The degree of substitution of the N-alkyl chitosan membranes used in this section was almost equal at about 3 mol%. In an N-ethyl chitosan membrane,
membrane, the permeation rate and the separation factor were almost equal to those in the chitosan membrane. But both the permeation rate and the separation factor of an N-propyl chitosan membrane were smaller than those of the chitosan membrane. In contrast, the permeation rate of an N-butyl chitosan membrane was slightly smaller than that of the chitosan membrane but the separation factor of the N-butyl chitosan membrane was about 1.5 times that of the chitosan membrane. Furthermore, in an N-pentyl chitosan membrane the separation factor was about two times greater than that in the chitosan membrane. In addition, both the separation factor and the permeation rate in the N-pentyl chitosan membrane showed a maximum.

From the aforementioned results, the model depicted in Scheme 16.5 is proposed to provide an understanding of the relationship between the permeation and separation characteristics for aqueous ethanol solutions through N-alkyl chitosan membranes in evapomeation and the changes in their membrane structure. Namely, the chitosan membrane has a very dense structure based on the hydrogen bonds among the hydroxyl groups, amino groups, and hydroxyl and amino groups in the chitosan chains as shown in Scheme 16.5a. However, introducing the N-alkyl group severs some of the hydrogen bonds, as shown in Scheme 16.5b and c, and the physical structure of the N-alkyl chitosan membrane becomes rough and the density of the N-alkyl chitosan membrane is decreased. Such an effect is remarkable for a chitosan membrane having bulky alkyl groups. On the other hand, the chitosan membrane becomes hydrophobic by alkylation of the hydrophilic amino groups. Therefore, the N-alkyl chitosan membrane has a strong affinity for an aqueous solution of 96 wt% ethanol, which is a relatively hydrophobic feed mixture, and has a high degree of swelling. Consequently, the permeation rate is increased and the separation factor is decreased with an increase in the number of carbon atoms.

The permeation and separation characteristics for an aqueous solution of 10 wt% ethanol are low because the N-alkyl chitosan membrane is hydrophobic to a relatively hydrophilic feed mixture. In the butyl and pentyl groups, however, the decrease in the degree of swelling of the membrane and the predominant incorporation of water molecules into these membranes due to the effect of the severing of hydrogen bonds leads to high water permselectivity.
q-Chito and cross-linked q-Chito cross-linked with DEDGE (see Scheme 16.1) membranes were prepared for the dehydration of an ethanol–water azeotrope. These membranes were highly water permeable [60]. The permeation rates of the q-Chito membranes decreased with an increasing degree of quaternization, and the cross-linked q-Chito membranes also decreased with an increase in the cross-linker concentration. The decrease in the permeation rate of the q-Chito membrane with an increase of the degree of quaternization was due to a lowering of the diffusivity of the ethanol molecule during the diffusion process, based on the introduction of bulky quaternary ammonium groups into the chitosan molecule chains. The decreased permeation rate of the amount of cross-linked
q-Chito membrane with an increase in the cross-linker could be attributed to a lowering of the diffusivity of the permeating molecules caused by the dense cross-link structure between the q-Chito molecule chains. The separation factors for the water permselectivity of the former membrane were mainly dependent on the sorption selectivity based on the solubility of the water molecule into the q-Chito membrane. In contrast, the cross-linked q-Chito membrane was significantly influenced by both sorption and diffusion selectivities. The separation factors of the cross-linked q-Chito membranes were very high, about 4100–4200. The degree of swelling of these membranes, the membrane density and the contact angle of the membrane surface were consistent with these permeation and separation characteristics for an ethanol–water azeotrope during evapomeation. The separation mechanism for an ethanol–water azeotrope during evapomeation through the q-Chito and cross-linked q-Chito membranes was analysed by the solution-diffusion model. The water permselectivity of the q-Chito membrane was mainly governed by the sorption selectivity and that in the cross-linked q-Chito membrane was dependent on both the sorption and the diffusion selectivities.

PIC cross-linked chitosan membranes (see Scheme 16.2), constructed from q-Chito and poly(ethylene oxydiglycolic acid) (PEO acid) on a porous poly(ether sulfone) (PES) (q-Chito–PEO acid PIC–PES), as shown in Figure 16.18, have been applied to the dehydration of an ethanol–water azeotrope in evapomeation [62].

Figure 16.19 shows the permeation rate and the separation factor for the water permselectivity of ethanol–water azeotrope (96.5 wt% ethanol) through q-Chito–PEO acid PIC–PES composite membranes as a function of the molar ratio of the carboxylate groups in PEO acid and the quaternized ammonium groups in q-Chito.

Figure 16.18 Scanning electron microscope image of the cross-section of the q-Chito–PEO acid PIC–PES composite membrane.

Figure 16.19 Permeation and separation characteristics for an ethanol–water azeotrope through q-Chito–PEO acid PIC–PES composite membranes during evapomeation as a function of the molar ratio between the carboxylate groups in PEO acid and the ammonium groups in q-Chito. (○) PEO acid 400; (●) PEO acid 1000; (□) PEO acid 4000.
In every \( q \)-Chito–PEO acid PIC membrane, the separation factors for water permselectivity were increased by cross-linking the \( q \)-Chito with PEO acids and reached a maximum at an equimolar ratio between the carboxylate and ammonium groups. The permeation rates were also affected by the molar ratios of the carboxylate and ammonium groups. With an increasing molecular weight of PEO acid, the separation factors at a molar ratio other than an equimolar ratio increased, but the separation factor at an equimolar ratio was not dependent on the molecular weight of PEO acid. This suggests that the PIC between the carboxylate and quaternized ammonium groups was not formed stoichiometrically. Such difference in the PIC formation due to different PEO acid molecules yields significant differences in chemical and physical structure of the resulting membrane. Therefore, a competing factor may be significantly related to these results.

Table 16.11 summarizes the total permeation rate, the partial permeation rates for water and ethanol, and the separation factor, sorption selectivity and diffusion selectivity, and evapomeation index for water permselectivity of an ethanol–water azeotrope through a \( q \)-Chito–PEO acid 400 PIC–PES composite membrane at various temperatures. As can be seen, the partial permeation rates for ethanol were very small, but those for water increased with increasing permeation temperature. This increase in the partial permeation rate for water was due to the increase in the motion of the permeating molecules and polymer chains comprising the membrane matrix. The sorption selectivity was not influenced all that much by the permeation temperature, but the diffusion selectivity was influenced significantly. The decrease in the water permselectivity with an increase of permeation temperature can be attributed to a lowering of the diffusion selectivity based on an increase in the diffusivity of the ethanol molecule.

Huang [76] reported that the pervaporation index, which is the product of the permeation rate and the separation factor, can be used as a measure of membrane performance during pervaporation. Because the membrane performance for evapomeation was estimated by the same method, the evapomeation index was also summarized in Table 16.11. The evapomeation index was the highest at a permeation temperature of 60 °C, and this suggests that there is an optimal temperature for the permeation of an ethanol–water azeotrope through the hydrophilic \( q \)-Chito–PEO acid PIC–PES composite membranes during evapomeation.

Rice straw is mainly composed of cellulose, hemicellulose and lignin. Rice straw typically includes glucose, xylose, arabinose, mannose and galactose. Therefore, the ethanol production process from rice straw involves three steps. First, polymeric substrates are degraded into monosaccharides with chemical or enzymatic treatment. Second, the sugars are converted into ethanol by bacteria or yeast (usually the strain \textit{Saccharomyces cerevisiae}). Third, the ethanol is purified from fermentation broth by processes such as adsorption, distillation and liquid–liquid extraction. Among these processes,

<table>
<thead>
<tr>
<th>Permeation temperature (°C)</th>
<th>Permeation rate ( \times 10^{-2} ) (kg m(^{-2}) h(^{-1}))</th>
<th>Separation factor</th>
<th>Sorption selectivity</th>
<th>Diffusion selectivity</th>
<th>Evapomeation index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total H(_2)O EthOH</td>
<td>( \alpha_{sep, H_2O/EtOH} )</td>
<td>( \alpha_{sorp, H_2O/EtOH} )</td>
<td>( \alpha_{diff, H_2O/EtOH} )</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>8.01 7.98 0.03</td>
<td>8000</td>
<td>850</td>
<td>9.4</td>
<td>640</td>
</tr>
<tr>
<td>60</td>
<td>35.12 34.96 0.16</td>
<td>6300</td>
<td>815</td>
<td>7.7</td>
<td>2205</td>
</tr>
<tr>
<td>80</td>
<td>91.03 87.60 3.43</td>
<td>800</td>
<td>727</td>
<td>1.1</td>
<td>728</td>
</tr>
</tbody>
</table>

Table 16.11 Evapomeation characteristics and performance of \( q \)-Chito–PEO acid 400 PIC–PES composite membrane for an ethanol–water azeotrope at various temperatures.
dehydration of water–ethanol mixtures using evapomeation process is a well-developed method [1,2]. In the vapour permeation process, the feed solution is vaporized first and then permeated through the membrane that has a hydrophilic nature and selectively transports water. This process can effectively concentrate the ethanol in the feed solution [77].

Tsai et al. [78] investigated the surfactant addition effect on the evapomeation of aqueous ethanol mixtures through polysulfone hollow-fibre membranes. Evapomeation, the membrane separation technique proposed by Uragami and Morikawa [41,45], can avoid the disadvantages caused by pervaporation. Through the evapomeation technique, the feed solution vaporizes first and then permeates through the membrane. Consequently, the swelling or shrinking of polymer membranes caused by direct contact with the feed solution can be prevented. The purification of individual acids could be accomplished using distillation. The differences in boiling points between water and these carboxylic acids are large enough that distillation is technically viable. However, because the acids are relatively dilute and water is the most volatile component of this mixture, distillation would be an energy-intensive process. Future work on the development of this process will focus on improving the energy efficiency of the purification steps by using processes such as evapomeation, which has been shown previously to be an effective method for the separation of water and acetic acid [79].

Figure 16.20 shows the relationship between the water concentration in the feed vapour under various feed vapour pressures and the ethanol concentration (C₂) in the permeate through GA cross-linked q-Chito membrane during high-temperature and high-pressure evapomeation. The separation performance for water permselectivity in the water–ethanol feed vapour increased with a decreasing difference between the total pressure P_T and the feed vapour pressure P₁ [61].

16.3.4 Concentration of Organic Liquid by Evapomeation

The effects of the ethanol concentration in the feed solution on the permeation rate and separation factor for ethanol permselectivity through a dense PDMS membrane by evapomeation are shown in Figure 16.21. As can be seen from this figure, a dense PDMS membrane in evapomeation shows moderately high ethanol permselectivity but the permeation rate is low [44,45].
When some methods which can improve the permeation rate in evapomeation are developed, it is greatly expected that the evapomeation process will serve for the concentration and removal of organic liquids in aqueous solutions such as the concentration of bio-alcohol and removal of aromatic and chlorinated hydrocarbons in the wastewater. One proper example is that a low-density membrane is applied to evapomeation for the concentration of organic liquid in an aqueous organic solution. The permeation rate and separation factor for ethanol permselectivity of a nonporous poly[1-(trimethylsilyl)-1-propyne] membrane in evapomeation were $5.3 \times 10^{-11}$ kg m$^{-2}$ h$^{-1}$ and 14.9 respectively [15]. This separation factor was almost same as that of a dense PDMS membrane but the permeation rate was 2.5 times higher than that in the latter membrane. It is well known that nonporous poly[1-(trimethylsilyl)-1-propyne] membranes have lower density, and hence higher free volume, than other polymer membranes [80].

**16.3.5 Separation of Optical Enantiomers by Evapomeation**

Racemates of 1,3-butanediol, 2-butanol and their derivatives were enantioselectively separated by evapomeation and pervaporation through (+)-poly[1-[dimethyl(10-pinanyl)silyl]-1-propyne] ([(+)-poly(DPSP)) membrane. The permeation rate $P$ and enantioselectivity (per cent enantiomeric excess (%ee) of the permeate) were very high. For example, the $P$ and %ee values in evapomeation for (+)/(−)-1,3-butanediol were $1.19 \times 10^{-3}$ g m$^{-2}$ h$^{-1}$ and 41.7%ee, and those in pervaporation for (+)/(−)-2-butanol were $8.37 \times 10^{-4}$ g m$^{-2}$ h$^{-1}$ and 44.6%ee respectively. This is the first example of vapor enantioselective permeation [32].

Aoki et al. [33] achieved the optical resolution of various racemates, such as (+)/(−)-tryptophan and (+)/(−)-1,3-butanediol, by membrane permeation through a self-supporting membrane of (+)-poly(DPSP) prepared by homopolymerization of (−)-1-[dimethyl(10-pinanyl)silyl]-1-propyne (−-DPSP). Almost complete optical resolution (%ee of the permeate 81–100%ee) was achieved at an initial period of concentration-driven permeation, and stable permeation with moderate permselectivity (%ee of the permeate 12–54%ee) continued for more than 600 h. In addition, by permeation of vapour permeant such as evapomeation and pervaporation, higher permeation rates were attained maintaining high enantioselectivity. The sign of the enantiomer that predominantly permeated through a (+)-poly(DPSP) membrane was opposite to that through a (−)-poly(DPSP) membrane. In the permeation through a (+)-poly(DPSP) membrane of a solute or a solvent having a high affinity for (+)-poly(DPSP)
and in the permeation through a membrane from the copolymer of (−)-DPSP with a small amount of 1-(trimethylsilyl)-1-propyne, their enantioselectivities were much lower. These findings suggest that the permeating route surrounding chiral pinanyl groups in a (+)-poly(DPSP) membrane that can enantioselectively separate various racemates was easily deformed by using a solute or solvent having a high affinity for (+)-poly(DPSP) or by removing a small amount of pinanyl groups.

Several new polymers for optical resolution membranes were synthesized and enantioselective permeabilities of the polymer membranes were examined for various racemates using four methods: concentration-driven permeation, pressure-driven permeation, pervaporation and evapomeation. (+)-Poly(DPSP) membranes showed high enantioselective permeabilities in concentration-driven permeation for various racemates and low permeation rates, which were improved by using pervaporation or evapomeation. (−)-Poly(2-(dimethyl(10-pinanyl)silyl)norbornadiene) had a higher permeability than (+)-poly(DPSP). Polymers having a chiral main chain showed poor enantioselective permeability. Highly and stably enantioselective permeations were observed through the blend membranes whose surface were modified by (−)-oligo-(methyl (10-pinanyl)siloxane (−)-OMPS). The graft copolymers with (−)-OMPS as the grafts are promising for a higher performance membrane [34].

16.3.6 Acceleration of Chemical Reaction by Evapomeation Technique

The pervaporation membrane separation technique has been applied to accelerate the conversion of chemical reactions, especially esterifications. In these applications, liquid by-product water is removed through water-permselective membranes [81-86]. We can easily presume that the evapomeation technique can be applied to those chemical reactions. For example, when a hydrophilic PVA membrane is applied to the esterification for dehydration of water, by-product, the conversion in esterification can be increased significantly [87]. These results are discussed in detail in Chapters 21 and 24.

References


17

Temperature-Difference Controlled Evapomeation

17.1 Principle of Temperature-Difference Controlled Evapomeation

As mentioned in Section 16.1, a novel membrane separation technique known as ‘evapomeation’ makes use of the advantages of pervaporation, but reduces the negative effects of swelling on membrane performance. In this technique, the feed solution is fed to the membrane without directly contacting the polymer membrane. This is accomplished by vaporizing the liquid feed so that only vapour is supplied to the polymer membrane. Therefore, swelling or shrinking of the polymer membranes due to contact with the feed solutions is minimized.

As just mentioned, a new evapomeation method for membrane separation that improves the shortcomings of pervaporation while keeping the advantages of this technique was developed. However, an improvement of the permeation rate in evapomeation by some methods was strongly required, as described in Section 16.3.4. As one method for this requirement, a novel method establishing the temperature difference between the feed solution and the membrane surroundings was proposed [1]. This novel membrane separation technique, called ‘temperature-difference controlled evapomeation’ (TDEV) [1–8, 23], is as follows. In evapomeation, the temperatures of the feed solution (A) and the membrane surroundings (B) are controlled, and consequently a differential between these temperatures can be established, as shown in Figure 17.1. Bernardo et al. [9] interestingly introduced the TDEV method in their chapter in the Concise Encyclopedia of High Performance Silicones.

This TDEV method is a very interesting technique for the separation of aqueous solutions and organic liquid mixtures using the difference between the freezing points of permeants. The separation mechanism in TDEV can be easily understood by Figure 17.2. When a mixture consisting of a component with lower freezing point and a component with higher freezing point is provided as the feed solution in the TDEV process, the latter components are easily aggregated on the membrane surroundings but the former components are difficult to aggregate on the membrane surroundings. In addition, if a membrane that has a high affinity for the former component can be selected, then an excellent permselectivity is obtained.

17.2 Membranes of Temperature-Difference Controlled Evapomeation

Hydrophilic, hydrophobic polymer and inorganic membranes which are applied to pervaporation and evapomeation can be applied to the TDEV process. As mentioned later, porous membranes can also be applied to TDEV.
17.3 Technology of Temperature-Difference Controlled Evaporative Condensation

17.3.1 Comparison of Membrane Performance in Evaporative Condensation and Temperature-Difference Controlled Evaporative Condensation

The TDEV experiments are performed using the TDEV cell shown in Figure 17.3 [10].

The ethanol concentration in the permeate, separation factor, apparent separation factor and permeation rate for an aqueous solution of 10 wt% ethanol through a dense poly(dimethylsiloxane) (PDMS) membrane by the TDEV method are shown in Figure 17.4, in which the temperature of the membrane neighbourhood is kept constant at 25 °C and the temperature of the feed solution was changed. Both the ethanol concentration in the permeate and the separation factor are increased with increasing temperature of the feed solution. As shown in Figure 17.4b, when the temperatures of both the feed solution and the membrane neighbourhood are 25 °C – that is, corresponding to the experiment in the evaporative condensation method – the separation factor \( \alpha_{\text{EtOH/H}_2\text{O}} \) based on the composition of feed vapour as expressed by

\[
\left( \alpha_{\text{EtOH/H}_2\text{O}} \right)_V = \frac{P_{\text{EtOH}}/P_{\text{H}_2\text{O}}}{V_{\text{EtOH}}/V_{\text{H}_2\text{O}}}
\]

is less than unity, where \( V_{\text{EtOH}} \) and \( V_{\text{H}_2\text{O}} \) are the weight fractions of ethanol and water vapour respectively from the feed solution, and \( P_{\text{EtOH}} \) and \( P_{\text{H}_2\text{O}} \) are the weight fractions of ethanol and water respectively in the permeate. This means that a PDMS membrane predominantly permeates water from aqueous ethanol solution.

But the ethanol concentration in the permeate is 38.2 wt% and thus higher than that in the feed solution. Therefore, an apparent separation factor \( \left( \alpha_{\text{EtOH/H}_2\text{O}} \right)_F \) based on the composition of feed mixture, is calculated:

\[
\left( \alpha_{\text{EtOH/H}_2\text{O}} \right)_F = \frac{P_{\text{EtOH}}/P_{\text{H}_2\text{O}}}{V_{\text{EtOH}}/V_{\text{H}_2\text{O}}}
\]
where $F_{\text{EtOH}}$ and $F_{\text{H}_2\text{O}}$ are the weight fractions of ethanol and water respectively in the feed solution. The apparent separation factor at a feed temperature of 25 °C is 5.6 and increases with increasing temperature of the feed solution, as shown in Figure 17.4c.

The total permeation rate and the permeation rates for ethanol and water are increased with an increase in temperature of the feed solution. The increase in these permeation rates is attributed to an increase in activity of the permeating molecules with a rise in temperature of the feed solution. The increment of the permeation rate for ethanol through a PDMS membrane with an increase of the feed temperature is greater than that for water, leading to an increase of the separation factor with the feed temperature.

The separation characteristics and the permeation rates for an aqueous solution of 10 wt% ethanol by the TDEV method are shown in Figure 17.5, in which the temperature of the feed solution is kept constant at 40 °C and that of the membrane neighbourhood is changed. The ethanol concentration in the permeate and the separation factors increase, and the permeation rates decrease, with decreasing temperature of the membrane neighbourhood. The decrease of the permeation rate is due to the lowering of both the activity of permeating species and the motions of polymer chains constituting the membrane. On the other hand, the increase of the separation factors is explained using the illustration in Figure 17.6. When the water and ethanol molecules vaporized from the feed mixture come close to the membrane neighbourhood, it is presumed that the water vapour aggregates much easier than the ethanol vapour and tends to be liquefied as the temperature of the membrane neighbourhood becomes lower. This aggregation between water molecules is responsible for the increase of separation factors.
As can be seen from Figures 17.4 and 17.5, a high permselectivity for ethanol through a PDMS membrane is achieved when the difference between the temperature of the feed solution and membrane neighbourhood is high.

The results in this study suggest that when the temperatures of feed solution and membrane neighbourhood in the separation of aqueous ethanol solution by the evapomeation method are reasonably controlled, the membrane performance is significantly improved. This suggestion can also be applied to the permeation of other organic liquid mixtures through other membranes.

Figure 17.4 Permeation and separation characteristics for an aqueous ethanol solution through a dense PDMS membrane during TDEV. Feed: aqueous solution of 10 wt % ethanol (25 °C).

Figure 17.5 Permeation and separation characteristics for an aqueous ethanol solution through a dense PDMS membrane during TDEV. Feed: aqueous solution of 10 wt % ethanol (40 °C).
To reconfirm the results of the permeation separation for an aqueous ethanol solution through a dense PDMS membrane in TDEV, modified silicone rubber membranes were prepared as follows: Silyl® 5B25 (see Scheme 17.1), produced by Kanegafuchi Chem., Ind., was employed as membrane material. The degree of polymerization of the propylene glycol chain was \( n = 130 \).

Modified silicone rubber membranes were made by pouring the casting solution – consisting of Silyl® 5B25 (2.5 g) of degree of polymerization \( n = 130 \) of the propylene glycol chain, catalyst (0.25 g) (produced by Kanegafuchi Chem., Ind.) and benzene (917 g) – onto a flat dish of stainless steel and allowing the solvent to evaporate completely at 25 °C. The membrane thickness was 80 μm. The formation of the modified silicone rubber membrane is as shown in Scheme 17.1.

This modified silicone rubber membrane was applied to the permeation and separation experiments for an aqueous ethanol solution in TDEV [4].

The effects of the temperature of feed solution on the permeation rate of total permeate (ethanol and water) and ethanol concentration in the permeate for the permeation of an aqueous solution of 10 wt% ethanol through a modified silicone rubber membrane by TDEV are shown in Figure 17.7.

Figure 17.6 Tentative mechanism of the separation for aqueous ethanol solutions through a dense PDMS membrane in TDEV.

\[
(CH_3O)_2Si(CH_3)CH_2CH_2O[\ldots CH(CH_3)CH_2O]_{\text{n}}CH_2CH_2CH_2(OH)(CH_3)Si(OCH_3)_2
\]

Scheme 17.1 Scheme of the preparation of the modified silicone rubber membrane.
in which the temperature of the membrane surroundings is kept constant at 25 °C. Both the total permeation rate and the ethanol concentration in the permeate increased with increasing temperature of the feed solution. The increase in the permeation rate is due to the increasing mobility of the permeants with increasing temperature of the feed solution. When the temperatures of the feed solution and the membrane surroundings are 25 °C, this experiment corresponds to the results in EV and the ethanol concentration in the permeate is 32.7 wt% and is higher than that in the feed solution. With increasing feed solution temperature, which correspond to TDEV experiments, both the permeation rate and ethanol in the permeate concentration increase remarkably. As can be seen from these results, it is interesting that the modified silicone rubber membrane is applied to TDEV experiments.

The total permeation rate, the ethanol concentration in the permeate and the ratio of the permeation rate of ethanol to that of water for the permeation of an aqueous solution of 10 wt% ethanol through a modified silicone rubber membrane by the TDEV method are shown in Figure 17.8 in which the temperature of the feed solution was kept constant at 40 or 70 °C and that of the membrane surroundings was changed. The total permeation rate decreased and the ethanol concentration in the permeate increased with decrease in temperature of the membrane surroundings. The decrease in the total permeation rate is attributed to the lowering of both the motions of polymer chains constituting the membrane and the activity of the permeants. On the other hand, the increase in the ethanol concentration in the permeate is explained as follows. When the molecules of the water–ethanol vapour come close to the membrane surroundings, it is presumed that the water vapour is condensed much easier than the ethanol vapour and tends to be liquefied as the temperature of the membrane surroundings becomes lower. This condensation of water molecules is responsible for the increase of permselectivity for ethanol through the modified silicone rubber membrane. These findings are corroborated by the fact that the ratio of permeation rates \( \frac{PR_{\text{EtOH}}}{PR_{\text{H}_2\text{O}}} \) increases with a decrease in the temperature of the membrane surroundings, as shown in Figure 17.8c.

As shown in Figure 17.8, the total permeation rates and the ethanol concentrations in the permeate at 70 °C feed solution temperature are greater than those at 40 °C. The greater permeation rates are caused by an increase of the motions of the polymer chains and permeants. The high concentrations of ethanol in the permeate at 70 °C feed temperature are due to the fact that the increment of the permeability of ethanol with an increase of the feed solution temperature is larger than that of water.

Figure 17.9 shows the total permeation rates and the ethanol concentrations in the permeate as a function of the temperature of the membrane surroundings. The increase in the ethanol concentration
Figure 17.8 Effects of temperature of the membrane surroundings on the total permeation rate, ethanol concentration in the permeate and ratio $PR_{\text{EtOH}}/PR_{\text{H}_2\text{O}}$ of permeation of ethanol to water through a modified silicon rubber membrane by the TDEV method. Feed solution: aqueous ethanol solution of 10 wt%; feed solution temperature: 40 °C (○), 70 °C (●).

Figure 17.9 Effects of temperature of the membrane surroundings on the total permeation rate, ethanol concentration in the permeate and permeation rate of ethanol (○) and water (■) through a modified silicon rubber membrane by the TDEV method. Feed solution and feed solution temperature are same as in Figure 17.7.
in the permeate with a drop in temperature of the membrane surroundings is similar to the result in Figure 17.8. The permeation rate, however, increased with decreasing temperature of the membrane surroundings. In order to elucidate this phenomenon, the relationships between the permeation rates of ethanol and water and the temperature of the membrane surroundings are shown in Figure 17.9c. The permeation rate of water (■) increased slightly but that of ethanol did so remarkably with a drop in the temperature of the membrane surroundings. When the temperature of the membrane surroundings diminishes, both the solubility of water vapour into the membrane and the aggregation of water molecules increase; consequently, the permeation rates of water at each membrane surroundings temperature become almost equal. On the other hand, since the solubility of ethanol vapour into the membrane increases but the aggregation of ethanol molecules scarcely changes, the permeation rate of ethanol (□) increases as the membrane surroundings temperature is lowered.

If the results in Figures 17.8 and 17.9 are combined, the permeation rate exhibits a maximum at a temperature of the membrane surroundings of about 0°C. A clear explanation for this phenomenon is still awaited.

When the temperatures of the feed solution and membrane surroundings are 70°C and −30°C respectively, the permselectivity for ethanol in an aqueous solution of 10 wt% ethanol through a modified silicone rubber membrane is the best in those experiments; that is, the ethanol concentration in the permeate was as high as ~70 wt%. Figure 17.10 shows the permeation and separation characteristics for aqueous ethanol solutions under the aforementioned permeation conditions as a function of ethanol concentration in the feed vapour. The permeation rate increased with increasing ethanol concentration in the feed vapour. This is due to the increase of the amount of ethanol vapour supplied to the modified silicone rubber membrane which has ethanol selectivity. Further, in the conditions mentioned, the ethanol concentrations in the permeate became significantly higher than those in the feed vapour or the feed solution. Also, when the ethanol concentration in the feed vapour is low, the concentration of ethanol in the permeate is higher.

Figure 17.11 shows the effect of the alcohol concentration in the feed vapour on the permeation rates and separation factors for permeation through a modified silicone rubber membrane by the TDEV method, in which the temperature of the feed solution was 70°C and that of the membrane surroundings was −30°C. The selectivity for alcohols decreases in the order methanol > ethanol > 1-propanol. The degree of swelling of the modified silicone rubber membrane for these alcohols is in the order 1-propanol > ethanol > methanol. From the results in Figure 17.11 and the degree of swelling of the membrane, the selectivity for alcohols through the modified silicone rubber membrane may mainly depend on the difference in diffusivity of the alcohol molecule in the membrane based on the molecular size of the alcohol.
The aforementioned results suggest that the TDEV method will be a powerful method to develop a higher selectivity in membrane separation and also able to be applied to the permeation and separation of other organic liquid mixtures through other membranes.

Table 17.1 summarizes the permeation and separation characteristics for an aqueous solution of 10 wt% ethanol through a PDMS membrane in TDEV, in which the temperatures of the feed and membrane surroundings are controlled. When the temperature in the membrane surroundings is kept constant and the temperature of the feed solution is increased (run nos. 1–5 in Table 17.1), both the permeation rate and separation factor increased. As the temperature of the feed solution is kept constant and the temperature in the membrane surroundings is changed (run nos. 2 and 6–10) the permeation rate decreases and the separation factor remarkably increases with lowering of the temperature in the membrane surroundings. However, when the temperature of the feed is kept constant and the temperature in the membrane surroundings is set higher than the temperature of the feed solution (run nos. 11–13), the selectivity for ethanol is very low.

Table 17.1 also includes the permeation and separation characteristics for an aqueous solution of 10 wt% ethanol through a PDMS membrane in pervaporation at 40 °C (run no. 15). The separation factors \( \alpha_{\text{EtOH/H}_2\text{O}} \) for TDEV in run nos. 2–5 and 6–11 are greater than those for pervaporation in run no. 15. In particular, when the temperature of the feed solution was 40 °C and the temperature in the membrane surroundings was −30 °C (run no. 6), \( \alpha_{\text{EtOH/H}_2\text{O}} \) is 85.7 and the ethanol concentration in the permeate is 90.5 wt%.

From these results in TDEV, it was found that the selectivity for ethanol in aqueous ethanol solutions through a PDMS membrane is improved as the temperature of the feed solution is raised, the temperature in the membrane surroundings is decreased, and also a larger difference between these temperatures is created. In order to provide a larger temperature difference, the temperatures of the feed solution and the membrane surroundings were set at 70 °C and −30 °C respectively. The result obtained is shown in run no. 14 in Table 17.1. However, contrary to expectations, a high selectivity cannot be obtained. This result may be due to the fact that the temperature in the membrane surroundings could not be kept at −30 °C because the temperature of the feed solution was too high.

Figure 17.12 shows the permeation and separation characteristics for an aqueous solution of 10 wt% ethanol through a dense PDMS membrane in TDEV, in which the temperature of the feed solution was kept constant at 40 °C and the temperature of the membrane surroundings was changed [5]. The permeation rate decreased but the ethanol concentration in the permeate increased with decreasing temperature in the membrane surroundings. The decrease in the permeation rate is attributed to the
Table 17.1 Effects of temperature of the feed and membrane surroundings on permeation and separation characteristics for an aqueous solution of 10 wt% ethanol through a dense PDMS membrane by the TDEV method.

<table>
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<tr>
<th>Run no.</th>
<th>Feed temperature (°C)</th>
<th>Membrane surroundings temperature (°C)</th>
<th>Ethanol concentration in permeate (wt%)</th>
<th>Separation factor ((\alpha_{\text{EtOH}}/\text{H}_2\text{O})_V)</th>
<th>((\alpha_{\text{EtOH}}/\text{H}_2\text{O})_F)</th>
<th>Permeation rate for total ((10^2 \text{ kg m}^{-2} \text{ h}^{-1}))</th>
<th>Permeation rate for ethanol ((10^3 \text{ kg m}^{-2} \text{ h}^{-1}))</th>
<th>Permeation rate for water ((10^2 \text{ kg m}^{-2} \text{ h}^{-1}))</th>
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<td>5.6</td>
<td>1.38</td>
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</table>
lowering of the motion of both the permeating molecules and polymer chains constituting the PDMS membrane. On the other hand, the increase in separation factor is explained by the illustration shown in Figure 17.6.

The permeation and separation characteristics for an aqueous solution of 10 wt% ethanol through the poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membrane in TDEV, in which the temperature of the feed solution was kept constant at 40 °C and the temperature of the membrane surroundings was changed to a temperature less than the temperature of the feed solution are shown in Figure 17.13 [11]. The permeation rate was a maximum at 20 °C of the membrane surroundings and the ethanol concentration in the permeate increased with decreasing temperature of the membrane surroundings. The behaviour for the permeation rates can be explained by the increases in the solubility of the vapours into the membrane and by the mobility of the permeants in the membrane as the temperature of the membrane surroundings changes. The increase in the ethanol concentration of the permeate (i.e. the increase in the ethanol permselectivity) can be understood by both an aggregation of water...
molecules on the membrane surroundings kept at lower temperature and by the high affinity for the PTMSP membrane of ethanol molecules. As can be seen in Figure 17.12, TDEV using a PTMSP membrane is very effective for the concentration in the ethanol permselectivity from aqueous ethanol solutions.

In the discussion of Figures 17.11–17.13 the permeation and separation characteristics for aqueous alcoholic solutions through hydrophobic polymer membranes such as PDMS, modified silicone rubber and PTMSP in TDEV were introduced and the mechanism of the permeation and separation for those membranes was discussed. Now we go on to experiment with the dehydration of organic solvent using a hydrophilic polymer membrane using the TDEV method to elucidate whether the mechanism of the permeation and separation that we discussed was correct.

Figure 17.14 shows the characteristics of permeation and separation for an aqueous DMSO solution through a chitosan membrane by the TDEV method [6]. In Figure 17.14, the feed is an aqueous solution of 50 wt% DMSO, the temperature of the feed solution is kept constant at 40 °C and the temperature of membrane surroundings is changed to a temperature less than the temperature of the feed solution. Both the total permeation rate and separation factor increased with decreasing temperature of the membrane surroundings. The increase in the total permeation rate may be due to the increase of the solubility of vapour in the membrane with a drop of the temperature of the membrane surroundings according to Henry’s law.

The increase in the separation factor (i.e. an improvement of the permselectivity for water) is explained by the illustration shown in Figure 17.15. When the DMSO and water molecules which had vaporized from the feed mixture come close to the membrane surroundings, the DMSO vapour aggregates much easier than the water vapour (because the freezing points of DMSO and water are 18.4 °C and 0 °C respectively) and tends to liquefy as the temperature of the membrane surroundings becomes lower. This aggregation of the DMSO molecules is responsible for the increase of permselectivity for water through the chitosan membrane. The increase in the separation factor with the TDEV method, in which the temperature of the membrane surroundings is lower than the temperature of the feed solution, is attributed to the influence of the degree of aggregation of the DMSO molecule on the membrane surroundings, which is significantly governed by the temperature of the membrane surroundings. The high water permselectivity of the chitosan membrane for aqueous DMSO solutions in TDEV is significantly enhanced by both a high affinity for water of the chitosan membrane and the decrease of the solubility selectivity for DMSO molecules into the chitosan membrane based on their aggregation on the membrane surroundings [12].
The permeation rates for water and DMSO for an aqueous solution of 50 wt% DMSO through a chitosan membrane in TDEV are shown in Figure 17.16, in which the temperature of the membrane surroundings is changed. As can be seen from these results, the permeation rates for DMSO were remarkably low compared with those for water; that is, it is about one hundred thousandth. The difference between the permeation rates for water and DMSO became larger with decreasing temperature of the membrane surroundings. These results support the discussion of the mechanism for permeation and separation in TDEV described earlier.

Şanlı and co-workers investigated the permeation and separation characteristics of acetic acid–water mixtures through itaconic acid grafted poly(vinyl alcohol) (PVA) [13], PVA–malic acid (85/15 v/v) membranes [14] and PVA–poly(acrylic acid) (75/25 v/v) membranes [15] during TDEV.

The permeation and separation mechanism for aqueous alcoholic solutions through dense hydrophobic polymer membranes in TDEV can be supported by that for an aqueous organic solvent solution through a dense hydrophilic polymer membrane.

**Figure 17.15** Tentative mechanism of permeation and separation for aqueous DMSO solutions through a dense chitosan membrane in TDEV.

**Figure 17.16** Effect of temperature of the membrane surrounding on the permeation rates for water (●) and DMSO (○) for aqueous DMSO solution through a chitosan membrane in TDEV. Feed solution: aqueous solution of 50 wt% DMSO; temperature of feed solution: 40 °C.
Table 17.2 shows the effect of the freezing point of the permeate in aqueous organic liquid solutions on the permselectivity through some polymer membranes by TDEV. This table gives us a certain important suggestion. When some membranes are applied in the TDEV method, we can prospect for an optimum combination of the membrane and the feed mixture to get a high permeation rate and high permselectivity. As can be seen from this table, a permeant having a lower freezing point (bold component) in the feed mixture is selectively permeated. In addition, the membrane has a stronger affinity to the permeant which is selectively permeated. Therefore, a much higher selectivity can be achieved in TDEV. Consequently, if we can select a suitable combination in the relationship between the chemical properties of the membrane and the physicochemical properties of the permeants, we can fabricate excellent membranes with both high permeation rate and high permselectivity [8].

Since it is well known that glassy, nanoporous PTMSP membranes have lower density, and hence a higher free volume than other polymer membranes [16], the characteristics of permeation and separation for an aqueous solution of 10 wt% ethanol through a PTMSP membrane, which is organic solvent selective, were operated in TDEV and pervaporation mode [12]. Our experimental results are shown in Table 17.3. The permeation and separation characteristics in TDEV and pervaporation at 40 °C are very similar. However, in TDEV with decreasing temperature of the membrane

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeant</th>
<th>Freezing point</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>C₂H₅OH–H₂O</td>
<td>C₂H₅OH &lt; H₂O (-114 °C)(0 °C)</td>
</tr>
<tr>
<td>PTMSP</td>
<td>C₂H₅OH–H₂O</td>
<td>C₂H₅OH &lt; H₂O (-114 °C)(0 °C)</td>
</tr>
<tr>
<td>PVC</td>
<td>CH₃COOH–H₂O</td>
<td>CH₃COOH &gt; H₂O (16.7 °C)(0 °C)</td>
</tr>
<tr>
<td>Chitosan</td>
<td>(CH₃)₂SO–H₂O</td>
<td>(CH₃)₂SO &gt; H₂O (18.5 °C)(0 °C)</td>
</tr>
</tbody>
</table>

Table 17.3 Permeation and separation characteristics for an aqueous solution of 10 wt% ethanol through a PTMSP membrane in TDEV.

<table>
<thead>
<tr>
<th>Temperature of membrane surroundings (°C)</th>
<th>TDEV</th>
<th>PV² (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol in permeate (wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Separation factor (\alpha_{\text{EtOH/H₂O}})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permeation rate (kg m⁻²h⁻¹)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Pervaporation.

\(^b\) \(\alpha_{\text{EtOH/H₂O}} = [Y_{\text{EtOH}}/(1 - Y_{\text{EtOH}})]/[X_{\text{EtOH}}/(1 - X_{\text{EtOH}})]\), where \(X_{\text{EtOH}}\) is the weight fraction of ethanol in the feed and \(Y_{\text{EtOH}}\) is the weight fraction of ethanol in the permeate. Feed temperature: 40 °C.
The permeation rate and the ethanol/water selectivity of the PTMSP membrane in TDEV are considerably higher than those of a dense PDMS membrane in TDEV in Figure 17.14. These results suggest that if a porous polymer membrane is applied to TDEV for the concentration of aqueous ethanol solutions, high permeation and separation characteristics can be obtained. Thus, Uragami et al. [12] tried to apply various commercial porous membranes to the concentration of aqueous ethanol solutions in TDEV.

It is well known that reducing membrane thickness leads to an increase in the permeation rate in membrane technology. The relationship between the permeation and separation characteristics for an aqueous ethanol solution through PTMSP membranes in TDEV and the membrane thickness is investigated by Uragami et al. [12]. The permeation rate in the PTMSP membrane of thickness of 20 μm is about nine times compared with that of 100 μm without a change in the ethanol permeability [17].

Table 17.4 lists the permeation rate and the ethanol concentration in the permeate for an aqueous solution of 10 wt% ethanol in TDEV. a)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Average pore size b) (μm)</th>
<th>EtOH in permeate (wt%)</th>
<th>Permeation rate (kg m⁻² h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(tetrafluoroethylene)</td>
<td>0.45</td>
<td>39.7</td>
<td>36.59</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>43.6</td>
<td>29.73</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>44.6</td>
<td>31.21</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>51.3</td>
<td>20.17</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>54.3</td>
<td>13.80</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>0.125 × 0.05</td>
<td>55.9</td>
<td>8.27</td>
</tr>
<tr>
<td></td>
<td>0.07 × 0.03</td>
<td>57.1</td>
<td>8.31</td>
</tr>
<tr>
<td>Cellulose nitrate</td>
<td>0.01</td>
<td>51.2</td>
<td>28.24</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>0.015</td>
<td>59.6</td>
<td>0.27</td>
</tr>
<tr>
<td>Polypropylene c)</td>
<td>0.125 × 0.05</td>
<td>20.0</td>
<td>1.02</td>
</tr>
<tr>
<td>PDMS d)</td>
<td></td>
<td>86.0</td>
<td>0.023</td>
</tr>
</tbody>
</table>

a) Temperatures of the feed solution and the membrane surroundings are 40 °C and −20 °C respectively.
b) Value in catalogue.
c) In pervaporation (40 °C).
d) Dense membrane.

The permeation rate and the ethanol/water selectivity increased remarkably. The permeation rate and the ethanol/water selectivity of the PTMSP membrane in TDEV are considerably higher than those of a dense PDMS membrane in TDEV in Figure 17.14. These results suggest that if a porous polymer membrane is applied to TDEV for the concentration of aqueous ethanol solutions, high permeation and separation characteristics can be obtained. Thus, Uragami et al. [12] tried to apply various commercial porous membranes to the concentration of aqueous ethanol solutions in TDEV.

It is well known that reducing membrane thickness leads to an increase in the permeation rate in membrane technology. The relationship between the permeation and separation characteristics for an aqueous ethanol solution through PTMSP membranes in TDEV and the membrane thickness is investigated by Uragami et al. [12]. The permeation rate in the PTMSP membrane of thickness of 20 μm is about nine times compared with that of 100 μm without a change in the ethanol permeability [17].

Table 17.4 lists the permeation rate and the ethanol concentration in the permeate for an aqueous solution of 10 wt% ethanol through various commercial porous polymer membranes in TDEV. In this table, the properties of the dense PDMS in TDEV are also included. From the results in Table 17.4, it is found that an aqueous solution of 10 wt% ethanol could be concentrated to about 40–60 wt% by applying porous polymer membranes using TDEV and the permeation rates were about 10–1000 times those of a dense PDMS membrane.

Figure 17.17 shows the effect of the average pore size of porous poly(tetrafluoroethylene) membranes on the ethanol concentration in the permeate for an aqueous solution of 10 wt% in TDEV. It can be presumed that there is a correlation between the pore size and the ethanol/water selectivity, because a porous poly(tetrafluoroethylene) membrane with smaller pore size had higher ethanol–water selectivity.
The contact angle for water on the surface of porous polymer membranes and the ratio of adhesion work of porous polymer membranes are listed in Table 17.5. A membrane that is highly water repellent but has affinity for ethanol can give high ethanol/water selectivity. On the basis of these aforementioned results, it was found that the ethanol/water selectivity of porous polymer membranes was significantly influenced by both the pore size and the character of the pore wall. Specifically, a microporous polymer membrane which has the smallest possible critical surface tension relative to the surface tension of water ($\delta_{\text{H}_2\text{O}}$: 72.8 dyne cm$^{-1}$) and is a little larger than that of ethanol ($\delta_{\text{EtOH}}$: 22.6 dyne cm$^{-1}$), is optimum. Thus, the preparation of porous PDMS membranes was investigated.

### Table 17.5 Contact angle for water and ratio of adhesion work of porous polymer membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Contact angle for water (deg)</th>
<th>Ratio of adhesion work$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(tetrafluoroethylene)</td>
<td>112–116</td>
<td>0.92–0.97</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>98–105</td>
<td>0.77–0.83</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>80</td>
<td>0.70</td>
</tr>
</tbody>
</table>

$^a$ Contact angle for 10 wt% ethanol/contact angle for water.

The contact angle for water on the surface of porous polymer membranes and the ratio of adhesion work of porous polymer membranes are listed in Table 17.5. A membrane that is highly water repellent but has affinity for ethanol can give high ethanol/water selectivity. On the basis of these aforementioned results, it was found that the ethanol/water selectivity of porous polymer membranes was significantly influenced by both the pore size and the character of the pore wall. Specifically, a microporous polymer membrane which has the smallest possible critical surface tension relative to the surface tension of water ($\delta_{\text{H}_2\text{O}}$: 72.8 dyne cm$^{-1}$) and is a little larger than that of ethanol ($\delta_{\text{EtOH}}$: 22.6 dyne cm$^{-1}$), is optimum. Thus, the preparation of porous PDMS membranes was investigated.

### 17.3.2 Preparation of Porous Poly(dimethylsiloxane) Membranes

When an aqueous emulsion of organopolysiloxane, which can be cured by removing water at room temperature or by heating to form a water-repellent elastomer, was frozen, a half-cured elastomer could be formed. Because this frozen elastomer was dried by a conventional method, an elastomer-like sponge with a dense skin layer was produced. However, when the water in the frozen elastomer was removed without the freeze–drying method, porous materials having a continuous pore structure were obtained,
as shown in Figure 17.18. Porous PDMS membranes were prepared by using this technique. In this membrane preparation method, the pore size and porosity can be controlled by changing the freeze conditions of aqueous emulsions of organopolysiloxane [12, 18–20].

Figure 17.19 shows the effect of the temperature of the membrane surroundings on the permeation rate and the ethanol concentration in the permeate for an aqueous solution of 10 wt% ethanol through a dense PDMS membrane (a) and a porous PDMS membrane (b) in TDEV [21]. In Figure 17.19, the temperature of the feed solution was kept constant at 40 °C and the temperature of the membrane surroundings was changed; the pressure on the downstream side was kept at 665 Pa. In Figure 17.19b, with decreasing temperature of the membrane surroundings, the permeation rate decreased and the ethanol concentration in the permeate increased. This decrease in the permeation rate can be explained by the permeation conditions in Table 17.6, where \( \Delta T \) is the temperature difference between the temperature of the feed solution \( T_f \) and that of the feed vapour \( T_v \), and \( \Delta P \) is the pressure difference between the pressure on the feed side \( P_f \) and that on the permeate side \( P_p \). In Figure 17.20, the relationships between \( \Delta T \) and \( \Delta P \), and of \( \Delta P \) and \( \Delta T \) and the characteristics of permeation and separation are shown. It is suggested that an increase in \( \Delta T \) results in a decrease in \( \Delta P \) and a decrease in the permeation rate. Consequently, the decrease in the permeation rate with decreasing temperature of the membrane surroundings in Figure 17.19b significantly depend upon a decrease in \( \Delta P \).

On the other hand, the increase in the ethanol concentration in the permeate shown in Figure 17.19b (i.e. the increase in the ethanol/water selectivity through a porous PDMS membrane with decreasing temperature of the membrane surroundings) can be attributed to the tentative mechanism shown in Figure 17.21.

When water and ethanol molecules, vaporized from the feed solution, come close to the membrane surroundings kept at lower temperature in TDEV, the water vapour aggregates much easier than the ethanol vapour, because the freezing point of water molecules (0 °C) is much higher than that of ethanol molecules (−114.4 °C), and the aggregated water molecules tend to be liquefied as the temperature of the membrane surroundings becomes lower. On the other hand, because the PDMS membrane has a relatively high affinity to the ethanol molecules, they are sorbed inside the pores in a porous PDMS membrane and this sorbed layer of the ethanol molecules is formed in an initial
Figure 17.19 Comparison of the permeation and separation characteristics for an aqueous solution of 10 wt% ethanol of a dense PDMS membrane (a) and porous PDMS membrane (b) in TDEV, in which the temperature of the feed solution was kept constant at 40 °C and the temperature of the membrane surroundings was changed.

Table 17.6 Permeation and separation characteristic for an aqueous solution of 10 wt% ethanol through a porous PDMS membrane during TDEV and the permeation conditions in TDEV with changing the temperature of the membrane surroundings as the temperature of the feed solution was kept constant.

<table>
<thead>
<tr>
<th>Temperature of membrane surroundings (°C)</th>
<th>Ethanol in permeate (wt%)</th>
<th>Permeation rate (kg m⁻² h⁻¹)</th>
<th>(T_L)</th>
<th>(T_V)</th>
<th>(\Delta T)</th>
<th>(\Delta P)</th>
<th>(P_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20</td>
<td>71.8</td>
<td>0.14</td>
<td>33.0</td>
<td>17.2</td>
<td>15.8</td>
<td>4934</td>
<td>5599</td>
</tr>
<tr>
<td>0</td>
<td>71.1</td>
<td>7.8</td>
<td>33.8</td>
<td>22.0</td>
<td>11.8</td>
<td>5692</td>
<td>6357</td>
</tr>
<tr>
<td>20</td>
<td>62.1</td>
<td>16.1</td>
<td>35.2</td>
<td>30.2</td>
<td>5.0</td>
<td>6357</td>
<td>7022</td>
</tr>
<tr>
<td>40</td>
<td>49.8</td>
<td>20.1</td>
<td>40.0</td>
<td>38.0</td>
<td>2.0</td>
<td>6903</td>
<td>7568</td>
</tr>
</tbody>
</table>

\[ \Delta T = T_L - T_V, \Delta P = P_f - P_p, T_f; \] temperature of the feed solution; \(T_V\); temperature of the feed vapour; \(P_f\); pressure on the feed side; \(P_p\); pressure on the permeate side.
Figure 17.20 Relationships between (a) the temperature difference $\Delta T$ and the pressure difference $\Delta P$, (b) $\Delta P$ and the permeation and separation characteristic, and (c) $\Delta T$ and the permeation and separation characteristics in TDEV.

Figure 17.21 Tentative mechanism of the separation for aqueous ethanol solutions through porous PDMS membrane in TDEV.
stage of the permeation. The vaporized ethanol molecule may be able to permeate across the mem-
brane by surface diffusion on the sorbed layer of the ethanol molecules inside the pores.

Both the aggregation of the water molecules and the surface diffusion of the ethanol molecules in the
pores are responsible for the increase in the ethanol/water selectivity through a porous PDMS membrane
in TDEV. The increase of the ethanol/water selectivity in TDEV can be attributed to both the degree of
aggregation of the water molecules on the membrane surroundings and the thickness of the sorbed layer
of the ethanol molecules inside the pores, which are significantly governed by the temperature of the
membrane surroundings. When the temperature of the membrane surroundings becomes lower, the
degree of aggregation of the water molecules and the thickness of the sorbed layer of the ethanol mole-
cules are increased. Therefore, an increase in the ethanol/water selectivity for aqueous ethanol solutions
was observed with decreasing temperature of the membrane surroundings.

As shown in Figure 17.19, the tendency of the decrease in the permeation rate and increase in the
ethanol/water selectivity with lowering temperature of the membrane surroundings through these
two PDMS membranes was very similar. In spite of the fact that the ethanol/water selectivity in these
PDMS membranes was almost equal, however, the permeation rates through these PDMS membranes
were remarkably different; that is, the permeation rates in a porous PDMS membrane were higher by
three orders of magnitude than those of a dense PDMS membrane.

A remarkable difference in the permeation rate between dense and porous PDMS membranes can
be attributed to the fact that the permeation through a dense PDMS membrane is due to the solution-
diffusion model and that through a porous PDMS membrane is based on pore flow, as shown in
Figure 17.21.

On the basis of these results, it is suggested that an application of porous hydrophobic polymer
membranes to TDEV for the concentration of aqueous ethanol solutions is very advantageous. To
evaluate the high performance of membrane materials in the concentration of an aqueous solution
of dilute bio-ethanol under TDEV, asymmetric porous cellulose nitrate and cellulose acetate mem-
branes were prepared by a phase inversion method. In the concentration of dilute ethanol under
TDE, these membranes showed a high permeation rate and high ethanol/water selectivity, as shown
in Figure 17.22. In membranes with almost a similar pore size, the ethanol/water selectivity was con-
siderably higher for the cellulose nitrate membrane than the corresponding cellulose acetate mem-
brane. This result suggested that the affinity between the membrane material and the permeant is
an important factor in the separation selectivity [10].

In Figure 17.23, in which the feed temperature is kept constant at 40 °C and the temperature of
membrane surroundings is changed, a porous PTMSP membranes prepared by freeze–dry and press
treatment is used. As can be seen, with decreasing temperature of the membrane surroundings,
although there is a small decrease in the permeation rate observed, the ethanol concentration in
the permeate remarkably increases. It is also found that when a porous PTMSP membrane is applied
to the TDEV method for the concentration of aqueous ethanol solutions, higher ethanol/water selec-
tivity and a considerably high permeation rate are achieved [22].

Figure 17.24 shows the effect of the temperature of the membrane surroundings on the permeation
rate and the separation factor $\alpha_{H_2O/DMSO}$ for the water/DMSO selectivity in an aqueous solution
of 50 wt% DMSO through a porous chitosan membrane in TDEV. In Figure 17.24, the temperature
of the feed solution has been kept constant at 40 °C, the temperature of the membrane surroundings
is changed and the pressure on the downstream side is kept at $2 \times 10^4$ Pa. As can be seen from
Figure 17.24, with decreasing temperature of the membrane surroundings, the permeation rate
decreased and the separation factor for the water/DMSO selectivity increased. This decrease in the
permeation rate can be explained by the permeation conditions. When the temperature difference
between the temperature of the feed solution $T_L$ and that of the feed vapour $T_V$, and the pressure
Figure 17.22 Effect of the temperature of the membrane surroundings on the permeation rates and ethanol concentration in the permeate for an aqueous solution of 10 wt% ethanol passed through symmetric porous cellulose nitrate (a) and cellulose acetate (b) membranes during TDEV. The temperature of the feed was kept at 40 °C and that of the membrane surroundings was varied. The reduced pressure on the downstream side was 650 Pa. The average pore diameters of asymmetric cellulose nitrate and cellulose acetate membranes were 280 Å and 284 Å respectively.

Figure 17.23 Effect of the temperature of the membrane surroundings on the permeation rates and ethanol concentration in the permeate for an aqueous solution of 10 wt% ethanol passed through porous PTMSP membranes during TDEV. Feed: 10 wt% ethanol (40 °C); pressure: $5.0 \times 10^2$ Pa.
difference between the pressure on the feed side $P_f$ and that on the permeate side $P_p$ are defined as $\Delta T$ and $\Delta P$ respectively, it is suggested that an increase in $\Delta T$ results in a decrease in $\Delta P$ and a decrease in the permeation rate. Consequently, the decrease in the permeation rate with decreasing temperature of the membrane surroundings in Figure 17.24 significantly depends upon a decrease in $\Delta P$.

On the other hand, the increase in the separation factor for water/DMSO selectivity shown in Figure 17.24 through a porous chitosan membrane with decreasing temperature of the membrane surroundings can be attributed to the tentative mechanism shown in Figure 17.25.

When water and DMSO molecules, vaporized from the feed solution, come close to the membrane surroundings kept at lower temperature in TDEV, the DMSO vapour aggregates much easier than the water vapour, because the freezing point of DMSO molecules (18.5 °C) is much higher than that of water molecules (0 °C), and the aggregated DMSO molecules tend to be liquefied as the temperature of the membrane surroundings becomes lower. Both the aggregation of the DMSO molecules and the surface diffusion of the water molecules in the pores of hydrophilic chitosan membrane are responsible
for the increase in the water/DMSO selectivity through a porous chitosan membrane in TDEV. The results in the separation for aqueous DMSO solutions through a water-selective porous chitosan membrane in TDEV could support the mechanism in the concentration of ethanol for aqueous ethanol solutions through an ethanol-selective porous PTMSP membrane in TDEV mentioned before.

The permeation rate and the separation factor for an aqueous solution of 50 wt% of DMSO through a dense chitosan membrane in TDEV shown in Figure 17.14 were 0.02–0.18 kg m$^{-2}$ h$^{-1}$ and 105–250 respectively [6]. As can be seen in Figure 17.24, those in a porous chitosan membrane are 0.05–0.28 kg m$^{-2}$ h$^{-1}$ and 110–1000 respectively. The remarkable difference in the permeation rate and the separation factor for water/DMSO selectivity between dense and porous chitosan membranes can be attributed to the fact that the permeation through a dense chitosan membrane is due to the solution-diffusion model and that through a porous chitosan membrane is based on pore flow, as shown in Figure 17.25.

On the basis of these results, it is also suggested that an application of porous hydrophilic polymer membranes to TDEV for the dehydration of aqueous DMSO solutions is very advantageous.

The membrane performance and the experimental conditions for an aqueous solution of 10 wt% ethanol through a porous PDMS membrane during TDEV in continuous long-term experiments using an automatically controlled TDEV system as shown in Figure 17.26 are shown in Figure 17.27, in which temperatures of the feed solution and membrane surroundings are 40 °C and 20 °C respectively. As can be seen in this figure, $T_L$, $T_V$ and $P_L$ do not change with time and a stable operation is observed. This result is advantageous for a long-term continuous operation. More importantly, both the permeation rate and the ethanol/water selectivity also are very stable.

Figure 17.26 Membrane performance and experimental condition for an aqueous solution of 10 wt% ethanol through a porous PDMS membrane during TDEV in continuous long-term experiments.
The concentration of an aqueous solution of dilute ethanol was tested by the TDEV bench plant connected in series with porous hydrophobic hollow-fibre membrane with the area of 20 m$^2$ shown in Figure 17.28.

From the earlier discussion, we can easily understand that a higher membrane performance can be given by combining the porous membranes and the TDEV method. Then, to get a much higher membrane performance we have to propose a method to give the most suitable membrane structure for TDEV. In this stage, the following method for the preparation of porous membranes is strongly recommended: use of the electrospinning method which fabricates nanofibres is one technique that

Figure 17.27 Automatically controlled TDEV system.

Figure 17.28 TDEV bench plant connected in series with porous hydrophobic hollow-fibre membrane.
can precisely control the pore size, pore size distribution, porosity, pore tortuosity and thickness of the membrane, as can be predicted readily from the scanning electron microscopy photographs in Figure 17.29b and f. As for this big expectation, it may greatly contribute to the preparation of the most suitable membranes in reverse osmosis, nanofiltration, ultrafiltration, microfiltration, forward osmosis, pervaporation, evapomeation, TDEV technology, and so on.

Applications to evapomeation and the TDEV method of inorganic membranes are not yet reported. The characteristics of inorganic membranes are that they are not swollen by the feed solution and can be used easily to prepare porous hydrophilic and hydrophobic membranes. It is hard to get rid of these characteristics. In particular, it is greatly expected that porous inorganic membranes will be applied to the separation and concentration of some liquid mixtures in TDEV.

We expect active suggestions for methods to improve membrane performance in TDEV other than for application of the TDEV method in porous membranes. To contribute to the improvement of human life is important, and many suggestions for new membrane technology from such a point of view are expected.

References


Membrane Distillation

Although membrane distillation (MD) is one of the membrane contactors shown in Chapter 22, it is the most important system of liquid–liquid membrane contactors. Therefore, MD is especially taken up in this chapter.

MD is a thermally driven separational programme in which separation is enabled due to phase change [1,2]. A hydrophobic membrane displays a barrier for the liquid phase, allowing the vapour phase (e.g. water vapour) to pass through the membrane’s pores (http://en.wikipedia.org/wiki/Membrane_distillation). The driving force for the MD processes is quite different from other membrane processes, being the vapor pressure difference across the membrane rather than an applied absolute pressure difference, a concentration gradient or an electrical potential gradient, which drives mass transfer through a membrane [1,3].

18.1 Principle of Membrane Distillation

The fundamental configurations in the MD system are of four types: direct contact MD (DCMD) (Figure 18.1a-1); vacuum MD (VMD) (Figure 18.1b); air-gap MD (AGMD) (Figure 18.1c); and sweep gas MD (SGMD) (Figure 18.1d-1) [4,5]. They differ based on the nature of the cold-side processing of the permeate [6,7].

18.1.1 Direct Contact Membrane Distillation

DCMD is when the membrane is in direct contact with liquid phases. An aqueous solution colder than the feed solution is maintained in direct contact with the permeate side of the membrane. This is the simplest configuration capable of producing reasonably high flux. It is best suited for applications such as desalination and concentration of aqueous solutions (e.g. juice concentrates) [1,8–12].

Liquid gap direct contact MD (LGDCMD) (Figure 18.1a-2), is one of the more recently distinguished process configurations providing ultrapure water at a lower yield compared with AGMD.

18.1.2 Vacuum Membrane Distillation

In VMD, vacuum is applied to the permeate side of the membrane module by means of a vacuum pump. The applied vacuum pressure is lower than the saturation pressure of volatile molecules to be separated from the feed solution. In this case, condensation takes place outside of the membrane module. This configuration is useful when volatiles are being removed from an aqueous solution [13,14].
18.1.3 Air Gap Membrane Distillation

In AGMD, an air gap is interposed between the membrane and a condensation surface. In this configuration the evaporated volatile molecules cross both the membrane pores and the air gap to finally condense over a cold surface inside the membrane module. The air gap configuration can be widely employed for most MD applications [15], particularly where energy availability is low.

Figure 18.1 Types of MD system: (a-1) DCMD; (a-2) LGDCMD; (b) VMD; (c) AGMD; (d-1) SGMD; (d-2) thermostatic SGMD.
18.1.4 Sweep Gas Membrane Distillation

In SGMD, a cold inert gas sweeps the permeate side of the membrane carrying the vapour molecules and condensation takes place outside the membrane module. This configuration type is used when volatiles are removed from an aqueous solution [16–20]. AGMD and SGMD can be combined in a process called thermostatic SGMD (Figure 18.1d-2) [21]. The inert gas in this case is passed through the gap between the membrane and the condensation surface. Part of the vapour is condensed over the condensation surface (AGMD) and the remainder is condensed outside the membrane cell by external condenser (SGMD) [7,16].

18.2 Fundamental Analysis of Membrane Distillation

18.2.1 Mass Transfer in Membrane Distillation

See Alkhudhiri et al. [21] for a comprehensive review. A schema of DCMD and AGMD is shown in Figure 18.2.

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**Figure 18.2** Schema of (a) DCMD and (b) AGMD.
18.2.1.1 Direct Contact Membrane Distillation

The mass flux $J$ in this case is assumed to be proportional to the vapour pressure difference across the membrane, and is given by

$$J = C_m (P_f - P_p)$$  \hspace{1cm} (18.1)

where $C_m$ is the membrane coefficient, and $P_f$ and $P_p$ are the vapour pressure at the membrane feed and permeate surfaces, which can found from the Antoine equation [22–25]. Therefore, Equation 18.1 can be rewritten in terms of temperature difference across the membrane surfaces when the separation process is for pure water or very diluted solution, and the temperature difference across the membrane surfaces is less than or equal to $10 \, ^\circ C$ [1,26–28]. Hence:

$$J = C_m \frac{dP}{dT} (T_f,m - T_p,m)$$  \hspace{1cm} (18.2)

The vapour pressure and temperature relationship can be expressed by the Clausius–Clapeyron equation as follows:

$$\frac{dP}{dT} = \frac{\Delta H_v}{RT^2} P_0(R)$$  \hspace{1cm} (18.3)

For a low concentration solution, the Antoine equation can be utilized to determine the vapour pressure, because it can be assumed that the vapour pressure is a function of temperature only (i.e. decreasing vapour pressure dependence on solution concentration). Martinez and Rodriguez-Maroto [29] and Godino et al. [30] estimated the effect of both concentration and temperature on the vapour pressures by considering the water activity at the feed and permeate sides, such that

$$P(T,x) = P_0(T) a_w(T,x)$$  \hspace{1cm} (18.4)

where $a_w(T,x)$ is water activity as a function of temperature and concentration, and $P_0(T)$ is the vapour pressure of pure water at a given temperature. Raoult’s law has also been used to estimate the vapour pressure [8,31], where

$$P(T,x) = P_0(T) a_w(1-x)$$  \hspace{1cm} (18.5)

Mass transfer through the membrane can be divided into three models. These models relate the mass transport with collisions between molecules and/or molecules with membrane. Ding et al. [32] proposed that Knudsen diffusion takes place when the pore size is too small, such that the collision between the molecules and the inside walls of the membrane suitably expresses the mass transport and the collision between molecules can be ignored. Molecular diffusion occurs when the molecules move corresponding to each other under the influence of concentration gradients. In Poiseuille flow (viscous flow), the gas molecules act as a continuous fluid driven by a pressure gradient. The Knudsen number $Kn$, defined as the ratio of the $\lambda$ of transported molecules to the membrane pore size, provides a guideline for which mechanism is active inside the membrane pore. According to the kinetic theory of gases, the molecules are assumed to be hard spheres with diameter $d_e$ and are involved in binary collisions only. It is worth noting that the collision diameters for water vapour and air are about $2.64 \times 10^{-10}$ and $3.66 \times 10^{-10}$ respectively [33]. The average distance travelled by molecules to make collisions $\lambda$ is defined as

$$\lambda = \frac{k_B T}{\sqrt{2nPd_e^2}}$$  \hspace{1cm} (18.6)
where \( k_B, T \) and \( P \) are the Boltzmann constant, absolute temperature and average pressure within the membrane pores respectively. The mean free path value of water vapour at 60 °C was estimated by Al-Obaidani et al. [34] to be 0.11.

For \( Kn > 1 \) or \( d_p < \lambda \) (Knudsen region), the mean free path of water vapour molecules is large compared with the membrane pore size, which means the molecule–pore wall collisions are dominant over molecule–molecule collisions. The mass transfer is reported by Khayet et al. [28], such that

\[
C_{Kn} = \frac{2\pi}{3} \frac{1}{RT} \left( \frac{8RT}{\pi M_w} \right)^{1/2} \frac{r^3}{\tau \delta}
\]

where \( \varepsilon, \tau, r, \delta \) and \( M_w \) are porosity, pore tortuosity, pore radius, membrane thickness and molecular weight of water vapour respectively.

If \( Kn < 0.01 \) or \( d_p > 100\lambda \) (continuum region), the ordinary molecular diffusion model represents the diffusion of the vapour flux through a stationary air film (the air that exists inside the membrane pores), and ordinary molecular diffusion is used to describe the mass transport:

\[
C_D = \frac{\pi}{RT} P_{air} \frac{D r^2}{P \tau \delta}
\]

where \( P_{air} \) is the air pressure within the membrane pore, \( D \) is diffusion coefficient and \( P \) is the total pressure inside the pore, which is equal to the partial pressure of air and water vapour.

In addition, Schofield et al. [35] presented the flux of water vapour molecules, which diffuse through the membrane pores (stagnant air), as

\[
J = \frac{1}{P_{air} \tau \delta} \frac{\varepsilon D P M_w}{RT} \Delta P
\]

where \( P_{air} \) and \( P \) are the average air pressure and average gas pressure within the membrane respectively.

Removing the stagnant air existing inside the pores by degassing the feed and permeate will reduce the molecular diffusion resistance, so the membrane permeability will increase [1].

However, if \( 0.01 < Kn < 1 \) or \( \lambda < d_p < 100\lambda \) (transition region), the water vapour molecules collide with each other, and also diffuse through the air film. Consequently, the mass transfer takes place by both the Knudsen and ordinary diffusion mechanism [28], where

\[
C_C = \frac{\pi}{RT} \frac{r^2}{\tau \delta} \left\{ \left[ \frac{2}{3} \left( \frac{8RT}{\pi M_w} \right)^{1/2} r^3 \right]^{-1} + \left( \frac{PD}{P_a r^2} \right)^{-1} \right\}^{-1}
\]

The diffusivity of water vapour through the stagnant air inside the pores is given by [36]

\[
PD = 1.895 \times 10^{-5} r^{2.072}
\]

In addition, the Fuller equation, which is a common equation to predict binary gas diffusion, can be used [37,38]:

\[
D = 1 \times 10^{-7} PD = 1.895 \times 10^{-5} r^{2.072} \frac{r^{1.75} \left( \frac{1}{M_{w_a}} + \frac{1}{M_{w_b}} \right)^{1/2}}{P \left[ \left( \sum v_a \right)^{1/3} + \left( \sum v_b \right)^{1/3} \right]^2}
\]
where $\sum v$ represents the diffusion volume, $T$ (K) is temperature and $P$ (atm) is pressure. The diffusion volumes of air and water are 20.1 and 12.7 respectively.

18.2.1.2 Vacuum Membrane Distillation

In order to remove air trapped in the membrane pores, the deaeration of the feed solution or a continuous vacuum in the permeate side should be applied. Consequently, the ordinary molecular diffusion resistance is neglected. The Knudsen mechanism is used to express the mass transfer [13,39–41], Poiseuille flow [42] or both together [22,42,43].

For example, when the ratio of the pore radius to the mean free path $r/\lambda < 0.05$, the molecule–pore wall collisions control the gas transport mechanism (Knudsen flow model) and the molar flow rate is

$$N_i = \frac{2\pi}{3} \frac{1}{RT} \left( \frac{8RT}{\pi M_w} \right)^{1/2} \frac{r^3}{\pi \delta} \Delta P_i$$

(18.13)

If $r/\lambda$ is between 0.05$\lambda$ and 50$\lambda$, both molecular–molecular and molecular–wall collisions should be considered. The total mass transfer is described by the Knudsen–viscous model and can be represented by

$$N_i = \frac{\pi r^4 P_{avg} 1}{8 \mu_i RT \pi \delta} \Delta P_i$$

(18.14)

where $\mu_i$ is the viscosity of species $i$ and $P_{avg}$ is the average pressure in the pore.

When $r/\lambda > 50$, molecular–molecular collision dominates and the mass transfer can be expressed by Poiseuille flow (viscous), such that

$$N_i = \frac{\pi r^4 P_{avg} 1}{8 \mu_i RT \pi \delta} \Delta P_i$$

(18.15)

18.2.1.3 Air Gap Membrane Distillation

Molecular diffusion theory is used to describe the transfer of vapour molecules through the membrane and the air gap. A stagnant gas film (air) is assumed to lie inside the membrane at the air gap side.

Kurokawa and Ebara [23] computed the flux by considering the diffusion in one direction through both membrane and air gap, where the air gap is below 5 mm:

$$J = \frac{PM_w}{RTP^*} \left[ \frac{D}{(\delta/e^{\delta}) + 1} \right] \Delta P$$

(18.16)

where $\Delta P$ is the water vapour pressure difference between the feed on the membrane and the condensation surface, and $P^*$ is the partial pressure of water.

Liu et al. [44] estimated the permeate flux for an aqueous solution when the average operating temperature $T_a$ was between 30 and 80 °C thus:

$$J = \frac{T_f - T_p}{\alpha T_a^{-2.1} + \beta}$$

(18.17)

where $\alpha$ and $\beta$ are parameters that can be determined experimentally.

Stefan diffusion was used to describe the diffusion through a stagnant gas film. It can be represented mathematically as [45]
where $D$, $y$, $c$ and $z$ are the diffusion coefficient, mole fraction of the vapour phase, molar concentration and diffusion length respectively. The Stefan equation was solved by Kimura et al. [46]:

$$N = \frac{CD}{1 - ydz}$$

(18.18)

where $y_m$ and $y_f$ represent the mole fraction of vapour at the membrane and the condensation film respectively.

18.2.1.4 Sweep Gas Membrane Distillation

Khayet [4] points out that the equations that illustrate the mass transfer of DCMD can be used in SGMD. A theoretical model was designed to predict the SGMD flux and temperature profiles in the system for two polytetrafluoroethylene (PTFE) membranes. Knudsen/molecular diffusion can be used to describe the mass transfer through the membrane pores. Moreover, the circulation velocity and feed temperature are significant parameters [18,19].

Sherwood correlation can be used to estimate the mass transfer coefficient $k$ across the boundary layers; the concentration at the boundary layer can then be evaluated. The empirical form of the Sherwood correlation is

$$Sh = \frac{kd}{D} = (\text{Constant})Re^aSc^b$$

(18.20)

where $Re$, $Sc$ and $D$ are the Reynolds number, Schmidt number and diffusion coefficient respectively. Schmidt numbers can be calculated by

$$Sc = \frac{\mu}{\rho D}$$

(18.21)

where $\mu$ is the viscosity. For a non-circular channel, these correlations can be utilized if the equivalent (hydraulic) diameter $d_{eq}$ is employed:

$$d_{eq} = 4r_H = \frac{4S}{L_p}$$

(18.22)

where $r_H$, $S$ and $L_p$ are the hydraulic radius, cross-sectional area of the flow channel and length of wetted perimeter of the flow channel respectively.

18.3 Membranes of Membrane Distillation

18.3.1 Membrane Materials

A large variety of membranes, including both polymeric and inorganic membranes of hydrophobic nature, can be used in the MD process; however, polymeric membranes have attracted much more attention owing to their possibility to modulate the intrinsic properties. PTFE, polypropylene and polyvinylidenefluoride (PVDF) are the most commonly used polymeric membranes owing to their low surface tension values [47]. Hydrophobic porous membranes can be prepared by different techniques, like sintering, stretching, electrospinning, phase inversion or thermally
induced phase separation, depending on the properties of the materials to be used. The useful materials should be selected according to criteria that include compatibility with the liquids involved, cost, ease of fabrication and assembly, useful operating temperatures and thermal conductivity [4,48]. Among them, PTFE membranes are the most hydrophobic ones, showing outstanding thermal stability and chemical resistance properties (they are not dissolved in all common solvents). The main disadvantage of PTFE membranes is the difficulty of processing. PTFE membranes are generally prepared by sintering or stretching. Polypropylene exhibits excellent solvent-resistant properties and high crystallinity. Polypropylene membranes are generally manufactured by stretching and thermal phase inversion. PVDF membranes exhibit good thermal and chemical resistance; however, this polymer easily dissolves at room temperature in a variety of solvents, including dimethylformamide and triethylphosphate. PVDF membranes are generally prepared by phase inversion [49].

18.3.2 Membranes of Membrane Distillation

18.3.2.1 Membrane Structure

There are some additional criteria that should be taken into consideration in the physical and chemical properties of membrane for selection of the appropriate membrane for a given MD application, such as (1) membrane pore size, (2) pore size distribution, (3) membrane porosity, (4) pore tortuosity, (5) membrane thickness and (6) thermal conductivity.

The relationship between the transmembrane flux and the different membrane-characteristic-related parameters is given by [50]:

1) **Membrane pore size** Membranes with pore sizes ranging from 10 nm to 1 μm can be used in MD [51]. The permeate flux increases with the increase in pore size as determined by the Knudsen model. However, in order to avoid wettability, small pore size should be chosen [7,52]. Thus, an optimum value for pore size has to be determined for each MD application depending on the type of feed solution.

2) **Pore size distribution** Pore size distribution affects uniformity of vapour permeation mechanism. In general, uniform pore size is preferable rather than distributed pore size [53].

3) **Membrane porosity** Membrane porosity is determined as the ratio between the volume of the pores and the total volume of the membrane. Evaporation surface area increases with the increase in porosity level of the membrane, resulting in higher permeate fluxes [54]. Membrane porosity also affects the amount of heat loss by conduction [55]. Conductive heat loss can be reduced by increasing porosity of the membrane, since the heat transfer coefficient of the gas/vapour $h_{mg}$ is generally an order of magnitude smaller than the heat transfer coefficient of the solid membrane $h_{ms}$. In general, the porosity of the membranes used in MD operations is in the range of 65–85%.

4) **Pore tortuosity** Tortuosity is the average length of the pores compared with membrane thickness. The membrane pores do not go straight across the membrane and the diffusing molecules must move along tortuous paths, leading to a decrease in MD flux. Therefore, permeate flux increases with the decrease in tortuosity. It must be pointed out that this value is frequently used as a correction factor for prediction of transmembrane flux due to the difficulties in measuring its real value for the membranes used in MD. In general, a value of 2 is frequently assumed for tortuosity factor [36,52,56].

5) **Membrane thickness** Permeate flux is inversely proportional to the membrane thickness in MD. Therefore, membrane must be as thin as possible to achieve high permeate flux. Thickness also plays an important role in the amount of conductive heat loss though the membrane. In order
to reduce heat resistances, it should be as thick as possible, leading to a conflict with the requirement of higher permeate flux. Hence, membrane thickness should be optimized in order to obtain optimum permeate flux and heat efficiency. The optimum thickness for MD has been estimated within the range of 30–60 μm [57].

6) **Thermal conductivity** Thermal conductivity of the membrane should be small in order to reduce the heat loss through the membrane from feed to the permeate side. Conductive heat loss is inversely proportional to the membrane thickness. However, selection of a thicker membrane decreases both the flux and permeability. One promising approach may be selection of a membrane with higher porosity, since the thermal conductivity of polymer membrane is significantly higher than the thermal conductivity of water vapour in the membrane pores [58]. The thermal conductivities of polymers used in MD generally vary in the range 0.15–0.45 W m\(^{-1}\) K\(^{-1}\) depending upon temperature and the degree of crystallinity [6].

The desired characteristics needed for a membrane to be used in DCMD are outlined. A new approach for the design of novel membranes for desalination by DCMD was proposed by Khayet et al. [58]. Porous hydrophobic–hydrophilic composite membranes have been prepared in one casting step, using the traditional phase inversion method of polymer solutions containing a hydrophilic host polymer and a fluorinated surface-modifying macromolecule. The membranes comply with the conditions and properties required in the DCMD process. Membranes of different mean pore sizes, pore size distributions, porosities, roughnesses, liquid entry pressures of water and thicknesses can be formed by varying the membrane preparation conditions. The structural characteristics and the DCMD performance of the first proposed porous composite membranes were compared with those of the commercial membranes most frequently used in this kind of process. The proposed membranes have potential to be used in DCMD for desalination because, compared with the commercial ones, these membranes possess a thinner hydrophobic porous top layer responsible for the water vapour transport in DCMD and a thicker hydrophilic porous sub-layer filled with water to lower the conductive heat loss. The thickness of the hydrophobic layer was found to be an order of magnitude lower than that of the commercial membranes.

Novel fluorosilanes grafted ceramic membranes were prepared and characterized in the AGMD process by Krajewski et al. The hydrophobic active layer was created by grafting 1H,1H,2H,2H-perfluorodecyltriethoxysilane (C\(_8\) compound) on a commercial ceramic membrane (zirconia layer on a microporous alumina support). Two kinds of commercial membranes were used with average pore diameter of the zirconia layer equal to 50 or 200 nm. Four hydrophobic membranes were prepared using different grafting conditions. The efficiency of the grafting process was characterized by thermogravimetric analysis, contact angle and liquid water entry pressure measurements. These new kinds of hydrophobic ceramic membranes were applied in the MD process. The influence of NaCl concentration and feed–permeate temperature difference on the efficiency of the MD process were determined. The rejection of NaCl was found to be close to 100%, indicating good hydrophobic behaviour of the FAS grafted ceramic membranes. The permeate fluxes were dependent on the NaCl concentration, pore diameter of the zirconia layer and the temperature difference between the feed and permeate sides of the membrane. The average flux of about 6.67 L m\(^{-2}\) h\(^{-1}\) was found for M1 and M2 membranes in contact with pure water and at feed and permeate temperatures equal 95 °C and 5 °C respectively. The flux of about 5.42 L m\(^{-2}\) h\(^{-1}\) was found for M3 membrane in contact with 1 M NaCl solution and feed and permeate temperatures equal to 99 °C and 5 °C respectively. This was the first broader study of the use of modified ceramic membranes in the MD process [59].
18.3.2.2 Electrospun Membranes in Membrane Distillation

Nanofibrous membranes of Matrimid were successfully fabricated using an electrospinning technique under optimized conditions [60]. Nanofibrous membranes are found to be highly hydrophobic with a high water contact angle of 130°. Field-emission scanning electron microscopy and pore size distribution analysis revealed the big pore size structure of electrospun membranes to be greater than 2 μm and the pore size distribution to be narrow. Flat-sheet Matrimid membranes were fabricated via casting followed by phase inversion. The morphology, pore size distribution and water contact angle were measured and compared with the electrospun membranes. Both membranes fabricated by electrospinning and phase inversion techniques were tested in a DCMD process. Electrospun membranes showed high water vapour flux of 56 kg m\(^{-2}\) h\(^{-1}\), which is very high compared with the cast membrane as well as most of the fabricated and commercially available highly hydrophobic membranes.

Rapid population growth has resulted in an imbalance in the supply and demand of fresh water for human consumption. As the sources of fresh water from surface water and fresh groundwater have been consistently depleting at an alarming rate, alternative sources such as seawater and brackish water are sought out. Desalination of water is considered as one of the most sustainable and best water resource alternatives. MD is an emerging and promising technology for water desalination and purification. It presents many advantages over common desalination technologies such as reverse osmosis. The two major factors hindering the application of MD are suitable membrane design and structure, and energy efficiency of the MD process. In recent years, membrane design has seen increasing research and interest. Advances in science and technology have led to new materials and techniques that could find potential application for membranes in MD. In the past few years, electrospinning of nanofibres has gained much interest and attention in their application for MD membrane, and so far with promising results. The review of Tijing et al. focuses on the recent progress in the application of nanofibrous membrane fabricated by electrospinning for MD application [61].

A bicomponent nanofibrous composite membrane was fabricated by electrospinning and was tested for desalination by DCMD by Tijing et al. [62]. The nanofibrous membrane was composed of a dual-layered structure of poly(vinylidene fluoride-co-hexafluoropropylene) (PH) nanofibres and polyacrylonitrile (PAN) microfibres. Morphological characterization showed slightly beaded cylindrical PH nanofibres with porosity of about 90%. The contact angles of PH and PAN nano- and microfibers were 150° and 100° respectively. The nanofibrous membranes were tested by DCMD and high water fluxes of 45 L m\(^{-2}\) h\(^{-1}\) and 30 L m\(^{-2}\) h\(^{-1}\) were obtained for distilled water and 35 g L\(^{-1}\) NaCl solutions as feed respectively using DL2 membrane (i.e. 25/75 PH/PAN thickness ratio). The present dual-layer membrane showed better flux performance compared with a commercial flat-sheet membrane. The results suggest the potential of the dual-layer nanofibrous membrane for DCMD applications.

Fibrous structures with nanoscale diameters offer a multitude of fascinating features, such as excellent mechanical behaviour and large surface area to volume ratio, making them attractive for many applications. Their large surface area also gives them high functionalization ability. Among the many techniques available for generating nanofibres, electrospinning is rapidly emerging as a simple process in which careful control of operating conditions and polymer solution properties enables the production of highly porous structures of smooth non-woven nanofibres. Compared with traditional phase inversion techniques for membrane fabrication, electrospinning allows the formation of interconnected pores with uniform pore size and porosities exceeding 90%. As a result, electrospun membranes are increasingly being applied to many water purification applications, such as MD and pretreatment of feed prior to reverse osmosis or nanofiltration processes by the removal of divalent metal ions, grease and other contaminants. Although the use of electrospinning for membrane fabrication had previously been reviewed, the rapid increase in developments over recent years necessitated the need for the review by Ahmed et al. on the preparation and application of electrospun
nanofibre membranes as the barrier layer for water treatment, with emphasis on the reinforcement and post-treatment of electrospun polymer membranes [63].

### 18.3.3 Membrane Modules

There are two major MD module configurations [2,64], which are the plate-and-frame module and the tubular module. Both of these modules have been used in pilot plant trials [65,66].

#### 18.3.3.1 Plate-and-Frame Module

This module is suitable for flat-sheet membranes and can be used for DCMD, AGMD, VMD and SGMD. In this configuration, the packing density is about 100–400 m$^2$ m$^{-3}$ [49,67]. Although this configuration has a relatively smaller effective area for the same volume when compared with the tubular modules, it is easy to construct and multiple layers of flat-sheet MD membranes can be used to increase the effective area. In this module it is easy to change damaged membranes from this configuration. Thus, this module is widely employed in laboratory experiments for testing the influence of membrane properties and process parameters on the flux or energy efficiency of MD [49]. Also, the flow dynamics can be improved by the use of spacers that increase turbulence and reduce temperature polarization.

#### 18.3.3.2 Tubular and Hollow-Fibre Module

This module can have a very high packing density (3000 m$^2$ m$^{-3}$) [65,68]. The feed is introduced into the shell side or into lumen side of the hollow fibres, and cooling fluid, sweeping gas or negative pressure can be applied on the other side to form VMD, SGMD or DCMD. Because of its large active area combined with a small footprint, hollow-fibre modules have great potential in commercial applications [65]. Although broken hollow fibres cannot be replaced, they can be detected by the liquid decay test [69–71] and pinned to remove broken fibres from service. Good flow distribution on the shell side can be difficult to achieve, with subsequent high degrees of temperature polarization. Crossflow modules have been developed to reduce this effect for hollow-fibre modules [72].

### 18.3.4 Solar-Powered Membrane Distillation


MD is very suitable for compact, solar-powered desalination units providing small- and medium-range output <10 000 L day$^{-1}$. In particular, the spiral-wound design patented by GORE in 1985 suits this application. Within the MEMDIS project, which kicked off in 2003, the Fraunhofer Institute for Solar Energy Systems ISE began developing MD modules as well as installing and analysing two different solar-powered operating systems, together with other project partners. The first system type is a so-called compact system, designed to produce a drinking water output of 100–120 L day$^{-1}$ from seawater or brackish water. The main aim of the system design is a simple, self-sufficient, low-maintenance and robust plant for target markets in arid and semi-arid areas of low infrastructure. The second system type is a so-called two-loop plant with a capacity of around 2000 L day$^{-1}$. Here, the collector circuit is separated from the desalination circuit by a saltwater-resistant heat exchanger. Based on these two system types, a various number of prototypes were developed, installed and observed.

The standard configuration of compact systems (as of 2011) is able to produce a distillate output of up to 150 L day$^{-1}$. The required thermal energy is supplied by a 6.5 m$^2$ solar thermal collector field. Electrical energy is supplied by a 75 W photovoltaic module. This system type is currently being developed further and marketed by the Solar Spring GmbH, a spin-off of the Fraunhofer Institute for Solar
Energy Systems. Within the MEDIRAS project – a further EU-project – an enhanced two-loop system was installed on the island of Gran Canaria. Built inside a 20 ft container and equipped with a collector array size of 225 m², a heat storage tank makes a distillate output of up to 3000 L day⁻¹ possible. Further applications with up to 5000 L day⁻¹ have also been implemented, either 100% solar powered or as hybrid projects in combination with waste heat.

In order to remit the membrane wetting in MD, PTFE flat membrane with low surface free energy and high water contact angle was prepared by a simple heat setting process by Wang et al. [73]. Membrane morphology evolution, such as breakage of fibrils and fusion of PTFE resin, and its influence on membrane characters, including pore size, porosity and roughness, were discussed. The effect of the heat setting process on the membrane wetting was evaluated by the membrane wetting time in a static absorption experiment and SGMD. The results showed that the crystallinity decreases with increasing heat setting temperature and time, which leads to low surface free energy and therefore low adsorbing capacity of penetrating agent and the long wetting time in the static absorption experiment and SGMD. In addition, pore size increases first and then decreases due to the breakage of fibrils and fusion of PTFE resin respectively, which further affects the permeate flux. Therefore, Wang et al. proposed that the antifouling property and separation performance of PTFE flat membrane in SGMD can be well handled and hoped that such a PTFE flat membrane would be potentially useful in seawater desalination.

18.4 Technologies of Membrane Distillation

18.4.1 Comparison of Various Membrane Distillations

DCMD and AGMD processes were modelled by Alklaibi and Lior as a two-dimensional conjugate problem in which a simultaneous numerical solution of the momentum, energy, and diffusion equations of the feed and cold solutions have been carried out. The results were validated in comparison with available experimental results. The two processes were compared in terms of their sensitivity to the main parameters and the mass transfer resistances of the common domains. The results showed, among other things, that the process thermal efficiency of AGMD is higher than that of DCMD by about 6% due to the presence of the air gap. The permeate flux of DCMD is higher than that of AGMD by about 2.3-fold and 4.8-fold for $T_h$ of 80 °C and 40 °C respectively. Increasing the thermal conductivity of the membrane material $k_m$ improves the DCMD process by mainly improving the process thermal efficiency and improves the AGMD process by mainly improving the permeate flux [74].

MD is an emerging separation process suitable for desalination of brackish or seawater. In this technique, hydrophobic membranes are required to allow only water vapour permeation through the porous barrier. In work by Cerneaux et al., zirconia and titania ceramic membranes with pore diameters of 50 nm (Zr50) and 5 nm (Ti5) respectively were chemically modified to change their hydrophilic feature into a hydrophobic one by grafting of the $C_8F_{17}(CH_2)_2Si(OC_2H_5)_3$ perfluoroalkylsilane molecule ($C_8$). Water contact angles around 160° were measured, indicative of highly hydrophobic membranes. Desalination of NaCl solutions of 0.5 and 1 M was performed using the AGMD, DCMD and VMD methods, with the aim to compare their efficiency. High salt rejection rates higher than 99% were obtained in all configurations investigated [75].

MD is a thermally driven membrane process using porous hydrophobic membranes. MD has been investigated as an alternative desalination technology due to its advantages over multistage flash and reverse osmosis. Nevertheless, it is difficult to design and optimize the MD systems under various
conditions, because both thermal and hydrodynamic effects play an important role. Therefore, the study of Koo et al. focused on performance analysis of MD systems in different configurations. DCMD and VMD were experimentally compared using laboratory-scale systems. A simple model was also applied to analyse the difference between the two configurations theoretically. Experimental results indicated that permeate flux in DCMD and VMD were sensitive to the operating conditions. Using the same membranes, the two MD systems showed different flux behaviours. The influences of operating parameters for DCMD and VMD on overall efficiency were also investigated. The model results also confirmed the difference between these two systems theoretically [76].

18.4.2 Desalination and Removal of Salt

18.4.2.1 Desalination

New MD configurations and a new membrane module were investigated to improve water desalination by Cath et al. [77]. The performances of three hydrophobic microporous membranes were evaluated under vacuum enhanced DCMD with a turbulent flow regime and with a feed water temperature of only 40 °C. The new configurations provide reduced temperature polarization effects due to better mixing and increased mass transport of water due to higher permeability through the membrane and due to a total pressure gradient across the membrane. Comparison with previously reported results in the literature revealed that mass transport of water vapours was substantially improved with the new approach. The performance of the new configuration was investigated with both NaCl and synthetic sea salt feed solutions. Salt rejection was greater than 99.9% in almost all cases. Salt concentrations in the feed stream had only a minor effect on water flux. The economic aspects of the enhanced DCMD process were briefly discussed and comparisons made with the reverse osmosis process for desalination.

MD is considered a promising technology for desalination applications. Usually, the investigations stated in MD literature cover lab-scale experiments to analyse the technology’s potential. The work of Winter et al. is focused on experimental studies on full-scale spiral-wound MD modules with a membrane surface area of 5–14 m². Module technology and module fabrication are introduced, as well as the fully automated performance test facility and the characterization procedures. Statements regarding module fabrication quality are given by a comparison of a four-module production charge. The experimental results consider module output rate and specific energy consumption for a broad variety of module operation points. The interaction of feed flow rate, temperature levels, feed water salinity and geometrical module design parameters are quantified and discussed. Special attention is given to the influence of salinity on module performance. The salt rejection rate throughout all experiments was very high and almost independent from any operational parameters studied. Finally, a preliminary approach showed the feasibility of high-purity distillate production with the spiral-wound modules. In an emulated double-stage process the distillate conductivity was dropped down to 0.19 μS cm⁻¹ [78].

The MD process constitutes one of the possibilities for a new method for water desalination. Four kinds of polypropylene membranes with different diameters of capillaries and pores, as well as wall thicknesses were used in the study by Gryta [79]. The morphology of the membrane used and the operating parameters significantly influenced process efficiency. It was found that the membranes with lower wall thickness and a larger pore size resulted in the higher yields. Increasing both feed flow rate and temperature increased the permeate flux and simultaneously the process efficiency. However, the use of higher flow rates also enhanced heat losses by conduction, which decreased the thermal efficiency. This efficiency also decreased when the salt concentration in the feed was enhanced. The influence of fouling on the process efficiency was considered.
18.4.2.2 Removal of Salt

PTFE flat-sheet membrane with the mean pore size of 0.1 μm was used to treat the high concentration (NH₄)₂SO₄ and NH₄Cl solutions by VMD. The permeate flux was varied in the range 8–48 L h⁻¹ m⁻² and was dependent on the operating conditions. The effects of permeate pressures and feed parameters in terms of pH values, feed temperature, flow rate and feed concentration on both the permeate fluxes and the permeate concentrations of total nitrogen (TN) were investigated. Experiment results showed the feed temperature had the most significant effect on the permeate flux. The feed pH value was observed to be the most dominant factor on permeate concentration of TN. Ammonium was rejected with low feed pH value, high feed temperature and low permeate pressure. When the feed pH value was 3, the permeate concentration of TN was kept in the range of 1–3 mg L⁻¹ and the ammonia nitrogen rejection rate was 99.95%, despite the feed concentration being increased [80].

Arsenite (As(III)) and arsenate (As(V)) removal by DCMD were investigated with self-made PVDF membranes by Qu et al. [81]. Permeability and ion rejection efficiency of the membrane were tested before the arsenic removal experiments. A maximum permeate flux 20.90 kg m⁻² h⁻¹ was obtained, and owing to the hydrophobic property the PVDF membrane had high rejection of inorganic anions and cations which was independent of the solution pH and the temperature. The experimental results indicated that the DCMD process had higher removal efficiency of arsenic than pressure-driven membrane processes, especially for high-concentration arsenic and arsenite removal. The experimental results indicated that the permeate As(III) and As(V) were under the maximum contaminant limit (10 μg L⁻¹) until the feed As(III) and As(V) achieved 40 mg L⁻¹ and 2000 mg L⁻¹ respectively. The 250 h simultaneous DCMD performance of 0.5 mg L⁻¹ As(III) and As(V) solution was carried out respectively. The permeate arsenic was not detected during the process, which showed the PVDF membrane had stable arsenic removal efficiency. Membrane morphology changed slightly after the experiments, however, the permeability and the ion rejection of the membrane did not change.

Hou et al. presented the DCMD application for fluoride removal from brackish groundwater [82]. The self-prepared PVDF membrane exhibited high rejection of inorganic salt solutes and a maximum permeate flux 35 kg m⁻² h⁻¹ was obtained. The feed concentration had no marked impact on the permeate flux and the rejection of fluoride. The precipitation of CaCO₃ would clog the hollow fibre inlets and foul the membrane surface with the increase of concentration factor when natural groundwater was used directly as the feed, which resulted in a rapid decline of the module efficiency. This phenomenon was diminished by acidification of the feed. The experimental results showed that the permeate flux and the quality of distillate obtained remained stable before the concentration factor reached 5.0 with the acidified groundwater as feed. The membrane module efficiency began to decline gradually when the feed continued to be concentrated, which can be mainly attributed to the formation of CaF₂ deposits on the membrane surface. Finally, a 300 h continuous fluoride removal experiment on acidified groundwater was carried out with the concentration factor at 4.0 and the permeate flux kept stable, and the permeate fluoride was not detected.

18.4.3 Drinking Water

PVDF nanofibre membrane could be used in MD to produce drinking water (NaCl concentration <280 ppm) from a saline water of NaCl concentration 6 wt% by AGMD [83]. This was the first attempt to use electrospun nanofibre membrane in MD. This new approach may eventually enable the MD process to compete with conventional seawater desalination processes such as distillation and reverse osmosis.

Two MD modes, DCMD and SGMD, were investigated for synthesized and real (Persian Gulf) seawater desalination by Shirazi et al. A commercial PTFE membrane with 0.22 μm pore size was
characterized (using atomic force microscopy and scanning electron microscopy) and was used for experiments. A multipurpose plate-and-frame MD module was used for desalination experiments. The effects of various operating conditions and MD module design, as well as feed type on the permeation flux, were studied. The feed temperature was found to be the most effective operating parameter. The flow rate in both sides of the MD module was found to be effective; however, the feed flow rate showed more influence. Both the modes investigated were successfully applied for seawater desalination, whilst the direct contact mode seemed to provide more permeation flux. The results indicated that the MD module design has a significant effect on the overall efficiency. At optimum conditions, a 99% salt rejection was achieved for both the investigated MD modes [84].

Fibrous membranes of poly(trimethyl hexamethylene terephthalamide) (PA6(3)T) were fabricated by electrospinning and rendered hydrophobic by applying a conformal coating of poly(1H,1H,2H,2H-perfluorodecyl acrylate) using initiated chemical vapour deposition (iCVD) [85]. A set of iCVD-treated electrospun PA6(3)T fibre membranes with fibre diameters ranging from 0.25 to 1.8 μm were tested for desalination using the AGMD configuration. Permeate fluxes of 2–11 kg m⁻² h⁻¹ were observed for temperature differentials of 20–45 °C between the feed stream and condenser plate, with rejections in excess of 99.98%. The liquid entry pressure was observed to increase dramatically, from 15 to 373 kPa with reduction in fibre diameter. Contrary to expectation, for a given feed temperature the permeate flux was observed to increase for membranes of decreasing fibre diameter. The results for permeate flux and salt rejection show that it is possible to construct membranes for MD even from intrinsically hydrophilic materials after surface modification by iCVD and that the fibre diameter is shown to play an important role in the MD performance in terms of permeate flux, salt rejection and liquid entry pressure.

18.4.4 Wastewater

DCMD was used by Gryta et al. for the separation of saline wastewater. Wastewater containing NaCl and protein as well as the effluents produced during the regeneration of ion exchangers was used as feed. During the concentration of these solutions by the MD process, severe fouling of the membranes was observed in several cases. The major reasons for fouling were associated with heating of the feed and increasing concentration of solutes. The membrane morphology and composition of the fouling layer were studied using scanning electron microscopy coupled with energy dispersion spectrometry. The application of appropriate pretreatment enabled the removal of foulants from the feed; hence, the treatment of such wastewaters by MD was possible [86].

DCMD was used by Liu and Wang to treat low-level radioactive wastewater. The dusty gas model was used to analyse the mass transfer mechanism and calculate the permeate flux. The operating parameters such as feed temperature, feed velocity and feed concentration were studied. The experimental results showed that the DCMD process can separate almost all Cs⁺, Sr²⁺ and Co²⁺ from wastewater. The permeate flux decreased linearly when NaNO₃ concentration increased from 1.0 to 200 g L⁻¹. The permeate flux remained about 60% of its initial flux even when NaNO₃ concentration in feed solution was as high as 200 g L⁻¹. The dusty gas model can be successfully applied to estimate the mass transfer, and the experimental permeate flux values fitted well with those calculated by the dusty gas model. Liu and Wang concluded that DCMD is a promising separation process for low-level radioactive wastewater treatment [87].

Experimental investigations were carried out by Peydayesh et al. to treat bentazon solutions by the VMD process. The effects of several parameters, including feed temperature, feed flow rate, vacuum pressure and initial bentazon feed concentration on flux quality and quantity, were studied. The VMD process was found to be effective in the treatment of the bentazon solutions as the
permeate was absolutely pure water. Results showed that increasing temperature and flow rate and decreasing vacuum pressure and bentazon concentration enhanced permeate flux. Temperature and vacuum pressure were found to be the most important factors for permeate flux. Under the best conditions (a feed temperature of 60 °C and a vacuum pressure of 30 mbar), a maximum permeate flux of 92.94 kg m⁻² h⁻¹ was obtained. Also, a mathematical model describing the variation of bentazon concentration with time was developed and validated with the experimental results [88].

18.4.5 Food

MD was applied by Hausmann et al. for the concentration of a range of dairy streams, such as whole milk, skim milk and whey. MD of a pure lactose solution was also investigated. DCMD-mode experiments were carried out in continuous concentration mode, keeping the warm feed/retentate and cold permeate stream temperatures at 54 °C and 5 °C respectively. Performance in terms of flux and retention was assessed. The flux was found to decrease with an increase of dry-matter concentration in the feed. Retention of dissolved solids was found to be close to 100% and independent of the dry-matter concentration in the feed. Fourier transform infrared spectroscopy of the fouled membranes confirmed organics being present in the fouling layer [89].

In further work, Hausmann et al. note that MD is an emerging membrane process based on evaporation of a volatile solvent and that one of its often stated advantages is the low flux sensitivity toward concentration of the processed fluid, in contrast to reverse osmosis. They looked at two high-solids applications of the dairy industry: skim milk and whey. Performance was assessed under various hydrodynamic conditions to investigate the feasibility of fouling mitigation by changing the operating parameters and to compare performance with widespread membrane filtration processes. Whereas filtration processes are hydraulic pressure driven, MD uses vapour pressure from heat to drive separation and, therefore, operating parameters have a different bearing on the process. Experimental and calculated results identified factors influencing heat and mass transfer under various operating conditions using PTFE flat-sheet membranes. Linear velocity was found to influence performance during skim milk processing but not during whey processing. Lower feed and higher permeate temperature were found to reduce fouling in the processing of both dairy solutions. Concentration of skim milk and whey by MD has potential, as it showed high rejection (>99%) of all dairy components and can operate using low electrical energy and pressures (<10 kPa). At higher cross-flow velocities (around 0.141 m s⁻¹), fluxes were comparable to those found with reverse osmosis, achieving a sustainable flux of approximately 12 kg h⁻¹ m⁻² for skim milk of 20% dry matter concentration and approximately 20 kg h⁻¹ m⁻² after 18 h of operation with whey at 20% dry matter concentration [90]. Hausmann et al. [91] also looked at fouling of membranes during MD of two model dairy feeds: skim milk and whey, as well as their major single components. Every MD experiment was conducted for 20 h at 54 °C feed inlet temperature and 5 °C permeate inlet temperature using PTFE membranes. Performance was assessed in terms of throughput (flux) and retention efficiency. Skim milk flux was found to be lower but combinations thereof revealed that fouling was primarily driven by proteins and calcium, but only in combination. Lactose also played a role to a lesser extent in the protein–membrane interactions, possibly due to preferential hydration, but did not interact with the membrane polymer directly. However, lactose was found to deposit once an anchor point to the membrane was established by other components. Skim milk showed strong adhesion from its principle proteins, caseins; however. salts were needed to form a thick and dense cake layer. Caseins seem to form a layer on the membrane surface that prevents other components from interacting with the membrane polymer. Whey proteins, on the other hand, deposited to a lesser extent. In general, MD was found to be a
process that generates high-quality water with retention of all tested components >99% while simultaneously concentrating whey or skim milk.

18.4.6 Concentration and Removal of Organics

18.4.6.1 Concentration

The MD process was applied by Tomaszewska et al. for the concentration of different mineral acids, such as sulfuric, phosphoric, hydrochloric and nitric acids. The MD of a citric acid solution as an example of an organic acid was also investigated [92]. The experiments were carried out keeping the warm feed and cold solution temperatures at 333 K and 293 K respectively. The data obtained indicate that the volume flux of a permeate decreased with an increase of acid concentration in the feed. The reduction of acid content in the permeate, close to 100%, for nonvolatile acids was independent of the acid concentration in the feed. The amounts of hydrochloric or nitric acids in the permeate increased with a rise of the acid concentration in the feed, reaching the azeotropic composition. The effect of the polarization phenomena on the concentration process of sulfuric acid was discussed. Later, batch fermentation combined with the removal of ethanol from the broth by means of the MD process was investigated by Tomaszewska and co-workers [93]. Porous capillary polypropylene membranes were used for the separation of volatile compounds from the feed (broth), formed as a result of fermentation. The elimination of these compounds allows an increase in the productivity and the rate of conversion of sugar to ethanol, since they act as inhibitors. In the case of fermentation combined with MD, an efficiency of 0.4–0.51 g of ethanol per gram of sugar and an ethanol production rate of 2.5–4 g dm⁻³ h⁻¹ were achieved in relation to 0.35–0.45 g of ethanol per gram sugar and ethanol production rate of 0.8–2 g dm⁻³ h⁻¹ obtained in classical batch fermentation. The ethanol flux obtained in MD varied in the range of 1–4 kg m⁻² day⁻¹ and was dependent on the temperature and the feed composition.

The economic competitiveness of fuel ethanol in comparison with fossil fuels depends on the effective lowering of costs on each step of the process. One of the most promising methods seems to be the application of membrane separation technology. In the study by Lewandowicz et al., the focus is on improvement of brewer’s wort fermentation. For this purpose, the MD process for ethanol recovery was implemented. The experimental system consisted of a bioreactor equipped with a capillary polypropylene microfiltration unit. Yeast cell count and viability, assimilation of sugars, production of ethanol and fermentation of by-products (glycerol and lactic acid) were monitored during fermentations. The intercellular trehalose as well as Hsp70 and Hsp104 heat shock proteins contents were determined. It was concluded that MD can be regarded as a straightforward method, which leads to an increase in ethanol production by facilitation of the continuous process, more complete fermentation of sugars, lowering the osmotic pressure in the fermentation broth, decreasing glycerol synthesis level and increasing yeast cell number and viability [94].

Separation of ethanol from solutions with different concentrations in a BIOTRON bioreactor integrated with the DCMD system was investigated by Tomaszewska and Białończyk [95]. The experiments were carried out using immersed, capillary polypropylene membranes. The permeability of the membrane at feed inlet temperatures of 308, 318 and 333 K was determined. The permeate and ethanol flux were strongly affected by the vapour pressure, which increased with the feed temperature and was also associated with ethanol concentration in the feed. It was found that MD can be successfully applied for the separation of volatile components such as ethanol.

Model parameters modification and numerical simulation based on the Knudsen–viscous transition model to predict the VMD performance of an ethanol–water mixture and experiments were studied in
a PTFE flat-sheet membrane module by Shi et al. [96]. The novel approach to determine the model parameters $K$ and $B$ (modified Knudsen diffusion and viscous flow membrane characteristics respectively) consisting of membrane morphological parameters was especially developed by fitting the water VMD experimental results. Furthermore, linear relations between the modified model parameter $K$ or $B$ and feed temperature were first established and then successfully employed to predict by simulation the separation performances of a 5 wt% ethanol–water mixture. The experiments with ethanol–water VMD demonstrated that the fluxes of ethanol and water both increased with temperature or vacuum degree, but the separation factor decreased. The simulation values agree quite well with experimental ones, with the minimum and maximum discrepancies being 0.5% and 9.6% for flux and separation factor respectively.

18.4.6.2 Removal

Water resources used for drinking water production are increasingly contaminated by volatile organic compounds (VOCs), particularly by halogenated VOCs (HOVs), like chloroform, trichloroethylene and tetrachloroethylene, because of industrial pollution. At the same time, new regulations and guidelines on drinking water quality are more stringent on toxic agents, especially on HOVs. Among the different membrane processes, VMD seems to be a promising one. The paper by Couffin et al. aimed to evaluate whether VMD could be used to remove HOVs at very low concentration from water from experimental results obtained with synthetic waters. It also dealt with the characterization of the influence of some process parameters on flux and selectivity according to two different approaches: experiments and simulation. The influence of temperature and downstream pressure on the process productivity was discussed in terms of selectivity, which characterizes the permeate concentration but also of equivalent flux of treated water, which here is the concentrate. As quite high equivalent fluxes can be expected, VMD appears to be a promising way to remove trichloroethylene and other HOVs from water at a low concentration [97].

The removal of VOCs from aqueous streams by VMD was also analysed by Sarti et al. VMD is an evaporation process which takes place through microporous hydrophobic membranes; at low pressure the mass transfer through the membrane is generally dominated by the Knudsen mechanism, while the process selectivity is essentially determined by the liquid–vapour equilibrium conditions existing at the interface. Dilute aqueous mixtures containing ethanol or methylterbutyl ether were investigated experimentally over a wide range of operating conditions. The role of concentration polarization phenomena on the separation factor was also investigated. A detailed model of the transport phenomena involved in the process was developed and compared with the experimental data. A VMD system was finally designed for the purification of wastewaters and the related treatment costs were evaluated [14].

The removal of trace organic compounds (TrOCs) by a novel MD–thermophilic bioreactor (MDBR) system was examined by Wijekoon et al. [98]. Salinity build-up and the thermophilic conditions to some extent adversely impacted the performance of the bioreactor, particularly the removal of total nitrogen and recalcitrant TrOCs. While most TrOCs were well removed by the thermophilic bioreactor, compounds containing electron-withdrawing functional groups in their molecular structure were recalcitrant to biological treatment and their removal efficiency by the thermophilic bioreactor was low (0–53%). However, the overall performance of the novel MDBR system with respect to the removal of total organic carbon, total nitrogen and TrOCs was high and was not significantly affected by the conditions of the bioreactor. All TrOCs investigated were highly removed (>95%) by the MDBR system. Biodegradation, sludge adsorption and rejection by MD contribute to the removal of TrOCs by MDBR treatment.
References


19

Gas Permeation

19.1 Beginning of Gas Permeation

In 1831, Mitchell [1,2] reported for the first time that gases permeated through rubber membranes and that the flux of each gas was different. At that time, very few polymer membranes had high gas permeabilities and excellent separation properties. In the early 1950s, research concerning the separation of helium from natural gas or for oxygen enrichment from air was begun. With progressing of technology for polymer syntheses, new many materials for practical gas separations were developed. Membranes that have both a high solubility and a high diffusivity of gases as well as easy membrane formation properties are now being used. In this chapter, we discuss in detail from the fundamentals to the technology of gas permeation membranes.

The study of the permeation of gas through a membrane had already been reported historically in 1831 by Mitchell [1,2]. And Graham [3] performed a quantitative study of the gas permeation afterwards in 1866.

Graham considered that the permeation of gas through a rubber membrane is due to three processes: (1) the condensation and dissolution of gas on the membrane side where the gas concentration is high; (2) the diffusion in the liquid state of the gas in the membrane; and (3) the evaporation in the gas state on the another side of the membrane. Barrer [4] expanded the transition state theory of diffusion that Eyring [5] had proposed for polymer membranes and explained that the diffusion of gases in the polymer occurs through vacancies between polymer chains produced by the vibration of polymer segments.

The synthetic membrane is classified roughly into porous and nonporous membranes. The former has pores more than 10 Å in diameter, and the gases move mainly through these pores. On the other hand, there are molecular vacancies less than 10 Å caused by the thermal motion of the polymer chain forming a membrane in the latter, and gases move there. The permeation mechanism of these two kinds of membranes is different. In other words, gases are permeated mainly by a pore flow and a convection flow in a porous membrane and, in the case of a nonporous membrane, they are permeated by active diffusion.

The term the permeability is used in general to represent the ease of permeation of a gas through the membrane. The permeability occurs from the high-pressure side to the low-pressure side on both sides of the membrane. When all pressure is equal, the gas moves from the high partial pressure side to the low partial pressure side. These phenomena to the move of gas are unrelated to the mechanism of gas permeation for the membrane.
19.2 Fundamentals of Gas Permeation

19.2.1 Permeation and Separation of Gas through a Rubbery Membrane

19.2.1.1 Permeability Coefficient

The permeation mechanism of gas through a nonporous membrane consists of the four processes shown in Figure 19.1: (I) when gas contacts the film; (II) where the gas dissolves in the surface of the film (dissolution process); (III) the gas which dissolves moves through the whole film along the concentration gradient (diffusion process), but this state is an unsteady state; (IV) the gaseous concentration gradient in the film gradually becomes a straight line in the thickness direction of the film, and it becomes a steady state.

Figure 19.2 shows a permeation curve when the increase in the pressure of the low-pressure side as a border of the membrane is measured. The point B in Figure 19.2 corresponds to process (I)—(III) in Figure 19.1.

The quantitative handling of the permeation phenomenon in the steady state of Figure 19.2 proceeds according to Equation 19.1 when a membrane of uniform thickness \( l \) and area \( A \) as shown in Figure 19.3 is set on a border between gases of different partial pressures, and after a set time the permeation amount of gas per a set time is a constant. Equation 19.1 is the diffusion equation known as the second law of Fick:

\[
\frac{dC}{dt} = D \frac{d^2C}{dx^2}
\]  

(19.1)

In Figure 19.3, when the following boundary conditions are given and Equation 19.1 is integrated, we obtain Equations 19.2 and 19.3:

a) \( \frac{dC}{dt} = 0 \)

b) \( C = C_1 \) at \( x = 0 \)

c) \( C = C_2 \) at \( x = l \)

---

Figure 19.1 Permeation mechanism of gas through a nonporous membrane [5].
\[ C_x = C_1 - \left( \frac{(C_1 - C_2)x}{l} \right) \]  
\hspace{1cm} (19.2)

\[ \frac{dC}{dt} = -\frac{C_1 - C_2}{l} \]  
\hspace{1cm} (19.3)

where \( C \) is the concentration of gas which permeates in the membrane and \( x \) is a position in the membrane from the high concentration side.

When Fick’s first law shown in Equation 19.4 is integrated, the amount of gas moved through the membrane \( Q \) is given by Equation 19.5:

\[ V = -D \frac{dC}{dt} \]  
\hspace{1cm} (19.4)

\[ Q = DA \int_{0}^{t} \left( -\frac{dC}{dx} \right)_{x=1} dt \]  
\hspace{1cm} (19.5)

where \( V \) is the permeation rate per set hour and unit area.

We then obtain Equation 19.6 by substituting Equation 19.3 into Equation 19.5:

\[ Q = \frac{D(C_1 - C_2)At}{l} \]  
\hspace{1cm} (19.6)

If equilibrium includes the gas concentrations on both sides of membrane, \( C_1 \) and \( C_2 \) and the partial pressure of gas, \( p_1 \) and \( p_2 \) which contact with a membrane, then by Henry’s law we have

\[ C_1 - C_2 = S(p_1 - p_2) \]  
\hspace{1cm} (19.7)

where \( S \) is the solubility parameter.

Equation 19.6 can be rewritten as

\[ Q = \frac{DS(p_1 - p_2)At}{l} \]  
\hspace{1cm} (19.8)

When CGS units are used for \( (p_1 - p_2), A, t, l \), Equation 19.8 becomes

\[ Q = DS \]  
\hspace{1cm} (19.9)

And when \( Q \) is expressed in \( P \) we have

\[ P = DS \]  
\hspace{1cm} (19.10)

where \( P \) is the permeability coefficient.

Equation 19.8 can be rewritten as follows:

\[ Q = \frac{P(p_1 - p_2)At}{l} \]  
\hspace{1cm} (19.11)

Equation 19.11 is the fundamental equation which is used the calculation of the gas permeation through a nonporous membrane.
19.2.1.2 Diffusion Coefficient

Steady-state permeation of gas is used for the measurement of the permeability coefficient. On the other hand, the diffusion coefficient at a time lag before reaching the steady state, shown by $\theta$ in Figure 19.2, can be determined [6].

Equation 19.12 is obtained when the following boundary conditions are introduced into Equation 19.1:

a) $x = 0$, $C = C_1$ at $t < 0$

b) $x = l$, $C = 0$ at $t > 0$

c) $t = 0$, $C = 0$ at all $x$

d) $dC/dt = 0$ at $t = \infty$

\[
C = C_1 \left( 1 - \frac{x}{l} \right) - \frac{2C_1}{\pi} \sum_{n=1}^{\infty} n^{-1} \sin \left( \frac{n\pi x}{l} \right) \exp \left[ - \left( \frac{n\pi}{l} \right)^2Dt \right] \tag{19.12}
\]

\[
Q = DA \left\{ \frac{C_1 t}{l} - \frac{C_1}{6D} \sum_{n=1}^{\infty} \left\{ 1 + \frac{12 - n}{\pi^2 n^2} \exp \left[ - \left( \frac{n\pi}{l} \right)^2Dt \right] \right\} \right\} \tag{19.13}
\]

When $C$ in Equation 19.12 is differentiated with respect to $x$ and $dC/dx$ in $x = 1$ is claimed, this solution is substituted for Equation 19.5 and then it is integrated about $t$, and the gaseous quantity $Q$ at $x = 1$ with unsteady state in time $t$ in membrane area $A$ is shown by Equation 19.13.

Equation 19.14 for the straight line indicating the permeation by the steady state is obtained at $t = \infty$

\[
Q = \frac{DAC}{l} \left( 1 - \frac{l^2}{6D} \right) \tag{19.14}
\]

The time lag $\theta$ at a point cutting the time axis of Figure 19.2 is connected with the diffusion coefficient and membrane thickness as in Equation 19.15, and the diffusion coefficient can be obtained easily if $\theta$ is measured:

\[
\theta = \frac{l^2}{6D} \tag{19.15}
\]

19.2.1.3 Separation Factor

As shown in Figure 19.4, if the molar concentration (or partial pressure) of components A and B of a mixed gas supplied to the highly concentrated side across a membrane are $X_A$ and $X_B$ and the molar concentration (or a partial pressure) of components A and B of the low-concentration side, namely the permeate side, are $Y_A$ and $Y_B$, the separation factor, $\alpha$ is given by

\[
\alpha = \frac{Y_A / Y_B}{X_A / X_B} = \frac{X_B Y_A}{X_A Y_B} \tag{19.16}
\]

Because $X_A / X_B$ is a molar ratio of the supply gas, naturally it is a known value, and $Y_A / Y_B$ is a value found by analysis of permeate gas. Therefore, $\alpha$ is an experimental value. However, $X$ may be estimated by a calculation. If A and B in a mixed gas penetrates a membrane
independently according to Equation 19.11, the molar ratio of A and B of the permeate side equals the ratio of the permeated quantity:

\[
\frac{Y_A}{Y_B} = \frac{Q_A}{Q_B} = \frac{P_A(p_{A_1} - p_{A_2})}{P_B(p_{B_1} - p_{B_2})}
\]

(19.17)

In addition, because the mixed gaseous molar ratio of the feed side is equal to the ratio of the partial pressure, we have

\[
\alpha = \frac{Y_A}{Y_B} = \frac{X_A}{X_B} = \frac{P_A(p_{A_1} - p_{A_2})p_{B_1}}{P_B(p_{B_1} - p_{B_2})p_{A_1}} = \frac{P_A}{P_B} \left[ 1 - \left( \frac{p_{A_2}}{p_{A_1}} \right) \right]
\]

(19.18)

\(\alpha\) shown in Equation 19.18 is a calculated value, and it may be said that it is a theoretical calculated value. When the pressure of the feed side is set to a high pressure or the pressure of the permeate side is very much smaller than the pressure of the feed side, since the value in square brackets in Equation 19.18 gets closer to 1, \(\alpha\) approaches \(P_A/P_B\). This is equivalent to the permeability coefficient ratio and is a theoretical separation factor.

Because this was not available when the gaseous pressure of the permeate side was small in the separation of a mixed gas by a practical gas separation membrane, Stern and Walawender [7] obtained Equation 19.19 indicating the separation factor that considered the pressure ratio \(\gamma\) of the feed side and the permeate side:

\[
\alpha = \frac{P_A}{P_B} \left[ \frac{(1-X_A)/(1-Y_A)}{(1-X_A)/(1-Y_A) + \frac{1}{\gamma} \left( \frac{P_B}{P_A} - 1 \right)} \right]
\]

(19.19)

\(\gamma\) in Equation 19.19 is the pressure ratio \(p_1/p_2\) of both sides of the membrane. In this case when \(p_1/p_2\) becomes large, \(\alpha\) approaches the permeability coefficient ratio \(P_A/P_B\). It may be said that the ideal separation factor is the permeability coefficient ratio.

### 19.2.2 Membrane Permeation of Gas through a Glassy Membrane

#### 19.2.2.1 Dual Sorption Model Theory

As mentioned earlier, the permeability coefficient \(P\) was determined from the slope of the straight-line part of the permeation curve with a rubbery membrane, and the diffusivity \(D\) was obtained from the time lag \(\theta\). In addition, the solubility coefficient \(S\) to a gas separation membrane is obtained from \(P\) and \(D\) using Equation 19.10, which is a rearrangement of Equation 19.10. On the other hand, a sorption experiment of gas also provides \(S\) directly. When the solubility coefficient is \(S'\), we obtain Equation 19.20:

\[
S = \frac{P}{D}
\]

(19.10')

\[
D = \frac{P}{S'}
\]

(19.20)

In these relation equations, when the membrane is in a rubber state, which is higher than the glass transition temperature, \(D\) and \(\bar{D}\) show relatively good agreement. However, with the membrane of the glass state in the temperature domain that is lower than a glass transition temperature, \(\bar{D}\) does not accord with \(D\). Consequently, the dual sorption model was introduced to elucidate this fact.

The adsorption of gas or vapour to a polymer in the dual sorption model is due to the dissolution of gas according to Henry’s law and Langmuir adsorption occurring simultaneously, as shown in Figure 19.5.
The concentration $C$ of gas in a membrane is expressed by the sum of the concentration $C_D$ by the law of Henry’s gas dissolution and the concentration $C_H$ by Langmuir adsorption:

$$C = C_D + C_H \quad (19.21)$$

The former shows dissolution by the gaseous mixture in the rubbery polymer, and the latter is due to the insertion of a gas in the microvoids or in a pore in the polymer.

According to dual sorption theory, Equation 19.21 becomes [8]

$$C = C_D + C_H = k_D p + \frac{C_H b p}{1 + b p} \quad (19.22)$$

where $p$, $k_D$, $C'_H$ and $b$ are the pressure of gas, Henry’s gas dissolution law constant (which is the same as the solubility coefficient $S$ mentioned earlier), the hole saturation constant and the hole affinity constant.

### 19.2.2.2 Partial Immobilization Model

Stannet [9] summarized the dual sorption theory and a hypothesis about the diffusion and permeation proposed by Vieth et al. [8]. In this report, the gas which undergoes Langmuir adsorption is completely immobilized and does not contribute to the diffusion and permeation. However, the Langmuir-shaped gas adsorption is necessarily not completely immobilized; it is labile from complete fixity; this was supposed as extensive, and a theoretical equation for the permeability and time lag was derived [10]. Paul and Koros [11] transformed this theory type and suggested a partial immobilization model based on the concentration gradient.

When this consideration of partial immobilization is reflected, the average diffusion coefficient $\bar{D}_{AV}$ (Equation 19.23) as the average value of diffusion coefficients of the sorption $D_s$ and desorption $D_d$ obtained from the cycle of sorption–desorption of gas, we obtain Equation 19.24 [12]:

$$\bar{D}_{AV} = \frac{D_s + D_d}{2} \quad (19.23)$$

$$\bar{D}_{AV} = D_D \left[ \frac{(1 + FK)/(1 + bp)}{(1 + K)/(1 + bp)} \right] \quad (19.24)$$
where $K$ and $F$ are given by Equations 19.25 and (19.26) respectively:

\[
K = \frac{C_H b}{k_D} \tag{19.25}
\]

\[
F = \frac{D_H}{D_D} \tag{19.26}
\]

where $D_D$ and $D_H$ are the diffusion coefficient for the solution mode of Henry and for the Langmuir mode respectively.

Equation 19.24 shows that the relation of $D_{AV} \left[1 + K(1 + bp)\right]$ versus $K(1 + bp)$ is a straight-line relation having slope $D_H$ and intercept $D_D$.

Table 19.1 lists the $D_H$ and $D_D$ values determined from $D_{AV}$ obtained from the sorption and desorption experiment of $CO_2$ by a Kapton membrane and dual sorption parameters $k_D$, $C_H$ and $b$ determined from a sorption isothermal line [13].

The permeability coefficient $P$ considering partial immobilization is given by [14]

\[
P = k_D D_D \frac{1 + FK}{1 + bp} \tag{19.27}
\]

Equation 19.27 means that $P$ is obtained when dual sorption parameters and $D_H$ and $D_D$ values are used. In addition, the relation of $P$ versus $1/(1 + bp)$ gives a straight line with a slope $k_D D_D FK$ and intercept $k_D D_D$ when $P$ is used, which is obtained from a permeation experiment. The transportation parameters $D_H$ and $D_D$ based on a permeation experiment are given within parentheses in Table 19.1.

The values of $D_H$ and $D_D$ determined by both the permeation and sorption experiments are considerably near to the values of $D_D$ and $D_H$ obtained by only the sorption experiment. This result suggests that the sorption and permeation of $CO_2$ by the Kapton membrane, which is a glassy polymer, can be explained by the partial immobilization sorption theory. The concentration dependency of the diffusivity coefficient of the permeation of gas in the steady state is given by [11]

\[
D_{eff}(C_2) = \left( P(p_2) + p_2 \frac{\partial P}{\partial p} \right) \frac{\partial p}{\partial C} \bigg|_{p_2} \tag{19.28}
\]

The effective diffusion coefficient $D_{eff}$ calculated using isothermal data for sorption and permeation data using Equation 19.28, shows concentration dependency, as shown in Figure 19.6.

---

**Table 19.1** Transport parameters of $CO_2$ in 0.5-mil Kapton membrane.a)

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$D_D \times 10^9$ (cm$^2$ s$^{-1}$)</th>
<th>$D_H \times 10^{10}$ (cm$^2$ s$^{-1}$)</th>
<th>$F = D_H/D_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>2.91 (2.84)</td>
<td>1.08 (1.15)</td>
<td>0.037</td>
</tr>
<tr>
<td>45</td>
<td>5.69 (5.81)</td>
<td>5.24 (5.14)</td>
<td>0.092</td>
</tr>
<tr>
<td>55</td>
<td>7.19 (6.57)</td>
<td>11.2 (12.6)</td>
<td>0.167</td>
</tr>
</tbody>
</table>

a) Values in parentheses were obtained from sorption and permeability data.
On the other hand, $D_{\text{eff}}$ is also given from dual sorption parameters and permeation parameters and is given by

$$D_{\text{eff}} = D_1 (1 + FK)/(1 + bp)^2$$  \hspace{1cm} (19.29)

The solid lines in Figure 19.6 were obtained from Equation 19.29.

If the diffusion coefficient is constant, the time lag of the permeation curve of a membrane producing dual sorption $\theta$ is given by

$$\theta = \frac{L^2}{6D} (1 + Kf(y))$$  \hspace{1cm} (19.30)

where $K$ is given by Equation 19.25, and

$$f(y) = 6y^{-3} \left[ \frac{1}{2} y^2 + y \ln(1 + y) \right]$$  \hspace{1cm} (19.31)

where $y = bp$. Equation 19.30 contains the added term $1 + Kf(y)$ to the time lag of a rubbery polymer $\theta$, and when the dual sorption parameters $k_D$, $C_H$ and $b$ and the permeation parameters $D_H$ and $D_D$ are applied to Equation 19.31, $\theta$ of a glassy polymer that occurs due to dual sorption can be predicted.

### 19.2.3 Application to Gas Separation

In the case of a rubbery polymer membrane, because each component in a mixed gas permeate independently, it was mentioned earlier that the values of diffusion and solubility coefficient measured in a single component are used in the calculation for a mixed gas. However, since there are two kinds in the sorption and diffusion mode in a glassy polymer membrane, the analysis of data of a mixed gas is complicated. Koros et al. [15] defined Equations 19.32 and 19.33, which demanded the permeation of each
component in the composition and the pressure by considering the characteristics of the sorption and diffusion of the glassy polymer, and it was explained well what the separation factor depended on for pressure, as shown in Equation 19.34:

\[
P_A = D_{DA}k_{DA} \frac{1 + F_A K_A}{1 + b_B p_T + Y_A p_T (b_A - b_B)}
\]

\[
P_A = D_{DB}k_{DB} \frac{1 + F_B K_B}{1 + b_B p_T + Y_B p_T (b_A - b_B)}
\]

\[
\alpha \equiv \frac{X_A/X_B}{Y_A/Y_B} \approx \frac{P_A}{P_B}
\]

Because the permeability coefficient of a glassy polymer membrane is low, a rubbery polymer membrane has been used for gas permeation conventionally. However, in recent years a thinning technology using a support has been developed, and glassy polymer membranes now play an active part as gas permeation membranes.

### 19.3 Membranes for Gas Permeation

Gas permeation membranes are fabricated from a variety of polymers and inorganics such as ceramics, zeolite and metals. There are two types of membrane separator, each working through a different mechanism. There are two types of nonporous and porous membranes, which operate by a different permeation mechanism. The former are known as dense membranes. Above the glass transition temperature amorphous segments of polymer exhibit liquid-like properties and allow gases to pass through by a solution diffusion mechanism. Temperature has a very significant effect, which gives transport rates according to the Arrhenius equation. They are highly selective but must be very thin to achieve reasonable capacities per unit area. This limits their mechanical strength [16]. Small molecules of penetrants move among polymer chains according to the formation of local gaps by thermal motion of polymer segments. The free volume of the polymer, its distribution and local changes in distribution are of the utmost importance. The diffusivity of a penetrant depends mainly on its molecular size.

Porous membranes typically contain larger voids than nonporous membranes do, having interconnected pores significantly larger than the molecular diameters of gases passing through them. Transfer through the pores depends on structure and size distribution. Since selectivity is determined primarily by the relative molecular sizes of the gases being separated, they suffer from poorer selectivity. Unlike nonporous membranes, porous membranes exhibit no molecular interaction between the membrane polymer and the diffusing species.

Porous membranes can be made much thicker than nonporous membranes and retain high capacities with good mechanical strength, so despite their reduced selectivity they are commonly used for bulk separation. The pore diameter must be smaller than the mean free path of gas molecules. Under normal conditions (100 kPa, 300 K), this is about 50 nm. In this case, the gas flux through the pore is proportional to the molecule’s velocity; that is, inversely proportional to the square root of the molecule’s mass. This is known as Knudsen diffusion. Gas flux through a porous membrane is much higher than through a nonporous one by three to five orders of magnitude. The separation efficiency is moderate; hydrogen diffuses four times faster than oxygen. Porous polymeric or ceramic membranes for ultrafiltration serve the purpose. Note that when the pores are larger than
the limit then viscous flow occurs, and hence there is no separation (see http://en.wikipedia.org/wiki/Membrane_gas_separation).

19.3.1 Membranes from Natural Polymers

The selectivity of the cellulose acetate (CA) membrane is ideally suited to the recovery of hydrogen from the purge gas of reactor recycle loops. For the separation of high-concentration carbon dioxide (CO₂) or hydrogen sulfide (H₂S), the test data show that the permeabilities of the individual components in mixed gas permeation are significantly different from those of pure gases [17]. The permeabilities of oxygen and CO₂ of chitosan membranes prepared from an aqueous solution of acetic acid by the dry and wet method were studied by Sakurai et al. [18]. The permeabilities of gases were remarkably influenced by the membrane preparation method and were dependent significantly on the fine structure of membrane. The permeability and the sorption amount of water vapour were also affected by the kind of acid as a casting solvent for chitosan, and the importance of the resulting membrane structure was suggested [19]. A CA reverse osmosis membrane was applied to perform the separation of nutmeg essential oil and dense CO₂ [20].

Silk fibroin–chitosan blend films had good oxygen and water vapour permeabilities, making them useful as biomaterials. In particular, the blend film containing 40–50% chitosan showed very high oxygen permeability [21]. The permeability of five pore gases through the blend membranes of poly(4-vinylpyridine) (PVP) with ethylcellulose (EC) was investigated [22]. The highest O₂/N₂, CO₂/methane (CH₄) and H₂/N₂ selectivity coefficients were respectively equal to 6.8, 25 and 70. The temperature and pressure dependencies of the permeability of the five gases through a PVP/EC (50/50) blend membrane were discussed. The CO₂ flux was linearly proportional to the transmembrane pressure applied and decreased as the essential oil concentration in the feed stream increased.

The transport of CO₂, O₂ and N₂ in amorphous membranes of vulcanized natural rubber reinforced with regenerated cellulose was investigated by Reis-Nunes et al. [23]. The isotherms representing the variation of both the permeability and diffusion coefficients of the gases with pressure presented a relatively sharp increase in the region of low pressures, which was attributed to changes in the free volume. The analysis of the permeability characteristics of the membranes in terms of the free-volume theory suggests that gas transport was severely hindered in both the cellulose phase and the cellulose–rubber interphase of the composites.

Films of chitosan glutamate and sodium alginate were obtained by a casting/solvent evaporation method and cross-linked with their counter ions tripolyphosphate and calcium chloride respectively, by Remuñán-López and Bodmeier [24]. The cross-linked films were water insoluble but permeable to water vapour. The water vapour transmission rate of chitosan films linearly decreased with increasing concentration of cross-linking agent; an optimum cross-linking agent concentration was found with alginate.

The permeation and separation of CO₂ through a water-swollen chitosan membrane were studied by Ito et al. CO₂ preferentially permeated through the swollen chitosan membrane with a permeability of \(2.5 \times 10^{-8}\) cm³ (STP) and a CO₂/N₂ separation factor of 70 at room temperature. This separation performance for CO₂ resulted from the basic properties of the chitosan amino groups. The membrane preparation conditions, such as acetic acid concentration of the casting solution, affected the membrane permeation rate [25].

Modified EC membranes were applied to the recovery of propylene from a gas mixture by Bai et al. The mixture contained C₁ and C₅ hydrocarbons and nonhydrocarbons such as CO, CO₂, H₂ and N₂. Various metals, such as silver, ruthenium, palladium and iridium, were incorporated into EC membranes to modify the membrane permeation properties for selectively increasing the propylene.
Among the metal-incorporated membranes, the best results were obtained with a silver (5 wt%–EC membrane, which yielded a permeate stream of around 65 mol% propylene [26].

The effect of polyethylene glycol (PEG) on gas permeabilities and selectivities was investigated by Li et al. in a series of miscible CA blend membranes [27]. It was determined that the blend membrane having 10 wt% PEG20000 exhibited higher permeability for CO₂ and higher permselectivity for CO₂ over N₂ and CH₄ than those of the membranes which contained 10% PEG of the molecular weight in the range 200–6000. The apparent solubility coefficients of all CA and PEG blend membranes for CO₂ were lower than those of the CA membrane. However, almost all the blend membranes containing PEG20000 showed higher apparent diffusivity coefficients for CO₂, resulting in higher permeability coefficients of CO₂ with relation to those of the CA membrane.

Supramolecular complex membranes were prepared by Lehmann et al. from soluble metal phthalocyanines with a cyanoethylated hydroxypropylcellulose polymer with nitrile groups on flexible spacers [28]. Composite membranes made from these complexes were enriched from a mixture of N₂ or CH₄. Optimal selectivity and permeability were found with membranes containing phthalocyanines with bulky substituents on the macrocycle and metal ions, which are able to coordinate with the nitrile groups of the polymer.

### 19.3.2 Membranes from Synthetic Polymers

#### 19.3.2.1 Polyamides, Polyimides, Poly(phenylene oxide) and Fluoropolymers

Polyamides, polyimides and poly(phenylene oxide) are used for thermal resistance, and fluoropolymers such poly(vinyl fluoride), poly(vinylidene fluoride) (PVDF) and poly(tetrafluoroethylene) (PTFE) for chemical resistance.

Interfacial polycondensed composite membranes are well known for reverse osmosis. The study by Petersen and Peinemann describes the preparation of interfacial polymerized composite membranes for gas separation obtained from new polyamides. The polymers were synthesized by derivates of terephthaloylchloride and commercially available multifunctional amines. The membrane polymers consisted of linear or cross-linked chains. A high flux of CO₂, 0.3 m³ m⁻² h⁻¹ bar⁻¹, was observed, combined with a CO₂/N₂ selectivity up to 30. The permeability to hydrocarbons increased with hydrocarbon vapour concentrations. The synthesis of the thin polyamide layer was transmitted to a continuous production [29].

Thin-film composite reverse osmosis membranes were dried under different membrane pretreatment procedures and evaluated at increased temperatures by gas separation tests. The permeance and selectivity values obtained indicated the presence of highly permeable regions in the dry samples of the commercial membranes. Treatment with ethanol–hexane in a solvent exchange process, as well as membrane immersion in tert-butanol followed by freeze drying, increased the gas permeance by a factor of 1.8 to 9 and from 1.6 to 3.2 respectively by comparison with room-temperature and oven drying. Nevertheless, a Knudsen-diffusion transport mechanism was dominant after both pretreatments. The permeation temperature remarkably influenced gas selectivity and permeance, and the maximum He/N₂ selectivity occurred at 150 °C with considerable high permeance results, which may suggest the use of polyamide membranes as alternative materials for high-temperature separation processes. The temperature-induced changes in the polymer structure and in the transport of compounds can be explained by Knudsen and activated diffusion mechanisms throughout the highly permeable regions and a dense polyamide matrix respectively [30].

CO₂ and CH₄ permeabilities were measured for dense film and asymmetric membrane prepared from an aromatic polyimide (4,4-hexafluoroisopropylidene diphthalic anhydride (6FDA)–dibenzoylmethane (DMB)) by White et al. [31]. Selectivities for CO₂/CH₄ of up to 55 were determined.
for a mixture of these gases. Permeability of gases through the membrane was found to be dependent upon the CO$_2$ and higher hydrocarbon concentrations that can also be present in natural gas streams. In addition to CO$_2$ having an impact on CH$_4$ permeability, the presence of hexane or toluene cut CO$_2$/CH$_4$ selectivities in half. Lowered selectivities from ideal test conditions were a result of plasticization of the polyimide by these components. Results for the polyimide were contrasted with values obtained from CA films, which are less impacted by hydrocarbon impurities. The polyimide depends more upon diffusivity factors than CA does to generate high selectivity. Thermal and physical properties of 6FDA–DMB polymer and membrane were also described.

A series of polyimides was obtained by Calle et al. from the experimental diamine 1,4-bis(4-aminophenoxy)2,5-di-tert-butylbenzene (TBAPB) and three commercial dianhydrides – pyromellitic dianhydride (PMDA), 3,3,4,4-biphenyltetraacarboxylic dianhydride (BPDA) and 6FDA – following classical polyimidation methods. Analogous polyimides with diamines 2,2-bis(4-aminophenyl) hexafluoropropane (6FpDA) and 1,4-bis(4-aminophenoxy)benzene (APB) were also prepared for comparative purposes. All polyimides showed high thermal stability, with decomposition temperatures above 490 °C and glass transition temperatures higher than 270 °C. The rigid, rod-like structure of PMDA, combined with bulky diamines TBAPB and 6FpDA, yielded polyimides with high fractional free volume, close to that of 6FDA–6FpDA. The high fractional free volume of PMDA–TBAPB contrasts with its structure, which has a fairly large degree of short-range order as evidenced by X-ray diffraction. The gas permeation properties were greatly dependent on the dianhydride moiety and, as a rule, they compared well with those of polyimides used for gas separation. The polymers from PMDA (PMDA–TBAPB and PMDA–6FpDA) showed the best gas productivity values. By means of molecular modelling calculations, it was observed that monomer TBAPB preferably adopts a contorted, rotation-restricted conformation, which can explain the special characteristics observed in the reported polyimides [32].

PVDF is a hydrophobic polymer, nontoxic, high thermal and chemical resistance. The solubility of PVDF is restricted, being more used to its dissolution strongly polar solvents such as N, N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), tetrahydrofuran and 1-methyl-2-pirrolydone (NMP). PVDF membranes with a fine structure can be easily using those solvents [35].

PVDF-based mixed matrix membranes (MMMs) comprising crystalline structures of metal organic frameworks, CuBTC, CuBDC, MIL-53(Al) and NH$_2$-MIL-53(Al), were fabricated and investigated by Feijani et al. for gas separation applications [34]. Metal organic frameworks and membranes were extensively characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) techniques. A 10 wt% loading of CuBTC in PVDF showed 43.6% and 118.7% permeability enhancement for He and CO$_2$ gases compared with the pure membrane. Moreover, a high selectivity enhancement of 96% was observed for CO$_2$/CH$_4$. With regard to CuBDC, 37.5% and 117% permeability increases for He and CO$_2$ gases was reported for 15% loading. Furthermore, the best selectivity was related to CO$_2$/CH$_4$, in which a 109.3% increase was achieved relative to the pure membrane. Since CuBTC and CuBDC exhibited interesting effects on CO$_2$ transport, they can be promising additives for polymer membranes. The membranes containing 10 wt% of NH$_2$-MIL-53(Al) showed 11.25% and 22.41% selectivity enhancement for He/CH$_4$ and CO$_2$/CH$_4$. However, selectivity decreased by 3.33% and 1.3% for those membranes containing MIL-53(Al), compared with the pure PVDF membrane. The different behaviours of NH$_2$-MIL-53 (Al) and MIL-53(Al) can be explained by their different surface properties related to the existence of amino groups on NH$_2$-MIL-53(Al).

Franco et al. [35] reported a study of the use of polypropylene membranes that had been sputtered with PTFE in a radio-frequency plasma reactor. Plasma treatment resulted in the deposition of an ultrathin microporous coating that has a high degree of fluorination and nano- and microscale
roughness. The treated membrane maintained similar pore characteristics and a similar thickness to untreated polypropylene, and therefore it is likely that the treatment film provides a negligible resistance to CO\textsubscript{2} mass transfer relative to that of the bulk polypropylene membrane. The absorption results presented in this paper showed that the plasma-treated membrane had a comparable or superior performance to that of PTFE for CO\textsubscript{2} mass transfer into monoethanolamine solvent. A flat-sheet membrane configuration was used to test the properties of the material and to show that the treated membrane had a comparable CO\textsubscript{2} mass-transfer rate to PTFE after 25 days of solvent exposure. Results suggested that all membrane materials were at least partially wetted but that the extent of wetting was lower in the PTFE and plasma-sputtered membrane, relative to untreated polypropylene.

19.3.2.2 Polysulfone
Polysulfone materials are superior for membrane formation.

Gas separation membranes can be physically or chemically modified to improve their separation characteristics. The ability of bromine to form charge-transfer complexes with unpaired electrons along a polymer backbone was utilized by Barbari and Datwani to tailor the gas separation properties of a polysulfone membrane. It was hypothesized that the bromine molecules would alter the free-volume distribution in such a way as to hinder the transport of large gas molecules without a significant reduction in the flux of the more permeable gas. Bromine was sorbed into the polymer from an aqueous solution at pH 2. The treated membranes developed a characteristic orange colour, indicative of charge-transfer complex formation, which remained after aqueous rinsing and vacuum drying. CO\textsubscript{2} and CH\textsubscript{4} permeability coefficients of the treated membranes were measured to determine the selectivity. After bromine treatment, the selectivity of a polysulfone membrane for CO\textsubscript{2} over CH\textsubscript{4} was increased over 100% at 10 atm upstream pressure with only a 36% reduction in CO\textsubscript{2} permeability. Membrane stability was inconsistent, with only one film appearing visually stable up to 1 year after treatment [36].

Integrally skinned asymmetric gas separation membranes were prepared by (i) dry, (ii) wet and (iii) dry/wet phase-inversion processes [37]. The membranes were cast from a polysulfone–methylene chloride–1,1,2-trichloroethane–2-methyl-2-butanol casting system. Wet and dry/wet phase-inversion membranes were quenched in methanol. Membranes made by dry/wet phase inversion using convective evaporation showed optimum gas separation performance. The average O\textsubscript{2}/N\textsubscript{2} and He/N\textsubscript{2} selectivities of these membranes were within 85% of those determined for a dense, solution-cast polysulfone film, suggesting that the ultrathin skin layers were essentially defect free. The average apparent skin layer thickness of all samples tested was 270 Å. Scanning electron micrographs revealed that optimum membranes made by dry/wet phase inversion consist of an ultrathin skin layer, a tightly packed nodular transition layer and an open-cell, sponge-like substructure. Dry/wet phase-inversion membranes prepared by free-standing evaporation resulted either in high flux and low selectivity membranes or essentially defect-free membranes with fluxes lower than those made by convective evaporation. Dry phase-inversion membranes exhibited extremely low gas fluxes due to thick (17.5 μm) skin layers. On the other hand, wet phase-inversion membranes showed O\textsubscript{2}/N\textsubscript{2} selectivities <1, indicating that gas transport was determined by pore flow through skin layer defects.

19.3.2.3 Silicon Polymers
Silicon polymers such as poly(dimethyl siloxane) and poly[1-(trimethylsilyl)-1-propyne] are selected because of their high permeability and high permselectivity. Copolymerization of these polymers, blending and compositing with them are applied to get high membrane performance.
A thin SiO<sub>x</sub> selective surface layer was formed on a series of cross-linked poly(dimethylsiloxane) (PDMS) membranes by exposure to ultraviolet (UV) light at room temperature in the presence of ozone. The conversion of the cross-linked polysiloxane to SiO<sub>x</sub> was monitored by attenuated total reflectance FTIR spectroscopy, X-ray photoelectron spectroscopy, energy-dispersive X-ray microanalysis, contact angle analysis, and atomic force microscopy. The conversion of the cross-linked polysiloxane to SiO<sub>x</sub> increased with UV–ozone exposure time and cross-linking agent content, and the surface possesses highest conversion. The formation of an SiO<sub>x</sub> layer increased surface roughness, but it decreased water contact angle. Gas permeation measurements on the UV–ozone-exposed PDMS membranes documented interesting gas separation properties: the O<sub>2</sub> permeability of the cross-linked PDMS membrane before UV–ozone exposure was 777 Barrer, and the O<sub>2</sub>/N<sub>2</sub> selectivity was 1.9; after UV–zone exposure, the permeability decreased to 127 Barrer while the selectivity increased to 5.4. The free-volume depth profile of the SiO<sub>x</sub> layer was investigated by novel slow positron beam. The results showed that free-volume size increased with the depth, yet the degree of siloxane conversion to SiO<sub>x</sub> does not affect the amount of free volume [38].

19.3.3 Blend, Composite and Hybrid Membranes

The separation of hydrocarbons from permanent gases is of considerable importance in the chemical industry. Poly(1-trimethylsilyl-1-propyne) (PTMSP) is extremely permeable to hydrocarbons and has high hydrocarbon/permanent gas selectivity. However, the poor chemical resistance of this material limits its use as a membrane for industrial applications. To overcome this problem, Morisato et al. studied an alternative acetylene-based polymer, poly(4-methyl 2-pentyne) (PMP), which exhibits much better chemical resistance than PTMSP. Several types of nonporous, nanosized, fumed silica fillers were incorporated in PMP to manipulate the molecular polymer chain packing. The pure and mixed gas permeation properties of the PMP–silica hybrid membranes were studied. The gas permeability and the hydrocarbon/permanent-gas selectivity increased simultaneously with increasing filler content. The n-butane/methane selectivity was 13 for pure PMP, but increased to 26 for 45 wt% silica-filled PMP. In addition, the n-butane permeability also increased three- to fourfold. Therefore, the silica-filled hybrid PMP membrane showed completely opposite gas permeation behaviour to that of conventional polymers filled with nonporous inorganic nanoparticles [39].

The preparation of gas separation hollow fibres based on polyethersulfone (PES) Sumikaexcel and polyimide Matrimid 5218 blends, for three different compositions (i.e. PES/polyimide: 80/20, 50/50 and 20/80 wt%), was reported by Kapantaidakis and Koops [40]. The dry/wet spinning process was applied to prepare asymmetric hollow fibres by using blends of two different polymers with a common solvent. Dope viscosity measurements were performed to locate the blend concentrations where significant chain entanglement occurs. Cloud-point measurements were carried out to estimate the tolerance of both pure components and blends in water. SEM was used to investigate the morphological characteristics and the structure of asymmetric hollow fibres. The permeation rates of CO<sub>2</sub> and N<sub>2</sub> were measured by the variable pressure method. In all cases, hollow fibres exhibited a typical asymmetric structure with a dense skin layer and a finely porous substructure. Macroporosity in the membrane substructure were observed only for the fibres spun at high PES concentration (80 wt%). After coating with a silicone rubber solution, the hollow fibres developed exhibited a CO<sub>2</sub> permeance varying from 31 to 60 gas permeation units and a CO<sub>2</sub>/N<sub>2</sub> selectivity varying from 40 to 35 at room temperature. The thickness of the skin layer, which corresponds to these permeation rates, varied from 0.1 to 0.15 μm. The effect of air-gap distance on hollow fibres structure and permeation performance was examined. The aforementioned permeation properties establish PES–polyimide hollow fibres as excellent candidate membranes for the separation of gaseous mixtures in industrial level.
Carbon molecular sieving membranes were prepared from a polymer blend of polyphenylene oxide (PPO) and polypyrrolidone (PVP) as thermally stable and labile polymers respectively. The permeation results for the carbon membranes derived from the polymer blends of PPO–PVP showed that the transport of gas species was affected by the molecular sieving effect and that the permeation performances had a strong dependency upon the pyrolysis temperature and PVP molecular weight. The PPO–PVP-derived carbon membranes with lower PVP molecular weight than 40,000 showed decreased gas permeances and increased permselectivities due to a decrease in the pore structure. Meanwhile, it was observed that gas permeance for the carbon membranes of higher molecular weights than 40,000 increased due to the enhanced diffusional pathways in the thermally labile polymer region. Lee et al. considered that the introduction of the thermally labile polymer leads to control of the pore structure through the permeation results for the carbon membrane derived from the PPO–PVP and that the permeance performance was affected by the molecular weight and pyrolysis temperature [41].

MMMs are based on polymeric membranes filled with inorganic particles as a means to improve their gas separation performance [42]. In the study by Ahn et al., MMMs were prepared from polysulfone containing embedded nonporous fumed silica nanoparticles and the gas permeation properties of the resulting membranes were investigated. Physical properties such as film density, thermal degradation and glass transition temperature of polysulfone–silica MMMs were characterized. The distribution of the silica nanoparticles in polysulfone was observed by transmission electron microscopy and SEM. Furthermore, the interface between the polymer and silica agglomerates was studied in relation to the gas transport properties. The gas permeabilities of H₂, He, O₂, N₂, CH₄ and CO₂ were measured as a function of silica volume fraction, and diffusion and solubility coefficients were determined by the time-lag method. The effect of silica nanoparticles in polysulfone membranes on gas permeability was in contrast with predictions based on the Maxwell model. The O₂ permeability was approximately four times higher and CH₄ permeability was over five times greater than in a pure polysulfone membrane. However, the performance comprising permeability versus selectivity of polysulfone–silica MMMs for O₂/N₂ and CO₂/CH₄ follows a similar slope to that of the trade-off upper bound with increasing silica content.

Carbon hollow-fibre membranes derived from polymer blend of polyetherimide and PVP were extensively prepared through stabilization under air atmosphere followed by carbonization under N₂ atmosphere by Salleh and Ismail [43]. The effects of the PVP compositions on the thermal behaviour, structure and gas permeation properties were investigated thoroughly by means of differential scanning calorimetry, thermogravimetric analysis, X-ray diffraction and pure gas permeation apparatus. The experimental results indicated that the transport mechanism of small gas molecules of N₂, CO₂ and CH₄ is dominated by the molecular sieving effect. The gas permeation properties of the prepared carbon membranes have a strong dependency on PVP composition. The carbon membranes prepared from polymer blends with 6 wt% PVP demonstrated the highest CO₂/CH₄ and CO₂/N₂ selectivities of 55.33 and 41.50 respectively.

A cross-linking agent containing silicon–hydrogen bonds and trimethoxysilicon groups was synthesized by a silicon–hydrogen addition reaction. Based on a convenient and mild sol–gel process as well as cross-linking reaction, a siloxane–PDMS hybrid membrane containing fluorinated side-chains was also prepared by using 13-fluorinated triethoxysilane and PDMS containing a vinyl group as matrix materials. The chemical structure, microstructure and mechanical properties of the hybrid membrane were characterized. The effects of gas pressure difference, temperature and fluorine content on permselectivity of the hybrid membrane were investigated. The results showed that the membrane had better membrane-forming and high permeability as well as selectivity than normal PDMS membranes. The oxygen permeability coefficient was 602 Barrer and oxygen/nitrogen separation
factor was up to 3.47. The permeation properties of the fluorinated hybrid membrane are higher obviously than those of Robeson’s upper bound and of unfluorinated PDMS membrane. Both a high permeability and a high selectivity of the hybrid membrane may be attributed to the introduction of fluorine atoms into the PDMS membrane, the cross-linking network of the molecule structure and the mild sol–gel process [44].

19.3.4 Membranes from Organic–Inorganic Hybridization

Selective gas permeation of porous organic–inorganic hybrid membranes via the sol–gel route and its thermal stability were reported by Okui et al. [45]. Separation performance of the hybrid membrane was improved compared with porous membranes governed by Knudsen flow, and gas permeability was still much higher than that through nonporous membranes. Additionally, it was shown that these membranes were applicable at higher temperatures than organic membranes. SEM observation demonstrated that the thin membrane was crack free. Nitrogen physisorption isotherms showed the pore size was in the range of nanometres. Gas permeability through this membrane including a phenyl group was around $10^{-8}$ cm$^3$ (STP) cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$ at 25 °C. The ratios of O$_2$/N$_2$ and CO$_2$/N$_2$ were 1.5 and 6.0 respectively, showing the permeation was not governed by Knudsen flow. The permeability decreased as the temperature increased. Furthermore, the specific affinity between gas molecules and surface was observed not only in the permeation data of the hybrid membranes but also in the physisorption data. These results suggested that the gas permeation through the hybrid membrane was governed by the surface flow mechanism. Thermal analysis indicated that these functional groups were still stable at higher temperatures. The phenyl group especially remained undamaged even at 400 °C.

Liu et al. patented an invention for cross-linked membranes and in particular for cross-linked poly(ethylene oxide)–CA–silsesquioxane (PEO–CA–Si) organic–inorganic hybrid membranes and their use in gas separation. These cross-linked PEO–CA–Si membranes were prepared by in-situ sol–gel co-condensation of cross-linkable PEO–organotrialkoxysilane and CA–organotrialkoxysilane polymers in the presence of acetic acid catalyst during the formation of membranes. The cross-linkable PEO– and CA–organotrialkoxysilane polymers were synthesized via the reaction between the hydroxyl groups on PEO (or on CA) and the isocyanate on organotrialkoxysilane to form urethane linkages under mild conditions. The cross-linked PEO–CA–Si membranes exhibited both increased selectivity of CO$_2$/N$_2$ and CO$_2$ permeability compared with a CA membrane, suggesting that these membranes are very promising for gas separations such as CO$_2$/N$_2$ separation [46].

Bis(triethoxysilyl)methane (BTESM), which consists of Si–C–Si bonds, was used as a membrane precursor to control the size of amorphous silica networks. The single-gas permeation characteristics of hybrid silica membranes were examined by Kanezashi et al. to determine the effect of silica precursors on amorphous networks. Pore size distribution, as determined by single-gas permeation, suggested that average pore size was in the following order: bis(triethoxysilyl)ethane-derived silica > BTESM-derived silica > tetraethoxysilane-derived silica, due to differences in the minimum units of the silica precursor. The high C$_3$H$_6$–C$_3$H$_8$ separation performance of BTESM-derived silica membranes in a wide temperature range (50–200 °C) can be due to the control of silica network size by the ‘spacer;’ method using an Si–C–Si unit. For example, a BTESM-derived silica membrane showed a high C$_3$H$_6$ permeance of $6.32 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ with a C$_3$H$_6$/C$_3$H$_8$ permeance ratio of 8.8 at 50 °C. The order of C$_3$H$_6$ and C$_3$H$_8$ permeances of BTESM-derived silica membranes was C$_3$H$_6$ > C$_3$H$_8$, independent of the number of sol coats and temperature (50–200 °C), although the kinetic diameter of C$_3$H$_6$ ($d_k = 0.45$ nm) was reported to be larger than that of C$_3$H$_8$ ($d_k = 0.43$ nm). For permeation of hydrocarbons through amorphous silica membranes, it is suggested that the kinetic
diameter, which is a minimum equilibrium cross-sectional diameter, is not applicable for effective molecular size, probably because diffusivity depends not only on the minimum cross-section but also on molecular length [47].

19.4 Membranes from Inorganic Materials

19.4.1 Metal Membranes


Dense, metal membranes are being considered for the separation of hydrogen from gas mixtures. Palladium (Pd) and its alloys are the dominant material used, due to its high solubility and permeability for hydrogen. Pd, however, is expensive. One alternative is to coat a thin layer of Pd on a tantalum or vanadium support film. Alternatives to Pd and less expensive are tantalum and vanadium, which are also quite permeable to hydrogen. Recent focus is on supported thin metallic membranes with thickness ranging from submicrometre to a few tens of micrometres. The advantages include reduced material costs, improved mechanical strength and possibly higher flux. The main developments have been the production of composite Pd membranes for use in catalytic membrane reactors (CMRs). This development is based on the concept of process intensification, one important aspect of which is the potential for combining the reaction and separation stages of a process in one unit. One such application is the CMR. Apart from the benefit inherent in cost reduction of plant and maintenance, there is also the potential attainment of higher conversions and product yields. The composite Pd membrane used in the CMR is composed of a thin layer of Pd, or Pd alloy, deposited onto a porous substrate, such as a ceramic or stainless steel. The composite Pd membrane is placed adjacent to a catalyst bed and effects the selective removal of hydrogen from the catalytic reaction source. Another application is the use of these membranes to control the feed rate during partial oxidation reactions (e.g. addition of hydrogen). A major problem associated with metal membranes is the surface poisoning effects (e.g. by a carbon-containing source), which can be more significant for thin metal membranes.

19.4.2 Ceramic Membranes

Ceramic membranes (see http://en.wikipedia.org/wiki/Ceramic_membrane) are a type of artificial membrane made from inorganic materials (such as alumina, titania, zirconia oxides, silicon carbide or some glassy materials). They are used in membrane operations. By contrast with polymeric membranes, they can be used in separations where aggressive media (acids, strong solvents) are present. They also have excellent thermal stability, which makes them usable in high-temperature membrane operations. Like polymeric membranes, they are either dense or porous.

Kamarudin et al. [52] introduced a shortcut in the method of design for a tubular ceramic membrane (TCM) for gas separation. Generally, it explains the permeation of the multicomponent gas using crossflow models in a porous membrane and the surface area of the membrane required. The novel aspect of this method is that the expression for the length of the membrane is simplified to a number unit (NTU) and a height of transfer unit (HTU). The HTU term for porous membranes is characterized by the physical properties of the membrane; the feed flow rate $n_F$, membrane thickness $l_M$, feed pressure $P_F$, $K$ the permeability of gas and the diameter of the membrane $D_M$. The integral for NTU of a porous membrane is the solution for the local permeate along the length of the membrane.
It is found that NTU mainly depends on the rejection stream $x_R$ along the membrane and it describes the relative degree of separation. The proton electrolyte membrane fuel cell (PEMFC) system is used as the case study. CO is the main culprit in reducing the performance of the PEMFC and will act as a catalyst poison for the fuel cell anode at a concentration as low as 100 ppm. Thus, the reformate, from primary reforming, contains a significant amount of CO and must be purified. The effect of some important parameters, such as temperature, pressure and the thickness of membrane, on the degree of separation are presented in this paper. From the results, it can be seen that the system could reduce the CO concentration from 2000 to 500 ppm. Basically, the TCM will operate, in series, with a pressure swing adsorber in order to further reduce the concentration of CO to less than 10 ppm before entering the fuel cell stack. However, this paper only focuses on the design of the TCM. Besides this, it is observed that the purity of the hydrogen increased from 72.8 to 96% (at $\theta = 0.5$) after the membrane. This paper presents the state of the art of ceramic membranes for gas separation, particularly for the separation of hydrogen from process streams. It includes an overview of recent literature and reveals the best types of membranes for hydrogen separation, with the strong and weak points as well as key players based on patent positions. Hollow-fibre ceramic membrane technology at CEPAration is also presented [53].

19.4.3 Zeolite Membranes

Methods that have been developed for the preparation of zeolite membranes are as follows [50]:

1) **Zeolite-filled polymeric membranes** One of the most direct methods of preparation of zeolite-containing membranes is to embed zeolite crystals in a matrix. Sealing the gaps between zeolite crystals with a gas-tight matrix can provide a membrane configuration [51,52].

2) **Free-standing zeolite membranes** For molecular sieving applications, dense, pin-hole free zeolite membranes with limited thickness (<1 mm) would be an ideal configuration. Such membranes have been grown on temporary supports like Teflon and cellulose or at the interface between two phases [51,52].

3) **Supported zeolite membranes** The most frequently used and probably the most promising seem to be the so-called composite membranes. This type of membrane is prepared by in-situ hydrothermal synthesis. A relatively thin zeolite layer is crystallized on the surface or in the pores of a pre-shaped porous support. Among different types of inorganic materials, like ceramics, metal glasses, carbon used as supports, porous alumina has been the most popular for these preparations. Zeolite-containing composite membranes have been prepared by a vapour-phase transport method. The zeolite layer in this case is prepared by conversion of a previously deposited silica or silica–alumina layer under joint action of vapours containing water and a structure-directing agent [53].

The zeolite type prepared most often as a membrane is MFI, which is interesting for industrial applications with its suitable pore diameter, high thermal and chemical stability, easy synthesis and modification of the chemical composition. The experience gained in the preparation of MFI and other zeolitic membranes has shown that as well as the pin-holes there are many factors critical for the performance of the composite membranes. Some of them are (i) the adhesion of the zeolite layer on the support surface, (ii) the difference of the thermal expansion coefficients of support and zeolite, (iii) the orientation of zeolite crystals, (iv) the thickness of the zeolite layer, (v) the anisotropy of mass transport due to an anisotropic pore geometry and (vi) the influence of crystal boundaries on the permeation properties.
19.4.4 Carbon Membranes

Carbon molecular sieve membranes (CMSMs) are inorganic membranes capable of withstanding high temperatures and harsh chemical conditions due to their ‘inert’ inorganic carbon matrix. Furthermore, CMSMs combine high selectivities with high permeabilities, when compared with dense inorganic membranes. CMSMs present a narrow pore size distribution with selective pores (constrictions) in the range of 0.3–0.5 nm, responsible for the molecular sieving properties of the membranes. These constrictions allow the passage of smaller permeants in detriment to bulkier permeants, which are retained. The preparation of such membranes involves several steps, the more important being the selection and preparation of the precursor and the pyrolysis step.

19.5 Modules of Gas Separation Membrane

Gas separation membranes are typically contained in one of three modules [16]:

1) Plate-and-frame module constructed like a plate-and-frame heat exchanger.
2) Spiral-wound bundles in a metal module.
3) Hollow-fibre bundles in a metal module.

19.6 Technology of Gas Permeation Membrane

Gas separation membranes are employed in the following fields [54]:

1) Separation of N₂ or O₂ from air (generally only up to 99.5%).
2) Separation of H₂ from gases like N₂ and CH₄.
3) Recovery of H₂ from product streams of ammonia plant.
4) Recovery of H₂ in oil refinery processes.
5) Separation of CH₄ from the other components of biogas.
6) Enrichment of air by O₂ for medical or metallurgical purposes.
7) Enrichment of ullage by N₂ in inerting systems designed to prevent fuel tank explosions.
8) Removal of water vapour from natural gas and other gases.
9) Removal of SO₂, CO₂ and H₂S from natural gas (polyamide membranes).
10) Removal of volatile organic liquids from air of exhaust stream.

19.6.1 Hydrogen Separation

See the article by Phair and Badwal [55].

Separation membranes are already being used for the separation of H₂ and N₂ in ammonia production and for separating H₂ from hydrocarbons in petrochemical plants [56]. Hybrid membrane reactors combining H₂ separation membranes with a water-gas shift reactor can drive the equilibrium of the water-shift reaction forward (e.g. in coal gasification, methane partial oxidation or steam reforming processes), thereby increasing the H₂ yield and resulting in significant cost reductions in the generation of H₂. For instance, an H₂ separation membrane reactor integrated for the steam reforming of
CH₄ would not only increase methane to H₂ conversions at lower operating temperatures (250–400 °C), but also reduce steam consumption.

Pd-based alloys with yttrium, copper, ruthenium or indium additions were investigated by Burkhanov et al. Their specific H₂ permeability, strength, linear thermal expansion in H₂ and corrosion resistance in a number of gas media were determined. This allowed effective membrane elements to be developed using membranes made from these alloys, which are used for the separation of high-purity H₂ from H₂-containing gas mixtures. Membrane elements with 93.5 wt% Pd–6 wt% indium–0.5 wt% ruthenium alloy membranes were developed by the authors’ research group, and their technical characteristics were described [57].

Diestel et al. [58] prepared three ‘neat’ supported membranes, ZIF-8, ZIF-90 and Matrimid 5218, on porous alumina disks and compared their permeation behaviours in the separation of H₂–CO₂ with the corresponding zeolitic imidazolate framework (ZIF)–Matrimid MMMs. These MMMs consist of ZIF-8 and ZIF-90 nanoparticles embedded in Matrimid. They found that the embedding of the nanoparticles modifies the separation performance of the Matrimid 5218 membrane for separating H₂ from CO₂. Transmission electron microscopy and SEM images of the ZIF-8 and ZIF-90–Matrimid MMMs show that the ZIFs are well embedded into the polymer. Thus, the separation behaviour of these MMMs can be described with the Maxwell model. However, better separation results could be obtained by binding ZIF-90 particles covalently with ethylenediamine to the Matrimid matrix. In comparison with the MMMs that contain nonbound ZIFs, the covalent amine binding between the ZIF-90 particles and the Matrimid matrix leads to slightly lower permeabilities but a much higher H₂/CO₂ separation factor.

19.6.2 Oxygen Production

See the article by Phair and Badwal [55].

O₂ separation membranes offer a simpler and flexible alternative, and there is an increasing global interest in such membrane-based conducting materials. These membranes can be used for separating O₂ from air or in syngas production, by combining O₂ generation with the partial oxidation of CH₄ in a single reactor [59–61]. Such membranes have also been considered for the production of H₂ by the electrolysis of steam [62].

Composite membranes composed of gadolinium-doped cerium oxide (Ce₀.₉Gd₀.₁O₂−δ, denoted CGO) as the main oxygen ion carrier and lanthanum strontium ferrite ((La₀.₆Sr₀.₄)₀.₉₈Fe₀.₀₂O₃−δ, denoted as LSF) as electronic conductor were fabricated and tested. A composite film (15 μm) was deposited on a bilayer tube consisting of a porous magnesium oxide support coated with a thin CGO layer. On top of the dense membrane layer another porous CGO layer was deposited. The CGO layers act as backbones for infiltration with a suitable catalyst that can facilitate the surface exchange processes on the membrane. Composite membranes (where no catalysts were infiltrated in the CGO layers) were tested and demonstrated oxygen fluxes close to 1 mL min⁻¹ cm⁻² at 900 °C when flowing air on one side and a gas with an oxygen partial pressure of log pO₂ = −2 on the other side of the membrane. Work is also ongoing to characterize membrane performance in the presence of different infiltrated catalysts [63].

Amorphous, high glass transition, cross-linkable poly(arylene ether)s for gas purification membranes were synthesized by Sundell et al. The polymers included a moiety capable of several oxidation reactions and UV cross-linking. Structural identification was confirmed by ⁱH nuclear magnetic resonance and infrared spectroscopy and molecular weights were determined by size exclusion chromatography. Two oxidation reactions of the polymers were identified, one by chemical treatment using
Oxone and KBr and one by elevated thermal treatment in air. Differential scanning calorimetry and thermogravimetric analysis were used for thermal characterization, and thermogravimetric analysis, $^1$H nuclear magnetic resonance and attenuated total reflectance FTIR revealed the progress of the thermal oxidation reactions. Both polymers produced tough, ductile films, and the gas transport properties of the non-cross-linked linear polymers and cross-linked polymer were compared. The O$_2$ permeability of one exemplary non-cross-linked poly(arylene ether) was 2.8 Barrer, with an O$_2$/N$_2$ selectivity of 5.4. Following UV crosslinking, the O$_2$ permeability decreased to 1.8 Barrer, and the O$_2$/N$_2$ selectivity increased to 6.2 [64].

19.6.3 Carbon Dioxide Separation

See the article by Phair and Badwal [55].

Separation membranes continue to offer considerable advantages for process integration, ease of operation and have a smaller environmental impact than other separation techniques, which often result in pollutant by-products (e.g. spent adsorbents, contaminated solutions and solids) requiring costly treatment and removal. Currently, membranes are being considered for separating CO$_2$ from natural gas.

Carbon molecular sieve (CMS) hollow-fibre membranes were investigated for CO$_2$/CH$_4$ separation. High-pressure (up to 1000 psia), mixed-gas feeds of 10% CO$_2$–90% CH$_4$ on the shell side were examined for three different temperatures (24, 35 and 50 °C). The mechanical, permeance and selectivity stabilities of the CMS membranes under high pressure were encouraging and could be industrially relevant for many high-pressure applications, such as CO$_2$ removal from natural gas. Two asymmetric polyimide precursor fibres, 6FDA–BPDA–2,4,6-trimethyl-1,3-phenylene diamine and Matrimid 5218, were pyrolysed under vacuum to form the CMS membrane fibres. When pyrolysed under identical protocols, the two types of CMS fibres had different permeation properties and physical characteristics. Modifications of the pyrolysis protocol and conditions were explored. Increasing the final pyrolysis temperature was shown to dramatically increase the CO$_2$/CH$_4$ selectivity (>600) of the CMS membranes but was detrimental to the CO$_2$ permeance. On the other hand, using a helium purge gas instead of a vacuum environment during pyrolysis did increase CO$_2$ permeance but resulted in a significant loss of CO$_2$/CH$_4$ selectivity. Shortening the thermal soak time at the final pyrolysis temperature was the most effective approach to increasing the CO$_2$ permeance while maintaining the CO$_2$/CH$_4$ selectivity [65].

Hill and co-workers [66] conducted an extensive study to investigate the effects of nonsolvent (methanol, ethanol, 1-propanol and 1-butanol) pretreatment of polyimide precursor before carbonization on membrane structure and on the separation performance of CMSMs. The measured gas separation properties show that carbon membranes prepared with nonsolvent pretreatment have a lower flux and higher selectivity, suggesting a narrower pore size distribution. X-ray diffraction data show a slightly smaller d spacing in pretreated CMSMs. Positron annihilation lifetime spectroscopy results indicated smaller pores in the CMSMs pretreated with nonsolvents. The best separation efficiency was obtained by carbon membranes pyrolysed from ethanol-treated polymers. The CO$_2$/CH$_4$ selectivity of Matrimid- and P84-derived carbon membrane increases significantly from 61 to 169 and 89 to 139 respectively after ethanol pretreatment compared with those carbon membranes when untreated. This study demonstrated for the first time that nonsolvent pretreatment of polyimide precursors can play an essential role in the transport properties of high-performance CMSMs.

Permeability coefficients for pure CO$_2$, pure CH$_4$, and CO$_2$–CH$_4$ mixtures containing 50% CO$_2$ were reported for a polyimide synthesized from 3,3′-dihydroxy-4,4′-diamino-biphenyl and 6FDA and for three thermally rearranged (TR) derivatives thereof. Permeability measurements were made
at 35 °C for fugacities ranging from 4 to 25 atm. The permeability of CO₂ and CH₄ increased as the degree of TR conversion increased. For example, CO₂ permeability at 10 atm increased by a factor of 30 between the unconverted polyimide and its TR analogue converted at 450 °C. In pure-gas experiments, CO₂ was observed to plasticize the unconverted polyimide, but it did not appear to plasticize the TR polymers. In mixed-gas experiments, dual-mode competitive sorption caused a depression in CH₄ permeability, with very little change in CO₂ permeability. In addition, plasticization by CO₂ was evident in the CH₄ mixed-gas permeability trends, but its impact was small in contrast with dual-mode competitive effects. Consequently, CO₂/CH₄ mixed-gas permeability selectivity was higher than the ideal selectivity, calculated as the ratio of pure gas permeability coefficients. The dual-mode sorption and permeation model was fit to the experimental data. Dual-mode model parameters and model predictions were reported, along with their confidence intervals. By comparing the dual-mode model predictions with the experimental mixed-gas data, the degree of CO₂-induced plasticization was observed to decrease as the degree of TR conversion increased and was completely absent (within experimental uncertainty) for the TR polymer converted at 450 °C [67].

19.6.4 Helium Separation

Helium purification has become more important for increasing demands in scientific and industrial applications. Hu et al. [68] demonstrated that porous silicene can be used as an effective ultimate membrane for helium purification on the basis of first-principles calculations. Pristine silicene monolayer is impermeable to helium gas with a high penetration energy barrier (1.66 eV). However, porous silicene with either Stone–Wales (SW) or divacancy (555, 777 or 585) defect presents a surmountable barrier for helium (0.33 to 0.78 eV) but formidable for neon (Ne), argon (Ar) and other gas molecules. In particular, the porous silicene with divacancy defects shows high selectivity for He/Ne and He/Ar, superior to graphene, polyphenylene and traditional membranes.

The permeability–selectivity upper bounds show that perfluoropolymers have uniquely different separation characteristics than hydrocarbon-based polymers. For separating He from H₂ these differences are particularly dramatic. At a given He permeability, the upper bound defined by perfluoropolymers has He/H₂ selectivities that are 2.5 times higher than that of the upper bound defined by hydrocarbon-based polymers. Robeson and co-workers hypothesized that these differences in transport properties resulted from the unusual sorption relationships of gases in perfluoropolymers compared with hydrocarbon-based polymers, and their paper seeks to test this hypothesis experimentally. To do so, the gas permeability, sorption and diffusion coefficients were determined at 35 °C for H₂ and He in a series of hydrocarbon-, silicon- and fluorocarbon-based polymers. Highly or completely fluorinated polymers have separation characteristics above the upper bound for He/H₂ separation because they maintain good diffusivity selectivities for He over H₂ and they have He/H₂ sorption selectivities much closer to unity than those of hydrocarbon-based samples. The silicon-based polymer had intermediate sorption selectivities between those of hydrocarbon-based polymers and perfluoropolymers. Comparisons of H₂ and He sorption data in the literature more broadly extend the conclusion that He/H₂ sorption selectivity is rather different in hydrocarbon and fluorocarbon-based media [69].

19.6.5 Methane Production

A membrane-based process was applied to simultaneously reclaim CH₄ and generate reused water from raw domestic wastewater. The system was comprised of an up-flow anaerobic sludge fixed bed (UAFB), an anoxic sink (AS) and an aerobic membrane bioreactor (MBR). The hydraulic retention time (HRT) of UAFB (HRT$_U$) was gradually shortened from 8 h to 6 h, 3 h and to 1 h, while the HRT of
the AS and MBR remained at 8 h. It was found that $HRT_U$ of 3 h was more suitable for the balancing production of biogas and volatile fatty acids, and the volatile fatty acids served as a carbon source for denitrification. The transmembrane pressure of the MBR kept lower than 0.04 MPa without wash or change of membrane sheet; however, SEM analysis indicated that microbes attached to the inner surface of the membrane, causing irreversible fouling after 133 days of operation. The denaturing gradient gel electrophoresis profiles of amplified 16S rDNA gene fragments proved that more functional bacteria and higher microbial diversity emerged at $HRT_U$ of 3 h and 1 h. Most bacteria belonged to Betaproteobacteria and were responsible for carbon and nitrogen removal [70].

The capability of functionalized graphene nanopores to efficiently separate CH$_4$ from air was analysed using density functional theory. Hauser and Schwerdtfeger [75] studied the interaction between selected gas molecules and two finite model pores. Saddle-point energies of the activated complexes were used to estimate transmission probabilities and selectivities as a function of temperature. They accounted for geometry distortions caused by the transient gas molecules and discussed the applicability and limitations of descriptions based on ‘molecular size’ for the judgement of quasi-two-dimensional membranes.

### 19.6.6 Separation of Some Gases

Zeolite T membranes were prepared by hydrothermal synthesis on porous mullite tubes seeded with zeolite T crystals, using milk-like aluminosilicate gel with a molar composition of SiO$_2$ : Al$_2$O$_3$ : Na$_2$O : K$_2$O : H$_2$O of 1 : 0.05 : 0.26 : 0.09 : 14. A zeolite T crystal layer of about 20 μm in thickness was formed on the outer surface of the support after the synthesis at 373 K for 30 h. Single-gas and mixed-gas permeation experiments through zeolite T membranes were carried out by a vacuum method at 303–473 K using He, H$_2$, CO$_2$, O$_2$, N$_2$, CH$_4$, C$_2$H$_6$ and C$_3$H$_8$ single-component gases and CO$_2$–N$_2$, CO$_2$–CH$_4$ and other CO$_2$–hydrocarbon mixtures. In single-gas permeation experiments, with increasing kinetic diameter from 0.33 nm for CO$_2$ to 0.43 nm for C$_3$H$_8$, the gas permeance decreased by four orders in magnitude, indicating a kind of molecular sieving behaviour for the zeolite T membranes prepared in this study; that is, they had few defects and their permeation behaviour was controlled by zeolitic pores of erionite. Permeance of CO$_2$ was much higher than those of N$_2$ and CH$_4$ and the ideal selectivities for CO$_2$/N$_2$ and CO$_2$/CH$_4$ were 31 and 266 respectively at 343 K. In mixed-gas permeation experiments, zeolite T membranes showed high selectivities for CO$_2$/N$_2$ and CO$_2$/CH$_4$ pairs of 107 and 400 respectively at 308 K. The selectivity $\alpha$ decreased with an increase in temperature, but was still at a high level of 20 and 52 for CO$_2$/N$_2$ and CO$_2$/CH$_4$ respectively even at 473 K. This was due to the synergetic effects of competitive adsorption of CO$_2$ and molecular sieving of zeolitic pores. Because of the increasing effect of single-file diffusion, the selectivities for CO$_2$/C$_2$H$_6$ ($\alpha = 61$) and CO$_2$/C$_3$H$_8$ ($\alpha = 17$) were rather low [72].

### 19.6.7 Olefin–Paraffin Separation

Tests with mixture of gases were carried out at room temperature (30 ± 2 °C) to determine selectivities and permeabilities of propylene and propane. The ideal selectivities of the membranes towards the olefin were also evaluated. Metal-incorporated poly(2,6-dimethyl-1,4-phenylene-oxide) membrane was used for facilitating transport of the olefin through the membranes. The metals incorporated were silver (Ag(I)), Pd (Pd(II)), ruthenium (Ru(III)) and iridium (Ir(III)). Poly(2,6-dimethyl-1,4-phenylene-oxide) showed high ideal selectivities with respect to propylene. Among the metal-incorporated poly (2,6-dimethyl-1,4-phenylene-oxide) membranes, significantly improved flux and selectivity were obtained, especially for Ru(III) and Pd(II). Pd–poly(2,6-dimethyl-1,4-phenylene-oxide) membranes
exhibited twofold improvement in propylene permeance with improved selectivity from 3.44 to 5.33. The membranes were characterized by FTIR spectroscopy, inductively coupled atomic emission spectroscopy, wide-angle X-ray diffraction and density measurements to understand the structural characteristics of the membrane responsible for the observed behaviour. From IR results the metals, particularly Ru, Pd, Ag and Ir, were found to interact with the polymer. The improved selectivity values of the metal-incorporated polymers was explained by a decrease in the effective distance $d_{eff}$ between the adjacent intersegmental chains due to formation of metal-ion complex with the polymer matrix and hence a decrease in the free volume of the polymer upon metal incorporation. However, the significant improvements in the propylene permeabilities were realized mainly due to the selective transport of propylene molecules mediated by the incorporation of selected metal ions [73].

The effect of pressure on solubility and the influence of temperature on solubility, permeability and diffusivity of C$_3$F$_8$ and its hydrocarbon analogue C$_3$H$_8$ were reported in rubbery PDMS and glassy PTMSP [74]. The solubility of C$_3$F$_8$ is lower than that of C$_3$H$_8$ in both polymers at all temperatures and pressures investigated. The isosteric enthalpy of mixing C$_3$F$_8$ with PDMS and PTMSP is higher than that of C$_3$H$_8$ due to less favourable polymer–fluorocarbon interactions in the case of C$_3$F$_8$, and it decreases with increasing C$_3$F$_8$ concentration. Assuming a coordination number of 10, the energy associated with mixing C$_3$F$_8$ molecules and PDMS segments is 4.5 kJ mol$^{-1}$ more than that required to mix C$_3$H$_8$ molecules with PDMS segments, in the limit of infinite dilution. The isobaric activation energy of permeation $E_P$ for C$_3$F$_8$ is positive for both polymers, and that for C$_3$H$_8$ is negative in both polymers. This result is particularly interesting for PTMSP since all previous studies of activation energy of gas permeation in PTMSP report values that are near zero or negative; this study provides the first report of a positive $E_P$ value in PTMSP. In PDMS, differences in both activation energy of diffusion $E_D$ and enthalpy change on sorption contribute significantly to the difference in $E_P$ values of C$_3$H$_8$ and C$_3$F$_8$. For PTMSP, the difference in $E_P$ values for C$_3$F$_8$ and C$_3$H$_8$ stems mainly from a substantially larger $E_D$ value for C$_3$F$_8$ than for C$_3$H$_8$.

Previous studies on gas/vapour separations using polymeric membrane contactors have always been accompanied with a membrane stability issue: either a wetting phenomenon or a membrane degradation concern because of extensive contact with the solvent. To possibly overcome these conventional challenges and provide extended stability, the use of a ceramic hollow-fibre membrane contactor was proposed by Faiz et al. where propylene/propane separation using silver nitrate as a carrier was investigated for a continuous period of 6 months. Alumina hollow fibres with asymmetric structures consisting of a spongelike outer layer and a fingerlike inner layer were successfully fabricated, modified, characterized and finally examined for propylene/propane separation. The modification step using silane solutions was critical in improving the membrane hydrophobicity to ensure that no wetting occurred during contact with the solvent. Initial studies on the separation performance confirmed that the membrane module was able to operate in a non-wetting mode, where the observed overall mass-transfer coefficient was the highest. Moreover, the ceramic membrane module proved to be stable throughout continuous experiments up to a period of 2 months, where no decline in the performance was observed. However, beyond this investigation period, deposition of silver on the membrane surface started to appear significantly where the membrane’s appearance becomes dark. This silver deposition seemed to diminish the membrane’s hydrophobicity as it continued to accumulate on the membrane surface, where a slight decline in the separation performance was finally observed by the end of the 6-month period. By exposing the advantages of ceramic membranes over their polymeric counterparts, a novel regeneration method was demonstrated where the membrane module undergoes treatment with strong nitric acid to remove silver deposits, followed by remodification of the membranes with silane solutions to restore its hydrophobicity. The performance of the membrane modules was regained completely.
after regeneration. Thus, this technology can be performed for an extended period without the need to replace the membranes whenever a drop in the performance is observed due to deformation of the membranes, an issue commonly found with polymeric materials [75].

References


The separation and concentration of materials are very important operations with a long history of improvements and diversity. Membranes for separation and concentration possess such characteristics as expediency of operation, advantages in energy, lack of side reactions, a largely functional capacity, and so on, and are very noticeable in a wide variety of fields. Separation membranes that are of practical use in membrane separation technology are applied to reverse osmosis, nanofiltration, ultrafiltration, microfiltration, dialysis, pervaporation, evapomeation, gas permeation, membrane reactor, membrane contactor, fuel cell, energy conversion and storage, and optical resolution. As for these separation membranes, a material in a solution or gas is mainly separated by the physical function of filtration or diffusion, a so-called ‘molecular sieve’ through pores and molecular gaps in the membrane. The separation membrane based on this principle occupies a very important position in practical use, but it is hard to say that this principle is sufficient from the viewpoint of selectivity. Therefore, the aim is one of high efficiency and precision in material transportation and the separation of the biomembrane. In other words, the fact that a biomembrane shows a high selectivity is of great benefit in transportation, and the separation function of the material is significantly dependent on the existence of a carrier having a selective interaction with the material; namely, having a material recognition ability. For the purpose of giving a function with selective transportation to an artificial membrane, studies that adopted a carrier which interacted selectively with a transported material in an artificial membrane system are carried out actively. In carrier transport membranes there are the facilitated transport membranes and the active transport membranes.

20.1 Fundamental Principle of Carrier Transport through Artificial Membranes

Material transport through artificial membranes, in general, is classified into three fundamental types, as shown in Figure 20.1 [1].

20.1.1 Passive Transport

Figure 20.1a is a model for the passive transport that transfers the substrate \( S \) from the left side (L), with high concentration, to the right side (R), with low concentration, according to its concentration...
gradient across the membrane. The concentration gradient of S in the membrane in the passive transport is represented by

\[
\frac{[S]_L - [S]_R}{l} = \frac{K_1}{l} ([S]_L - [S]_R) \tag{20.1}
\]

where \([S]_L\) and \([S]_R\) are the concentrations of S on the interface of the membrane on the L side and the R side, \([S]_L\) and \([S]_R\) the concentrations of S outside the membrane on the L side and the R side, \(l\) the membrane thickness, and \(K_1\) the equilibrium constant of S inside and outside the membrane (\(K_1 = [S]_i/[S]_o\)). The flux of S from the L side to the R side is given by

\[
J_S = \frac{D_s K_1}{l} ([S]_L - [S]_R) \tag{20.2}
\]

where \(J_S\) is the flux of S and \(D_s\) is the diffusion coefficient of S in the membrane. It is easily understood from Equation 20.2 that transport cannot occur since the concentration gradient across the membrane is zero (i.e. \([S]_L = [S]_R\)).

### 20.1.2 Facilitated Transport

In Figure 20.1b, the carrier C in the membrane positively incorporates the substrate S into the membrane by forming a complex CS between C and S. In this transport system, in addition to the passive transport in Figure 20.1a, transport with the formation of complex is added. Consequently, since the transport of material is facilitated, it is called facilitated transport. In such transport, if the carrier can form a complex with a specific substrate, selectively facilitated transport is possible. In both Figure 20.1a and b the substrate could be transported from the high-concentration side (L side) to the low side (R side) but is never transported because the concentrations are equal on the two sides of the membrane.

Under the usual conditions of transport, the concentration of carrier inside the membrane is extremely low compared with that of transported substrate outside the membrane. Also, when the formation of a complex between the transported substrate and the carrier and dissociation of the complex are very fast and transport of the complex in the membrane is the rate-determining step, it is presumed that the concentration of the complex inside the membrane obeys the Michaelis–Menten equation as well as the enzyme reaction. From this discussion, the concentration gradient of a complex inside the membrane in facilitated transport is represented by
\[
\frac{[\text{CS}]_L - [\text{CS}]_R}{l} = \frac{K_2 [\text{C}]_0}{l} \left( \frac{[\text{S}]_L}{1 + K_2 [\text{S}]_L} - \frac{[\text{S}]_R}{1 + K_2 [\text{S}]_R} \right) \tag{20.3}
\]

where \([\text{CS}]_L\) and \([\text{CS}]_R\) are the concentration of the complex on the interfaces of the L and R sides respectively, \([\text{C}]_0\) is the total concentration of carrier (i.e. \([\text{C}]_0 = [\text{C}] + [\text{CS}]\) ), and \(K_2\) is the formation constant of CS.

The flux of S from the L side to the R side is given by

\[
J_S = \frac{D_{\text{CS}} K_2 [\text{C}]_0}{l} \left( \frac{[\text{S}]_L}{1 + K_2 [\text{S}]_L} - \frac{[\text{S}]_R}{1 + K_2 [\text{S}]_R} \right) \tag{20.4}
\]

where \(D_{\text{CS}}\) is the diffusion coefficient of CS in the membrane. As can be seen from Equation 20.4, when the condition

\[
[S]_L \neq [S]_R \tag{20.5}
\]

is maintained, transport similar to passive transport occurs from the higher concentration side of S to its lower-concentration side. However, since the transport condition becomes Equation (20.6), the transport cannot occur because the concentration gradient is zero.

\[
[S]_L = [S]_R \tag{20.6}
\]

The facilitated transport for the substrate due to the existence of a carrier in the membrane can be explained as follows. The relationships between the diffusion fluxes and the chemical potentials for the transported substrate S, carrier C and complex CS are represented by the phenomenological equations

\[
- \nabla \mu_S = L_S J_S
- \nabla \mu_C = L_C J_C
- \nabla \mu_{\text{CS}} = L_{\text{CS}} J_{\text{CS}} \tag{20.7}
\]

where \(\nabla \mu\), \(L\) and \(J\) are the difference in chemical potential, the phenomenological coefficient and the flux for the component respectively.

The formation of complex in the membrane is given by

\[
S + C = \text{CS} \tag{20.8}
\]

The power of interaction for this complex \(I\) is represented by

\[
I = \mu_S + \mu_C - \mu_{\text{CS}} \tag{20.9}
\]

By assuming the steady state:

\[
J_C + J_{\text{CS}} = 0 \tag{20.10}
\]

Since \(J\) is the flux of transported substrate outside the membrane, \(J\) corresponds to the sum of the flux of transported substrate and the flux of the complex inside the membrane:

\[
J = J_C + J_{\text{CS}} \tag{20.11}
\]

When the formation and dissociation of the complex are very fast, the power of interaction \(I\) for the complex is zero:

\[
I = 0 \tag{20.12}
\]
Also, as \( I \) is zero, \( \nabla I = 0 \); therefore:

\[
\nabla \mu_S + \nabla \mu_C - \nabla \mu_{CS} = 0 \tag{20.13}
\]

Equation 20.7 is substituted in Equation 20.13 and then Equations 20.10 and 20.11 are used:

\[
(L_C + L_{CS}) J = (L_S + L_C + L_{CS}) J_S \tag{20.14}
\]

Furthermore, if \( J_S \) in Equation 20.14 is represented by \( \nabla \mu_S \), we obtain

\[
J = -\frac{\nabla \mu_S}{L_S} \left( 1 + \frac{L_S}{L_C + L_{CS}} \right) \tag{20.15}
\]

The value of \(-\nabla \mu_S / L_S\) on the left side of Equation 20.15 corresponds to the diffusion flux in passive transport. Therefore, the amount inside the parentheses in Equation 20.15 implies the increment of transport due to the carrier. Since the phenomenological coefficients \( L_S, L_C \) and \( L_{CS} \) are positive values, it is easily understood from Equation 20.15 that the transport of substrate is facilitated since the carrier exists in the membrane [2].

### 20.1.3 Active Transport

A model of active transport is shown in Figure 20.1c. In this case the substrate is actively transported from the low-concentration side (L side) to the high-concentration side (R side) across the membrane against the concentration gradient between both sides. In this transport form, the substrate \( S \) is transported according to the concentration gradient of the complex \( CS \) in the membrane. This active transport of \( S \) is attributed to the conjugated energy for the transport of the complex \( CS \) between the species \( S' \) on the R side and the carrier \( C \) from the R side to the L side.

The concentration gradient inside the membrane in active transport is represented by

\[
\frac{[CS]_L - [CS]_R}{l} = \frac{K_2[C]_{i0}}{l} \left( \frac{[S]_L}{1 + K_2[S]_L + K_3 [S']_L} - \frac{[S]_R}{1 + K_2[S]_R + K_3 [S']_R} \right) \tag{20.16}
\]

where \( K_3 \) is the formation constant of the complex \( CS \) and \([S']_L\) and \([S']_R\) are the concentrations of \( S' \) on the L and R sides respectively. The flux of the complex \( CS \) is expressed as

\[
J_{CS} = \frac{D_{CS}[C]_{i0}}{l} \left( \frac{[S]_L}{1 + K_2[S]_L + K_3 [S']_L} - \frac{[S]_R}{1 + K_2[S]_R + K_3 [S']_R} \right) \tag{20.17}
\]

Even if transport is begun under the condition expressed in Equation 20.18, it is found from Equation 20.17 that the inequality given in Equation 20.19 holds, and consequently we obtain Equation 20.20:

\[
[S]_L = [S]_R \tag{20.18}
\]

\[
[S']_L < [S']_R \tag{20.19}
\]

\[
J_S > 0 \tag{20.20}
\]

Therefore, \( S \) is actively transported against its concentration gradient from the L side to the R side until the condition

\[
[S]_L - [S]_R + K_2 \left( [S]_L [S']_L - [S]_R [S']_R \right) = 0 \tag{20.21}
\]

is satisfied.
There are two types of active transport, as shown in Figure 20.2 [1]. Figure 20.2a is an antiport (counter transport) for active transport of the species \( S \) and \( S' \). Figure 20.2b is a symport (cotransport) for active transport of the species \( S \) and \( S' \). The active transport of species \( S \) in both cases requires conjugated energy due to the transport of species \( S' \).

## 20.2 Carriers in Membrane Transport

### 20.2.1 Role of Carrier

When we want to transport material selectively by carrier transport, selection of an energy source to transport the material and a carrier to provide selectivity in material transport are very important. Dynamic, electrical, thermal, optical, physical and chemical energies are used as the energy source for active transport. The existence in the membrane of a chemical material that can respond to these energy sources is the most important factor in a carrier transport membrane. That is, this chemical material corresponds to the carrier. For example, when pH changes (i.e. chemical energy) are used as the driving force and the chemical material used as the carrier is changed rapidly and reversibly by the changes in pH, a transported material and the transport species can be transferred to one side, and the transport of material occurs with a volume change of membrane due to membrane swelling and shrinking resulting from the changes in pH.

In active transport the carrier is a medium that transports the material selectively and actively. In the material transport of biomembranes, transport with high selectivity and efficiency is dependent on the existence of a carrier that specifically recognizes the material and on rapid and reversible variation of the carrier as it is supplied with a certain energy. For example, in a biomembrane, barinomysin, nonactin and monensin transport metal ions selectively and efficiently [3].

In Figure 20.3a, which models monensin, this carrier incorporates the metal ion centripetally by moving some of the hydrophobic bonds in the alkaline solution to the outside of the carrier, and releases the metal ion in the acidic solution by changing into a linear structure, as shown in Figure 20.3b. The incorporation of material into a membrane is due to chemical or physical interaction between the material and the carrier, but when such interactions are strong it is very difficult to release the material to the outside of the membrane. Accordingly, to plan for high performance in material transport, the selection of effective transport systems is very important.
transport, a mechanism must be designed for incorporation of material into the membrane and release of material from the membrane. That is, in a carrier transport membrane based on chemical interaction, it is very important to change the mechanism of chemical reaction for incorporation into the membrane and release to the outside of the membrane. Also, in a carrier transport membrane based on physical interaction, it is very important to provide a sufficiently large morphological change in the membrane, such as a change in conformation.

20.2.2 Membranes for Carrier Transport

When selective transport in material concentration or removal is achieved through a membrane having a carrier, the carrier plays an important role, as mentioned earlier. Since selection of the carrier significantly influences membrane performance, it is necessary to select the carrier after the interaction between the carrier and the transported material (the formation of complex), the behaviour of a carrier in the membrane, the physicochemical property of the complex, and so on have been investigated sufficiently.

Artificial carrier transport membranes for material transport are of two types: mobile and fixed. In a mobile carrier membrane the carrier can move freely in the membrane; a liquid membrane corresponds to this type. In a fixed carrier membrane the carrier is fixed on the polymer matrix or included in the polymer matrix and cannot move; a polymer solid membrane is of this type, which is homogeneous, transparent and flexible and usually consists of a base polymer, a carrier and a plasticizer [4]. In some cases the carrier can also act as the plasticizer. The polymer provides mechanical support to the membrane, while the plasticizer increases its flexibility and target solute permeability [5].

The advantages and disadvantages of carrier membranes of the mobile and fixed types are summarized in Table 20.1 [6].

The energy required for the transport of material in a carrier membrane of the fixed type is higher than that in a carrier membrane of the mobile type because the transported material must be transferred onto the fixed carrier with the repetition of adsorptive and desorptive interactions. Since a mobile carrier membrane need not be as thick as a fixed membrane, the energy barrier is advantageous. Furthermore, since a mobile carrier can move freely in a thin membrane, the transport of material is more efficient. However, in a mobile carrier membrane, the transported material, incorporated
in the membrane due to the formation of a complex between the carrier and the material, is released to the outside of the membrane without an exchange of carrier. Therefore, selectivity in material transport depends on a one-time complex formation between the carrier and the material, and consequently it is not very high. On the other hand, since the transported material moves with transfer on the fixed carrier, there are many chances for the carrier and the material to interact. Consequently, it is possible to improve selectivity of transport.

Concerning the stability of a membrane, since the carrier is fixed with a chemical bond in the membrane in a fixed carrier membrane, the chance of the carrier defecting to the outside of the membrane is not entirely absent. However, there is also a possibility of defection in a mobile carrier membrane. Mobile carrier membranes are of three types: cation exchanger, anion exchanger and coordination compound. In the cation exchangers, acid ester phosphates, chelating reagents, carboxylic acid, sulfonic acid, and so on are involved. Monensin, which is a well-known ionophore in biomembranes, is a typical carrier in carboxylic acid.

The anion exchangers include primary, secondary and tertiary amines and quaternary ammonium salts. These carriers form a stable complex with anions in an acidic solution and become free amine in an alkaline solution. These characteristics are utilized in material transport.

In the coordination compounds, neutral ester phosphates, crown ethers, cyclic polyethers, and so on are included. Figure 20.4 shows some examples of crown ethers, namely 18-crown-6, dibenzo-18-crown-6 and dicyclohexyl-24-crown-8, that incorporate the metal ion inside the crown ether ring and form a stable complex as a molecular pair. The selectivity for transport depends on the diameter of the crown ether ring and the size of the metal ion. Cyclic polyethers are derivatives of poly(ethylene glycol) and form a complex with the transported material by forming a pseudocyclic structure.

If the carriers in a fixed carrier membrane can interact selectively and reversibly with the transported material, they can use functional groups in the same way as in a mobile carrier membrane. It is a difficult problem to fix these functional groups covalently on a polymer chain. Even if the functional groups are fixed on the chain, the function of the carrier sometimes changes. For example, fixed carrier membranes prepared from compounds I and II in Scheme 20.1 introduced in the crown ether on the main and side chains of the polymer as shown here are inferior to the transport performances of a cation for mobile carrier membranes with the corresponding crown ethers [7,8].

<table>
<thead>
<tr>
<th>Membrane performancea)</th>
<th>Mobile carrier</th>
<th>Fixed carrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane preparation</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Energy for transport</td>
<td>A</td>
<td>C</td>
</tr>
<tr>
<td>Efficiency of transport</td>
<td>A</td>
<td>C</td>
</tr>
<tr>
<td>Selectivity for transport</td>
<td>C</td>
<td>B</td>
</tr>
<tr>
<td>Stability of membrane</td>
<td>D</td>
<td>A</td>
</tr>
<tr>
<td>Modulation</td>
<td>C</td>
<td>A</td>
</tr>
</tbody>
</table>

a)  A: best; B: better; C: good; D: bad.
The carrier structures of typical fixed carrier membranes, such as a cation-exchange membrane and a polymer membrane with a lactone ring, are listed in Table 20.2 [6]. The ion-exchange membranes are the most stable carrier membrane of the fixed type. These polymer membranes can actively transport some cations, as described later. The sulfo, carboxyl and phosphate groups in the polymer membranes of the fixed carrier (nos. 1–3) in Table 20.2 can respond reversibly and rapidly as a result of pH changes; consequently, the cationic materials are transported by the dissociation–equilibrium cycle of those functional groups. Membrane nos. 4–6 actively transport the cationic materials, due to utilization of the reversible and rapid opening–dosing function of the lactone ring by pH changes. In the carrier membrane no. 7, in which both the carboxyl group and the lactone ring are fixed, both the ion exchange of the carboxyl group and opening–closing of the lactone ring act as the carrier; consequently, selectivity in the active transport of alkali metal ions is improved.

The chemical structures for a fixed carrier membrane that actively transport anions are summarized in Table 20.3 [6]. Carriers other than the polymer membrane of no. 2 incorporate the transporting species into the membrane with the formation of a complex and the release of the transporting species due to its changing into a free amine. Such a change in the fixed carrier shows the function of active transport. The fixed carrier of no. 2 can actively transport anions due to utilization of the tautomerism function of the N-hydroxyethyl amide group by pH changes as expressed by [27,32]

\[
\text{RCONHCH}_2\text{CH}_2\text{OH} \xrightleftharpoons[\text{OH}^-]{H^+} \text{RCONHCH}_2\text{CH}_2\text{NH}_3
\]  (20.22)
Table 20.2 Fixed carrier membranes that actively transport cations.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fixed carrier membrane</th>
<th>Chemical structure of carrier</th>
<th>Material transported</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Poly(styrenesulfonic acid)—poly(vinyl alcohol)</td>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>Alkali metal ions, amino acids, nucleic acid bases, phenols, aldehydes</td>
<td>[9–11]</td>
</tr>
<tr>
<td>2</td>
<td>Poly(isobutylene-alt-maleic anhydride)—poly(vinyl alcohol)</td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>Alkali metal ions, ammonium ion, aniline, amino acids, nucleic acid bases</td>
<td>[12–18]</td>
</tr>
<tr>
<td>3</td>
<td>Poly(phosphorized vinyl alcohol)</td>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>Alkali metal ions</td>
<td>[13,14]</td>
</tr>
<tr>
<td>4</td>
<td>Poly(3-vinyl-4-butenolid-co-acrylonitrile)</td>
<td><img src="image4" alt="Chemical Structure" /></td>
<td>Alkali metal ions</td>
<td>[19]</td>
</tr>
<tr>
<td>5</td>
<td>Poly[3-(4-hydroxyphenyl)-3-(2-hydroxy-5-vinylphenyl) phthalide-co-4-hydroxystyrene]—cellulose acetate</td>
<td><img src="image5" alt="Chemical Structure" /></td>
<td>Alkali metal ions</td>
<td>[20]</td>
</tr>
<tr>
<td>6</td>
<td>Poly[3-(4-vinylphenoxy) phthalide-co-acrylonitrile]</td>
<td><img src="image6" alt="Chemical Structure" /></td>
<td>Alkali metal ions</td>
<td>[21]</td>
</tr>
<tr>
<td>7</td>
<td>Poly(maleic anhydride-alt-2-methyl-2-propen-1-ol)—poly (acrylonitrile)</td>
<td><img src="image7" alt="Chemical Structure" /></td>
<td>Alkali metal ions</td>
<td>[22]</td>
</tr>
</tbody>
</table>
20.3 Technology of Carrier Transport Membranes

20.3.1 Mobile Carrier Membranes

20.3.1.1 Transport and Separation of Inorganic Cations

Monensin, a typical ionophore of biomembranes, is a polyether carrier of the carboxylic acid type. This carrier incorporates the metal ion into the pseudocyclic structure in an alkaline solution and releases the metal ion by changing into a linear structure in acidic solution, as shown in Figure 20.3. A model of

Table 20.3 Fixed carrier membranes that actively transport anions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fixed carrier membrane</th>
<th>Chemical structure of carrier</th>
<th>Transported material</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chitosan–poly(vinyl alcohol)–glutaraldehyde</td>
<td>(\text{NH}_2)</td>
<td>Halogen ions, benzenesulfonic acid, benzoic acid, amino acids, nucleic acid bases</td>
<td>[23–26]</td>
</tr>
<tr>
<td>2</td>
<td>Poly(styrene-co-N-hydroxyethylacrylamide)</td>
<td>(\text{CH}_2\text{CHCONHCH}_2\text{HOCH}_2)</td>
<td>Halogen ions</td>
<td>[27]</td>
</tr>
<tr>
<td>3</td>
<td>Poly(styrene-co-pyridine)</td>
<td>(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)</td>
<td>Halogen ions, chloroacetic acid</td>
<td>[28]</td>
</tr>
<tr>
<td>4</td>
<td>Poly(N-propenoyl-9-acridinylamine-co-acrylnitride)</td>
<td>(\text{CH}_2\text{CHCONHNH}_2)</td>
<td>Halogen ions</td>
<td>[29]</td>
</tr>
<tr>
<td>5</td>
<td>Poly(1-vinylimidazole-co-styrene)</td>
<td>(\text{CH}_2\text{CH}_2\text{N}_2)</td>
<td>Halogen ions</td>
<td>[30]</td>
</tr>
<tr>
<td>6</td>
<td>Poly(quaternized-4-vinylpyridine-co-styrene)</td>
<td>(\text{CH}_2\text{CH}_2\text{N}_2\text{R}\text{I}^-)</td>
<td>Acetic acid</td>
<td>[31]</td>
</tr>
</tbody>
</table>
active transport of the metal ion through a mobile carrier membrane with such conformation changes of carrier structure due to pH changes in the monensin is shown in Figure 20.5 [33].

This carrier membrane is impregnated with an octanol solution containing sodium monensin in glass-fibre paper and dialysis paper. The concentration of Na\(^{+}\) ions due to active transport consists of four steps. Step 1 is the formation of a complex between the monensin molecule and the Na\(^{+}\) ions on the interface of the alkaline side due to the rapid reaction. Step 2 is the slow diffusion of the complex in the membrane to the right side according to its concentration gradient. Step 3 is the release of the Na\(^{+}\) ions due to the rapid exchange reaction between the Na\(^{+}\) ions and the protons on the interface of the acidic side. Step 4 is the reverse diffusion of monensin based on its concentration gradient to the left side across the membrane. In this transport system, the transfer of the protons from the right side to the left side acts as the conjugated energy for active transport of the Na\(^{+}\) ions. Consequently, the Na\(^{+}\) ions are transported from the left side to the right side against the concentration gradient across the membrane. The transport in Figure 20.5 corresponds to the antiport model shown in Figure 20.2a.

Cyclic and acyclic crown ether derivatives [34–38] were synthesized in the model of the cyclic barinomysin and the acyclic monensin, which are natural ionophores and were used as mobile carriers. The former crown ethers could actively transport amino acids.

Table 20.4 summarizes the transport rate and selectivity of Li\(^{+}\)/Na\(^{+}\) in the active transport of alkali metal ions through carrier membranes containing synthetic polyethers [39]. The active transport of K\(^{+}\) ions, which utilized both cis–trans isomerization of azobenzene by light and ion selectivity of the
Table 20.4 Active transport of alkali metal ions by acyclic polyethers.

| Carrier | Transport rate (μmol h⁻¹) | Selectivity | | | |
|---------|---------------------------|-------------|---|---|
|         | Li⁺ | Na⁺ | K⁺ | Li⁺/Na⁺ | Li⁺/K⁺ |
| III     | 20  | 6.2 | 3.4 | 5.9 | 5.9 |
| IV      | 18.2| 3.8 | 3.2 | 4.8 | 5.8 |
| V       | <3  | <1  | <1  |       |       |
| VI      | 44  | 17  | 16  | 2.9  | 2.8  |

![Structures](image1.png) ![Structures](image2.png)
crown ether, and in addition, the driving force of proton flow, has been reported [40]. This active transport was due to the fact that the light isomerization and structural change in an acidic–alkaline aqueous solution occurred simultaneously, as shown in Figure 20.6.

A plasticized cellulose triacetate (CTA) membrane consisting of \( N-6-(t\)-dodecylamido\)-2-pyridine carboxylic acid (\( t\)-DAPA) as a new carrier to facilitate membrane transport of Cu(II) was prepared by Tasaki et al. to develop a selective recovery system for Cu (II) from other divalent metal ions [42]. First of all, the solid (CTA)–liquid extraction equilibrium of Cu(II) was examined to obtain information concerning Cu(II)–\( t\)-DAPA complex stoichiometry and its extraction constant in the CTA membrane. Membrane transport studies were performed in a two-compartment cell. The CTA–\( t\)-DAPA membrane exhibited uphill transport of Cu(II) against the concentration gradient. The influences of the aqueous and membrane components on the permeability of Cu(II) were studied to elucidate its transport mechanism. Their results suggest that the transport mechanism consists of a diffusion process through an aqueous diffusion film, a fast interfacial chemical reaction, and diffusion through the membrane itself. The mass-transfer coefficients in the aqueous film phase \( k_a \) and membrane phase \( k_m \) were determined based on the diffusion model, using the stoichiometric relationship of the extracted species of Cu(II) and the extraction equilibrium constant \( K_{ex} \) determined independently by solid–liquid extraction. Their mass-transfer coefficients obtained were \( k_a = 7.8 \times 10^{-6} \text{ m s}^{-1} \) and \( k_m = 2.0 \times 10^{-9} \text{ m s}^{-1} \).

Sakai et al. [43] studied the effect of four counter anions (\( \text{CH}_3\text{COO}^- \), Cl\(^-\), NO\(_3^-\), ClO\(_4^-\)) of the trioctylmethylammonium cation on the rate of solvent extraction of thiourea and its transport across poly(vinyl chloride) (PVC)-based polymer inclusion membranes (PIMs). The membranes also contained 2-nitrophenyl octyl ether (NPOE) as the plasticizer, while chloroform was used as diluent in the solvent extraction studies. It was demonstrated that the counter anion affects substantially the rate of membrane transport, and the degree of extraction follows the order \( \text{CH}_3\text{COO}^- > \text{Cl}^- > \text{NO}_3^- > \text{ClO}_4^- \). The transport rate is negligible for the perchlorate anion. This order is consistent with thiourea interacting with the counter anion through hydrogen bonding to form a heteroconjugate anion.

Selective distribution of cobalt(II), nickel(II), zinc(II) and cadmium(II) ions from chloride solutions through PIMs was studied by Gajda et al. The carrier was 1-decylimidazole. The effect of chloride ion concentration on the ion permeation was analysed. The results suggest that the selectivity of some of the metal ions changes for the worse in the separation process. In particular, selectivity of the ion separation process for zinc(II) and cadmium(II) ions decreased fivefold [44].

**20.3.1.2 Transport and Separation of Inorganic Anions**

New PIM carriers to facilitate membrane transport of anions were prepared by Gardner et al. consisting of bis(pyridylmethyl)amine compounds coordinated to transition metal ions (Fe\(^{3+}\), Cu\(^{2+}\),

![Figure 20.6 Structural change by both light isomerization and pH of azobenzocrown ether derivative [41].](image)
One of the carriers was based on a resorcinarene bonded to four bis(pyridylmethyl)amines. These carriers were included in CTA-based PIMs to study competitive transport among halides (F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\)) and oxoanions (SO\(_4^{2-}\), SeO\(_4^{2-}\), NO\(_3^-\) and ReO\(_4^-\)). Several compounds, tris(2-butoxyethyl)phosphate, dibutyl phthalate and ethylbenzoate, ethyl phthalyl ethyl glycolate and benzoic acid 2-ethoxyethyl ester, were used as plasticizers in the membranes to provide solubility of the metal carrier complexes. Separations were performed with and without antiport anions. Permeabilities of oxoanions increased with the use of 0.05 M KCl as an antiport solution. In some cases, Cl\(^-\) was selectively transported over F\(^-\), Br\(^-\) and I\(^-\) in contradiction to the usual Hoffmeister-based selectivities. Excellent ReO\(_4^-\) transport over NO\(_3^-\), SO\(_4^{2-}\) and SeO\(_4^{2-}\) was observed for certain systems. Permselectivity for ReO\(_4^-\)/NO\(_3^-\) was 312 for a PIM using ethyl phthalyl ethyl glycolate as plasticizer, zinc complex as carrier and an antiport solution of 0.05 M KCl.

A new type of synthetic membrane transporter was described by McNally et al. and shown to operate in vesicles by a relay mechanism. The transporter structure is a phosphatidylcholine derivative with a urea group appended to the end of its sn-2 acyl chain. The urea can bind a chloride ion at the membrane surface via hydrogen bonds and then relay it through the bilayer interior to an acceptor molecule located in the opposite membrane leaflet. Three phosphatidylcholine derivatives were studied and transport rates increased with transporter affinity for chloride. The results of various controls studies were consistent with an anion counter transport process using a relay mechanism and a kinetically active aggregate of two or four transporter molecules. Transport was inhibited if the transporter resides in only one leaflet of the membrane, if the bilayer is too thick, and if the counter anion is a sulfate dianion. The expected favourable formulation properties of these amphiphilic compounds should facilitate efforts to transform them into tools for biomedical research and perhaps as therapeutic agents [46].

The technique of supported liquid membranes (SLMs) was used by Benjjar et al. to achieve the facilitated transport of Cr\(_2O_7^{2-}\), using the amphiphilic organic molecule methyl cholate – widely used for facilitated transport of metal ions and carbohydrates (sugars and alditols) – as carrier. They prepared their SLM using toluene as the organic phase and a film of polyvinylidene difluoride (PVDF) as microporous and hydrophobic polymer support with 100 \(\mu\)m thickness and 0.45 \(\mu\)m diameter pores. The effects of the macroscopic parameters permeability \(P\) and initial flux \(J_i\) on the facilitated transport of the Cr\(_2O_7^{2-}\) anions were determined for several acidities of the medium of three mineral acids: hydrochloric acid (HCl), nitric acid (HNO\(_3\)) and sulfuric acid (H\(_2\)SO\(_4\)). For the different environments studied, the SLM prepared was highly permeable for the transported substrate (Cr\(_2O_7^{2-}\)), and a clear evolution of these parameters was observed for the carrier used. The initial flux on the facilitated transport of the Cr\(_2O_7^{2-}\) anions is related to the initial concentration of this substrate in the feed phase by a saturation law, which allowed the determination of the microscopic parameters apparent diffusion coefficient \(D^*\) and the association constant \(K_{ass}\) of the (carrier–substrate) complexes, formed in the organic phase for the SLM used. The experimental results clearly indicated that the (carrier–substrate) complexes formed in the organic phase were unstable, which resulted in higher apparent diffusion coefficients \(D^*\) and thus a high permeability of this membrane type for facilitated transport with this type of oxygen anion (Cr\(_2O_7^{2-}\)) [47].

### Transportation and Separation of Organic Compounds

White et al. [48] studied the transport of saccharides through CTA membranes that included some carriers. Table 20.5 shows the transportation fluxes for the saccharides. They concluded that the transport mechanism was not based on carrier diffusion alone but was more in agreement with a jumping transport mechanism similar to the one proposed by Riggs and Smith [49].
Zwitterionic silver nitrate salts of 1-(1-methyl-3-imidazolio)propane-3-sulfonate, 1-(1-methyl-1-pyrrolidinio)propane-3-sulfonate and 1-(4-methyl-4-morpholio)propane-3-sulfonate were prepared and tested as carriers for facilitated olefin transport membranes in the separation of ethylene–ethane, propylene–propane, and C4 mixtures. The interactions of olefins with silver ions bound to sulfonate groups were investigated by Fourier transform infrared (FTIR) spectroscopy as well as the correlation between the binding affinity of olefins and facilitated transport [50].

Research about citric acid transport through PIMs was carried out by Gajewski and Bogacki. Two different plasticizers – NPOE and tri-butyl phosphate (TBP) – and a series of carriers of tri-octylamine and 1-alkylimidazoles with carbon chain lengths of 10, 11, 12, 14 and 16 atoms were used. It was found that for 1-alkylimidazoles the values of the permeability coefficients obtained for TBP as plasticizer changed in the range $8.81 \times 10^{-7}$ to $1.92 \times 10^{-6}$ m s$^{-1}$. When NPOE was used as the plasticizer, the values changed in the range $1.43 \times 10^{-9}$ to $2.24 \times 10^{-8}$ m s$^{-1}$. The value of the permeability coefficient for the membrane with TBP was $3.49 \times 10^{-7}$ m s$^{-1}$ and is comparable to the value obtained for the tri-octylamine with this plasticizer, which equals $4.77 \times 10^{-7}$ m s$^{-1}$ TBP; therefore, it is able to

Table 20.5 Maximum flux for saccharide transport through CTA membrane.

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Maximum flux ($10^{-8}$ mol m$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Glucose</td>
</tr>
<tr>
<td>VII</td>
<td>18 800</td>
</tr>
<tr>
<td>VIII</td>
<td>2 500</td>
</tr>
<tr>
<td>IX</td>
<td>1 600</td>
</tr>
<tr>
<td>X</td>
<td>1 080</td>
</tr>
<tr>
<td>XI</td>
<td>1 060</td>
</tr>
<tr>
<td>XII</td>
<td>340</td>
</tr>
<tr>
<td>XIII</td>
<td>R = H</td>
</tr>
<tr>
<td>XIV</td>
<td>R = CH$_3$</td>
</tr>
</tbody>
</table>
simultaneously act as a plasticizer and carrier in a membrane. The membranes tested were characterized by a high durability. The five-times repeated 24 h cycles of research did not show any decrease in transport capacity of citric acid [51].

Fallanza et al. [52] proposed the use of novel PVDF–HFP–BMImBF4–Ag+ (HFP: hexafluoropropylene; BMImBF4: 1-butyl-3-methyl imidazolium tetrafluoroborate) facilitated transport membranes to carry out the separation of olefin–paraffin gas mixtures. These membranes exhibited good thermal, chemical and mechanical stability, good separation properties and ease of manufacture. The effect of membrane composition was evaluated, concluding that the membrane with 80% polymer–20% ionic liquid (w/w) showed the best compromise between separation properties and mechanical resistance. The separation performance of membranes containing different concentrations of Ag+ in the range 0–80% w/w at temperatures between 293 and 323 K and different operational conditions was evaluated. The facilitated transport membranes prepared provided very promising results when tested with 50/50% v/v C3H8/C3H6 mixtures obtaining C3H6 permeabilities up to 6630 Barrer and C3H8/C3H6 selectivities over 700, placing these membranes well above the Robeson upper bound for polymeric and inorganic membranes. Moreover, these membranes showed excellent stability during long-term experiments carried out for 10 days.

Facilitated transport membranes containing silver cations and metallic Ag nanoparticles (NPs) as an olefin carrier have high olefin permeability and selectivity over propane. Silver ions are known to readily react with acetylene in aqueous conditions to produce silver acetylide, which can explosively decompose at temperatures over 160 °C, and therefore its formation should be avoided. In this regard, Kim et al. examined whether silver acetylide from olefin carriers such as free silver cations and surface-activated Ag NPs by 7,7,8,8-tetracyanoquinodimethane is formed upon exposure to acetylene, which is present as a minor impurity in many petrochemical feeds. The results showed that silver acetylide was not formed from the activated Ag NPs under their experimental conditions, while free silver cations of polymer electrolyte produced silver acetylide by reacting with acetylene. Therefore, it was concluded that the activated Ag NPs showed superior chemical stability, compared with free silver cations [53].

Investigations concerning transport of chosen organic acids (oxalic, succinic, malonic and adipic) through PIMs was conducted by Gajewski et al. CTA as a polymer matrix and 1-alkyl-1,2,4-triazoles with alkyl chain lengths of 8–12, 14 and 16 carbon atoms as carriers were used. The results obtained showed that both the alkyl chain length and the structure of the organic acids considerably influenced the transport rate through the PIM [54].

20.3.1.4 Transport and Separation of Gas
Ethylene and propylene are produced in larger quantities than any other organic compound. Production of these olefins requires separation of the olefins from the corresponding paraffins. Distillation is currently used, but this is an extremely energy-intensive process due to the very low relative volatility of the components. Previous studies have shown that facilitated transport membranes can have high selectivity for olefin/paraffin separation. However, four problems have limited the commercial application of facilitated transport membranes: (i) poor mechanical stability, (ii) the difficulty in preparing thin, high-flux composite membranes, (iii) the requirement of a water-vapour-saturated feed to provide mobility for the olefin-selective carrier and (iv) poor chemical stability due to carrier poisoning. Solid polymer electrolytes are a novel class of facilitated transport membranes for olefin/paraffin separation. These membranes solve the first three problems listed. Solid polymer electrolyte membranes are based on rubbery, polyether-based polymers containing a dissolved olefin-complexing metal salt. Solid polymer electrolyte composite membranes made from poly(ethylene oxide) loaded with silver tetrafluoroborate showed an ethylene/ethane selectivity of
up to 240 and an ethylene permeance of $8 \times 10^{-6}\text{cm}^3(\text{STP})\text{cm}^{-2}\text{s}^{-1}\text{cmHg}^{-1}$ with a dry feed gas mixture [55].

The effect of convective flow of a carrier solution through a facilitated transport membrane on the CO$_2$ permeation behaviour was investigated using diethanolamine as a carrier of CO$_2$. A dead-end-type filtration cell, equipped with an ultrafiltration membrane, was used as a gas permeation cell. A carrier solution was supplied to the feed side (high-pressure side) of the cell and was allowed to permeate to the receiving side (low-pressure side) and was circulated between the receiving and the feed side by a pump. The feed gas was a mixture of CO$_2$ and CH$_4$. The convective flow of the carrier solution through the membrane enhanced the gas permeance. For example, the CO$_2$ permeance $R_{CO_2}$ increased with increasing volumetric permeation flux of the carrier solution $u$, and when $u$ was $1.9 \times 10^{-5}\text{m}^3\text{s}^{-1}$ and the CO$_2$ partial pressure was 4.0 kPa, $R_{CO_2}$ was $6.23 \times 10^{-5}\text{mol m}^{-2}\text{s}^{-1}\text{kPa}^{-1}$. This value was about 10 times that at $u = 0$ with no convective flow of the carrier solution across the membrane. The selectivity of CO$_2$ over CH$_4$ was as high as 1970. This type of membrane was very stable during the experiments for more than 2 months [56].

The addition of silver tetrafluoroborate to a Nylon-12–tetramethylene oxide block copolymer dramatically reduced paraffin solubility in the polymer electrolyte, contributing significantly to overall olefin/paraffin selectivity [57].

The CO$_2$-facilitated transport highway in the membrane was designed through an amino carrier containing polyaniline nanorods and polyvinylamine. CO$_2$ molecules could transfer quickly owing to the reversible reaction with amino groups. This strategy may have great inspiration for constructing ideal membrane structure and offering the possibility to fabricate highly permeable and selective membrane [58].

20.3.1.5 Transport of Radioactive Ions

Figure 20.7 shows one model of active transport with a tertiary amine $R_3N$ used as the mobile carrier and a proton gradient created between the two sides across the membrane [59–61]. The $\text{UO}_2(\text{SO}_4)_3^{4-}$ and the $\text{H}^+$ on the L side form the complex $(R_3N)_4\text{UO}_2(\text{SO}_4)_3$, with $R_3N$ on the interface of the L side. This complex maintained an equilibrium state as expressed by

$$4R_3N(\text{org}) + 4\text{H}^+(\text{org}) + \text{UO}_2(\text{SO}_4)_3^{4-}(\text{aq}) \rightleftharpoons \text{(R}_3\text{NH})_4\text{UO}_2(\text{SO}_4)_3(\text{aq})$$

(20.23)

The complex was diffused to the R side due to its concentration gradient and dissociated into the $\text{UO}_3(\text{SO}_4)_3^{4-}$ ions and $\text{H}^+$ ions on the R side. The net result is concentration from the L side to the R side against its concentration difference across the membrane. The $\text{H}^+$ ions in this transport also acted as the conjugated energy for active transport. This is one example of the symport shown in Figure 20.2b.

Extraction and stripping of uranium ions from nitrate media using a hollow fibre liquid membrane contactor was studied by Ramakul et al. In this study, TBP diluted in kerosene was used as extractant and sodium hydroxide was applied as a stripping solution. Uranium ions were extracted using TBP 5% (v/v) by rejecting thorium ions into raffinate with a maximum percentage of extraction for the uranium being 67%. The mathematical model was focused on the extraction side of the liquid membrane system. The permeability for each concentration of HNO$_3$ was investigated by mass transfer theory. When the concentration of HNO$_3$ increased, more uranium ions were extracted; however, when the concentration of uranium and thorium in the feed solution was increased, the percentage of extraction and stripping slightly decreased because the permeability decreases when the concentration of the feed solution increases due to membrane fouling and concentration polarization [62].
The extraction of uranium(VI) from phosphoric acid medium using (2-ethylhexyl)phosphonic acid mono 2-ethylhexyl ester (PC-88A) and tri-n-octylphosphine oxide (TOPO) individually as well as from their synergistic mixture was studied by Singh et al. [63]. With an increase in phosphoric acid concentration in the aqueous phase, the distribution ratio was found to decrease in all cases. Synergy was observed when a mixture of PC-88A and TOPO was used. The synergistic mixture in the mole ratio of 4 : 1 (1.80 M PC-88A : 0.45 M TOPO) in xylene was found to be most suitable for uranium extraction. Among the various strip liquors used, 5% (w/v) solution of ammonium carbonate was found to be the most suitable. Using a mixture of 1.8 M PC-88A and 0.45 M TOPO as the extractant system and 0.5 M ammonium carbonate as the stripping agent, uranium recovery was found to be better than 97 ± 3% in multiple contacts \( (n = 2) \) from actual Davies Gray Waste, while in the case of wet phosphoric acid more than 52 ± 3% \( (n = 3) \) only could be recovered, where \( n \) is the number of contacts.

Carrier facilitated transport of U(VI) from HNO3 medium across an SLM was studied by Biswas et al. by varying the experimental conditions, such as feed, carrier, receiver phase compositions, pore size and membrane thickness [64]. Microporous polytetrafluoroethylene membranes were used as a solid support and dinonyl phenyl phosphoric acid (DNPPA) either alone or in combination with neutral donors dissolved in \( n \)-paraffin was used as carrier. Receiver phases like H2SO4, oxalic acid, citric acid and Na2CO3 were evaluated. Under the conditions of this study, 2 M H2SO4 appeared to be most effective as receiver for U(VI) transport across an SLM. The permeability coefficient \( P \) evaluated for 0.1 M DNPPA in combination with 0.05 M neutral donors showed the U(VI) transport order to be Cyanex 923 ~ TOPO \( > \) TBP \( > \) tris-2-ethylhexyl phosphate (TEHP). The permeability \( P \) of U(VI) decreased with increase in HNO3 concentration and with metal ion concentration in the feed solution. The variation of Cyanex 923 concentration at fixedDNPA concentration (0.1 M) revealed that U(VI) permeation across the SLM was a maximum at 1 : 2.5 mole ratio. The synergistic mixture of 0.1 M DNPPA + 0.05 M Cyanex 923 was used for uranium recovery from uranyl nitrate raffinate solution.

Biswas et al. also studied the permeation of U(VI) from HNO3 solution across an SLM using bis [2,4,4 trimethyl pentyl] phosphinic acid (Cyanex 272) either alone or in combination with neutral donors like Cyanex 923 (a mixture of four trialkyl phosphate oxides viz. \( R_3PO, R_2R'PO, RR'R_2PO \) and \( R'_3PO \), where \( R \) is \( n \)-octyl and \( R' \) is \( n \)-hexyl chain), TBP and TEHP dissolved in \( n \)-paraffin as carriers. The effect of various other parameters, such as nature and concentration of receiver phase, feed acidity, uranium concentration, pore size and membrane thickness on U(VI) transport across an SLM.
were also investigated. The transport behaviour of U(VI) was also compared with other derivatives of phosphoric acids, like PC-88A and DNPPA under identical conditions, and it followed the order Cyanex 272 > PC-88A > DNPPA. 2 M H₂SO₄ was suitable for effective U(VI) transport across the SLM. The presence of neutral donors in the carrier showed significant enhancement in U(VI) permeation in the order Cyanex 923 > TBP > TEHP. U(VI) transport decreased with increased membrane thickness as well as decrease in pore size. The optimized conditions were tested for recovery of U(VI) from uranyl nitrate raffinate waste generated during purification of uranium [65].

20.3.2 Fixed Carrier Membranes

20.3.2.1 Transport and Separation of Inorganic Cations

Typical fixed carrier membranes which transfer cations are the cation-exchange membranes with sulfonate, carboxylate and phosphate groups. Figure 20.8 shows the results where a cation-exchange membrane having a sulfonic acid group as the fixed carrier – prepared from a poly(styrenesulfonic acid) (PSA)–poly(vinyl alcohol) (PVA) ratio of 2 : 3 – was employed; the L side was 0.1 M KOH, and the R side was 0.1 M KCl and 0.1 M HCl [9,17].

The concentration of K⁺ ion on the R side, which is acidic, increased, while that on the L side decreased. The increase in the K⁺ ion concentration on the R side suggests the active transport of K⁺ ions from the alkaline side to the acidic side through the membrane because the initial concentration of K⁺ ions was the same on both the L and R sides. Such a result is similar to transport of a metal ion through a mobile carrier membrane. Cation-exchange membranes with carboxylic acid and phosphoric acid groups could also actively transport alkali metal ions [12–14].

The extent of active transport of the metal ion though the PSA–PVA membrane is estimated by

\[
\text{transport fraction (\%)} = 100 - \left(\frac{C_{\text{max}} - C_0}{C_0}\right) \times 100
\]

(20.24)

where \( C_0 \) (mol L⁻¹) and \( C_{\text{max}} \) (mol L⁻¹) are the initial and maximum concentrations of metal ions on the R side respectively. The transport fraction of the K⁺ ions is plotted against the initial H⁺ ion concentration on the R side in Figure 20.9, in which the L side is 0.1 M KOH and the R side is 0.1 M KCl in aqueous HCl. The transport fraction of the K⁺ ion concentration increased as the pH approached 1.0 on the R side and then remained approximately 90% constant as the initial pH on the R side dropped below unity.

Some examples of the pH changes with time on both the L and the R sides are shown in Figure 20.10. These results suggest that OH⁻ ions on the L side and H⁺ ions on the R side diffuse through the
Figure 20.9 Transport fraction of $K^+$ ions plotted against the initial $H^+$ ion concentration on the R side.

Figure 20.10 Changes in pH on both sides with time. (●) L side; (○) R side. Initial pH on the R side: (a) 0.2; (b) 1.0; (c) 2.0.
membrane according to the concentration gradients of their ions and, consequently, neutralization occurs. Under the condition of initial pH 1.0 on the R side, both sides become acidic with time because the acidic equivalent is greater than the alkaline equivalent. In contrast, when the initial pH on the R side is higher than unity both sides become alkaline with time. From these results it is predicted that the transport of K⁺ ions through the membrane may be attributed to the pH difference between the two sides.

The relationship between the decreased amount of H⁺ ions on the R side \(\Delta[H^+]\) and the transported amount of K⁺ ions from the L side to the R side \(\Delta[K^+]\) is summarized in Table 20.6 against the initial H⁺ ion concentration on the R side; the relationship between the ratio \(\Delta[H^+] / \Delta[K^+]\) and the initial H⁺ ion concentration is also included. Both values of H⁺ and \(\Delta[K^+]\) increased with an increase in the initial H⁺ ion concentration on the R side, and these values are equal except at pH 0.2.

When H⁺ ions transferred from the R side to the L side, it would be expected that the Cl⁻ ion, which is a counter ion for the H⁺ ions, would also diffuse from the R side to the L side because of the concentration gradient. The diffused amount of Cl⁻ ions from the R side to the L side is very small compared with that of H⁺ ions. This is caused mainly by the Donnan membrane relationship. However, H⁺ ions are transferred easily by a proton-jump mechanism [66].

A Donnan equilibrium is set up between both sides and the membranes, because the membrane used here has fixed charges. It is expected that an electric potential difference between both sides of the membrane occurs and that this potential difference may be related to transport of the metal ions. Figure 20.11 shows the changes in electric potential difference with time. In all conditions other than the initial pH 3 on the R side, where the transport of K⁺ ions is not observed, as shown in Figure 20.9, the electric potential difference occurs between both sides. When the extent of this potential difference is increased, the transport fraction of K⁺ ions increases. This result suggests that the transport of K⁺ ions is influenced significantly by the electric potential difference.

From these results, a tentative mechanism for the active transport of alkali metal ions through a PSA–PVA membrane is shown in Figure 20.12. When one side is alkaline and the other side is acidic, on the alkaline (OH⁻) side the metal ions are incorporated into the membrane by the ion-exchange reaction, and H⁺ ions become H₂O by neutralization with OH⁻ ions:

\[
\text{SO}_3^- + H^+ + M^+ + OH^- \rightarrow \text{SO}_3^2^- + M^+ + H_2O
\]  

Then the metal ions are transferred through the membrane by the sulfonic acid groups fixed to it. On the other hand, since the dissociation of the sulfonic acid group on the acidic (H⁺) side is very low compared with that on the alkaline side, the membrane surface on this side is very dense. Therefore, it is difficult for the metal ions, particularly the Cl⁻ ions, to permeate into the membrane. However, the H⁺ ions can be transferred through the membrane from the acidic side to the alkaline side by

<table>
<thead>
<tr>
<th>log[H⁺]</th>
<th>Δ[K⁺] (mol L⁻¹) ×10³</th>
<th>Δ[H⁺] (mol L⁻¹) ×10³</th>
<th>Δ[H⁺]/Δ[K⁺]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.2</td>
<td>1.70</td>
<td>2.90</td>
<td>1.7</td>
</tr>
<tr>
<td>-0.5</td>
<td>1.75</td>
<td>1.75</td>
<td>1.0</td>
</tr>
<tr>
<td>-1.0</td>
<td>1.65</td>
<td>1.63</td>
<td>1.0</td>
</tr>
<tr>
<td>-1.5</td>
<td>0.55</td>
<td>0.56</td>
<td>1.0</td>
</tr>
<tr>
<td>-2.0</td>
<td>0.15</td>
<td>0.16</td>
<td>1.1</td>
</tr>
</tbody>
</table>
a proton-jump mechanism [66]. When such H⁺ ions reach the region where the metal sulfonate is formed, the metal ions are released by the ion-exchange reaction:

\[
\text{SO}_3\text{H}^+ + \text{H}^+ \rightarrow \text{SO}_3^\text{−} + \text{H}^+ + \text{M}^+
\]

The metal ions released are transferred to the acidic side by the electric potential gradient between both sides, as mentioned earlier.

If the transport of metal ions proceeds by this mechanism, it is presumed to be influenced significantly by two factors: (1) the reversible adsorption–desorption cycle reaction of metal ions by the sulfonic acid group in the membrane; and (2) the occurrence of an electric potential gradient between the two sides caused by the impermeability of the membrane to Cl⁻ ions. In considering factor (1), it is required to provide transport conditions that shows the difference in dissociation of the sulfonic acid
group in the membrane. In the systems investigated, when the L side is the alkaline aqueous solution of constant concentration and the R side is the acidic aqueous solution, the effect of factor (1) can be maximized. On the other hand, for factor (2) it is important to prevent the diffusion of Cl\(^{-}\) ions into the membrane by forming a membrane that is denser and has many fixed charges. The membrane used, which is prepared with PSA–PVA in the ratio 2 : 3 and heat treated at 100 °C for 3 h, is very dense. Even the diffusion of K\(^{+}\) ions through the membrane caused by their concentration gradient is not easy, and the ionic concentration in this membrane is relatively high. Therefore, it is expected that Cl\(^{-}\) ions do not transfer completely across the membrane. However, Cl\(^{-}\) ions on the R side are transferred to the L side through the membrane as described earlier. The effect of factor (2) may be supported by using more bulky anions, such as alkylbenzene sulfonate, which cannot permeate physically through the membrane as the anionic species instead of Cl\(^{-}\) ion in the acidic side.

To clarify the foregoing expectation, benzene sulfonate (BS\(^{-}\)) and poly(styrene sulfonate) (PSA\(^{-}\)) anions whose ionic sizes are larger than that of halogen ions are used as anion species on the R side. The results obtained are shown in Figures 20.13 and 20.14 [13]. As can be seen from these results, the transport fractions of Na\(^{+}\) ions on the R side through the ISBN–PVA membrane, which was prepared from ISBN and PVA, and the PSA–PVA membrane in the systems of BS\(^{-}\) and PSA\(^{-}\) anions were greater than those in the Cl\(^{-}\) ion system. In particular, use of the PSA\(^{-}\) anions on the R side increased remarkably the transport fraction of Na\(^{+}\) ions on the R side; in addition, the transport rate and transport period of Na\(^{+}\) ions were significantly facilitated. It is suggested from these results that the permeation fraction of anions from the R side to the L side significantly governs the transport fraction of Na\(^{+}\) ions on the R side. The transport fraction of Na\(^{+}\) ions and the permeation fraction of the anions may be related to the electric potential difference between the two sides of the membrane. This potential difference becomes higher as the permeation fraction of anions from the R side to the L side is smaller. The increase in this potential difference corresponded to the increase in the transport fraction of the Na\(^{+}\) ions. This fact suggests that the rate, fraction and period of the active transport of Na\(^{+}\) ions were influenced significantly by an electric potential gradient in the membrane.

**Figure 20.13** Effect of anion species on the transport fraction of Na\(^{+}\) ions through PSA–PVA and poly(isobutylene-alternative co-maleic anhydride) (ISBN)–PVA membranes [13].
The changes in K⁺ and Na⁺ ion concentrations on both sides of the PSA–PVA membrane with time are shown in Figure 20.12, where the L side is a mixed solution of 0.05 M KOH and 0.05 M NaOH and the R side is aqueous HCl of different concentration [9,17]. In an initial stage of transport, both K⁺ and Na⁺ ions are passively transported from the L side to the R side according to their concentration gradients. Transport of these ions was facilitated by the sulfonic acid group and corresponds to the facilitated transport in Figure 20.1b. In Figure 20.15, after the concentration of K⁺ and Na⁺ ions on both sides of the left and right solutions became equal, both K⁺ and Na⁺ ions were also transported from the L side to the R side. These transports are against their concentration gradients and correspond to the active transport in Figure 20.1c.

Permeation fractions and selectivities, calculated from Equations 20.27, 20.28 and 20.29, are summarized in Table 20.7 in K⁺–Na⁺, Li⁺–Na⁺, and K⁺–Li⁺ systems:

\[
\text{permeation fraction (\%)} = \frac{[M_1^+]_{R,t}}{[M_1^+]_{L,t}} \times 100
\]  
(20.27)

\[
\text{permeation fraction (\%)} = \frac{[M_2^+]_{R,t}}{[M_2^+]_{L,t}} \times 100
\]  
(20.28)

\[
\text{selectivity} = \frac{[M_1^+]_{R,t}/[M_1^+]_{L,t}}{[M_2^+]_{R,t}/[M_2^+]_{L,t}}
\]  
(20.29)

The permeation fraction of alkali metal ions in all binary systems increased with an increase in the initial H⁺ ion concentration on the R side and was approximately constant at pH less than 1.0. The trend in the permeation fraction is similar to that of the transport fraction of K⁺ ions shown in Figure 20.9. Under the condition of higher H⁺ ion concentration on the R side, it is suggested that both alkali metal ions in all binary systems are actively transported through the membrane from the L side to the R side.
The $K^+$/Na$^+$ and $K^+$/Li$^+$ selectivities are always greater than unity; that is, $K^+$ ions are permeated preferentially to Na$^+$ ions or Li$^+$ ions. In the Li$^+$–Na$^+$ binary system the Li$^+$/Na$^+$ selectivity is smaller than unity; that is, the Na$^+$ ions permeate more rapidly than Li$^+$ ions. As mentioned earlier, if the transport of metal ions is dependent on the reversible adsorption–desorption reaction of metal ions, it is expected that the selective transportability of metal ions may be governed by an affinity between the membrane and the metal ions. The amount of metal ions adsorbed on the membrane in various metal binary systems is summarized in Table 20.7. The difference in the amount of metal ions adsorbed corresponds to the selectivity for each metal ion binary system. That is, it is found that the metal ions which are selectively adsorbed into the membrane were permeated preferentially.

In the K$^+$–Li$^+$ binary system, the K$^+$/Li$^+$ selectivity increased as the initial H$^+$ ion concentration on the R side decreased and was higher than those of K$^+$–Na$^+$ and Li$^+$–Na$^+$ binary systems. Since the hydrated ionic radius for these alkali metal ions is in the order of $K^+ < Na^+ < Li^+$ [67], this is attributed to the difference between the hydrated ionic radii of $K^+$ and Li$^+$, which was greater than those of the other two binary systems. In particular, when the initial H$^+$ ion concentration on the R side became

Table 20.7 Effect of H$^+$ ion concentration on the R side on the permeation fraction of alkali metal ions and the selectivities $K^+$/Na$^+$, Li$^+$/Na$^+$, and K$^+$/Li$^+$.  

<table>
<thead>
<tr>
<th>log[H$^+$]</th>
<th>Permeation fraction (%)</th>
<th>Selectivity $K^+$/Na$^+$</th>
<th>Permeation fraction (%)</th>
<th>Selectivity Li$^+$/Na$^+$</th>
<th>Permeation fraction (%)</th>
<th>Selectivity K$^+$/Li$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>−0.2</td>
<td>80.8</td>
<td>71.5</td>
<td>1.13</td>
<td>78.9</td>
<td>80.5</td>
<td>0.98</td>
</tr>
<tr>
<td>−0.5</td>
<td>86.2</td>
<td>80.6</td>
<td>1.07</td>
<td>78.1</td>
<td>79.8</td>
<td>0.97</td>
</tr>
<tr>
<td>−1.0</td>
<td>90.2</td>
<td>83.5</td>
<td>1.08</td>
<td>76.8</td>
<td>81.7</td>
<td>0.94</td>
</tr>
<tr>
<td>−1.5</td>
<td>58.5</td>
<td>54.2</td>
<td>1.08</td>
<td>48.7</td>
<td>55.3</td>
<td>0.88</td>
</tr>
<tr>
<td>−2.0</td>
<td>9.0</td>
<td>8.1</td>
<td>1.11</td>
<td>18.4</td>
<td>21.4</td>
<td>0.86</td>
</tr>
<tr>
<td>−3.0</td>
<td>3.1</td>
<td>2.8</td>
<td>1.12</td>
<td>1.9</td>
<td>2.1</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Figure 20.15 Changes in Na$^+$ and K$^+$ ion concentration on both sides of the membrane with time. Na$^+$–K$^+$ binary system: (●) Na$^+$ ions on the L side; (○) Na$^+$ ions on the R side; (◇) K$^+$ ions on the L side; (◇) K$^+$ ions on the R side. Initial pH on the R side: 1.0.
lower, the permeation of metal ions was dependent on the diffusion through the membrane due to the concentration gradient between the two sides, as shown in Figure 20.15. Therefore, under such conditions, a metal ion that has a larger hydrated ionic radius decreased the permeation fraction because the permeation resistance between the membrane and the hydrated ion is increased.

It was found that the selectivity of permeation for alkali metal ions through the membrane from the alkaline side to the acidic side is given by the following order: K\(^+\) > Na\(^+\) > Li\(^+\). This order of selectivity was identical to that for alkali metal ions through the ISBN–PVA membrane containing carboxyl groups as the fixed carrier [14].

Development of a novel fixed site carrier membrane, supported by polyethylene terephthalate (PET) fabric for metal ion separation was reported by Jin and Mah. The membranes were prepared by dipping PET fabric into the methylene chloride solution of poly(5-vinyl-\textit{m}-phenylene-\textit{m}'-phenylene-32-crown-10) (P(VCE)), a polymeric metal ion carrier. It was found that the flux of monovalent metal ions transported across the membrane differed significantly from each other and the flux decreased in the order Cs\(^+\) > Rb\(^+\) > K\(^+\) > Na\(^+\) > Li\(^+\) irrespective of the anion except for perchlorate anion. This was explained in terms of the stability of the complex, formed by the crown ether unit of the P(VCE) and the various metal ions; meanwhile, the lower rate of transport in the presence of perchlorate anions was ascribed to its low hydrophilicity [68].

Professor Thunhorst’s group (see http://stripe.colorado.edu/~bowmanc/PROJECTS/KLT/KLT.html) is developing fixed site carrier membranes which will facilitate the removal of specific metal cations from aqueous streams. This removal method is based on the pH-dependent complexation of a specific metal in the feed solution with reactive sites in the membrane and the release of the metal ions from the reactive sites at the receiving side of the membrane due to low pH. The membranes developed in this work are of a solid polymeric nature, they are nonporous and do not permit bulk water flow. The reactive sites have been chosen based on their selective adsorption properties for the metal ion of interest, and have been incorporated into a poly(styrene)-like polymer matrix. It has been shown mathematically and with SLMs that selective complexation within membranes can lead to the ability to ‘pump uphill’. One of the goals of this project is to remove ions from a dilute feed stream and transport them to a more concentrated receiving stream. The ability to selectively separate and concentrate a desired species would be quite useful in a variety of applications, including wastewater treatment, process water treatment, catalyst recycling and remediation efforts. The starting material for many of these functionalized membranes is poly(vinylbenzyl chloride), and the reactive sites are attached via organic synthesis reactions. To date, several reactive sites have been tested, including methyl phosphonate esters, isopropyl phosphonate esters, phosphonic acids and various phosphate sites. These functionalized polymers, as shown in Figure 20.16, were chosen based on the literature, which indicates that they selectively adsorb ferric ions. The quaternary amine polymer (also presented in Figure 20.16) was studied to provide information about polymer swelling. In Professor Thunhorst’s group’s studies, ferric and neodymium ions are used to model plutonium. Plutonium is the target metal of these studies because it is present in low concentrations in many waste streams, and because of the difficulties and expenses associated with current treatment.

Ferric ions can be actively transported by a similar mechanism to Figure 20.12, and ion selectivity also is possible.

Ammonium cations other than metal cations are also actively transported through ISBN–PVA membrane, cation-exchange membrane according to the mechanism shown in Figure 20.17 [15]. When the carboxyl groups in the membrane become the carboxylate groups on the L (OH\(^−\)) side, ammonium ions are incorporated into the membrane by the carboxylate groups in the membrane. Then ammonium ions are transferred by the carboxyl groups, which are the functional carrier fixed to the membrane. On the other hand, since the dissociation of the carboxyl groups in the acidic (H\(^+\))
side is very low, the membrane surface on the acidic side becomes very dense. Therefore, a permeation of ammonium ions and especially Cl\(^-\) ions into the membrane is very difficult. However, H\(^+\) ions can be easily transferred from the acidic side to the alkaline side through the membrane by a proton-jump mechanism [33]. When such H\(^+\) ions reach the region of ammonium carboxylates, ammonium ions are released by the ion exchange between ammonium ions and H\(^+\) ions. Such released ammonium ions are transferred to the acidic side by an electric potential gradient between both sides. On the other hand, the ISBN–PVA swelled in alkaline solution and shrunk in acidic solution. Therefore, a swelling–shrinking cycle of the membrane caused by pH changes brings about a physical active transport of ammonium ions from the alkaline side to the acidic side.

### 20.3.2.2 Transport and Separation of Inorganic Anions

Anion-exchange membranes containing amino groups, insoluble in acidic and alkaline aqueous solutions, were prepared from chitosan, PVA and glutaraldehyde. Using the membrane in a diaphragm...
cell, one side being adjusted to be acidic and the other alkaline, it was possible to transport actively halogen ions such as Cl$^-$, Br$^-$ and I$^-$ through the membrane from the acidic side to the alkaline side against the concentration gradient between both sides of the membrane. The active transport of halogen ions through the membrane was significantly influenced by the pH difference and electric potential difference between both sides of the membrane [23,24].

The transport amount of each ion through the membrane against the initial pH on the L side is summarized in Table 20.8. When the initial pH was 13.0, the rate of transported amount of ions and OH$^-$ ions was unity. This result is caused by the neutralization between H$^+$ ions and OH$^-$ ions in the membrane.

Under this condition, the amount of OH$^-$ ions transferred from the L side to the R side was greater than that of Na$^+$ ions, because OH$^-$ ions were easily diffused by a specific diffusion mechanism [66], but Na$^+$ ions were repelled by the charge fixed to the membrane. On the other hand, the amount of H$^+$ ions transported from the R side to the L side was significantly greater than that of Br$^-$ ions. This result is attributed to ions being easily transferred by a proton-jump mechanism. At the initial pH 13.5, OH$^-$ ions were transported the greatest of all ions, and H$^+$ ions the greatest at pH 11.0. Since there is a difference between the transported amounts of each ion and a Donnan equilibrium is set up between the solution and the membrane, which has a fixed charge, it is expected that an electric potential difference between both sides occurs, and, consequently, its potential difference may be related to the transport of halogen ions. The change of the electric potential difference between both sides with time is shown in Figure 20.18. In all conditions an electric potential difference occurred between both sides. The extent of transport fraction of Br$^-$ ions was dependent on that of its potential difference. The decrease of electric potential difference with time was due to the diffusive transport of Na$^+$ ions from the L side to the R side.

A tentative mechanism of the active transport of halogen ions is shown in Figure 20.19. In order to simplify the explanation, we use the example of the transport of Br$^-$ ions. When the Br$^-$ ions are incorporated into the membrane on the R (H$^+$) side, the hydrobromide is formed in the presence of hydrobromic acid and transferred through the membrane. As this hydrobromide reaches the L (OH$^-$) side, the hydrobromide changes to the amino group by neutralization and the Br$^-$ ions are released. The released Br$^-$ ions are transferred to the L side by the electric potential gradient between both sides. Consequently, it is suggested that the Br$^-$ ions are actively transported through the membrane from the acidic side to the alkaline side.

If a greater pH difference and electric potential difference between both sides could be kept for a longer time — that is, if the diffusive transport of metal ions from the L side to the R side were to be prevented –the active transport of Br$^-$ ions might be promoted. This expectation was revealed by

<table>
<thead>
<tr>
<th>Initial pH$^b$</th>
<th>13.5</th>
<th>13.0</th>
<th>11.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br$^-$ (mol L$^{-1}$ × 10$^4$)</td>
<td>3.5</td>
<td>7.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Na$^+$ (mol L$^{-1}$ × 10$^4$)</td>
<td>16.6</td>
<td>10.0</td>
<td>4.5</td>
</tr>
<tr>
<td>H$^+$ (mol L$^{-1}$ × 10$^4$)</td>
<td>—</td>
<td>14.3</td>
<td>9.8</td>
</tr>
<tr>
<td>OH$^-$ (mol L$^{-1}$ × 10$^4$)</td>
<td>23.3</td>
<td>14.3</td>
<td>—</td>
</tr>
</tbody>
</table>

a) ←: transport from the R side to the L side; →: transport from the L side to the R side.

b) On the L side.
Ogata et al. [69]. Diffusional transport properties of hydrophobic anion-exchange membranes were studied using the PIM. This class of membranes is extensively used in chemical sensors and membrane-based separation processes. The samples of PIMs were prepared by physical containment of the trioctylmethylammonium chloride (Aliquat-336) in a plasticized matrix of CTA. The plasticizers NPOE, dioctyl phthalate and TEHP having different dielectric constant and viscosity were used to vary the local environment of the membrane matrix. The morphological structure of the PIM was obtained by atomic force microscopy and transmission electron microscopy (TEM). For TEM, Pt NPs were formed in the PIM sample. The formation of Pt NPs involved in situ reduction of PtCl$_6^{2-}$ ions with

**Figure 20.18** Changes of the electric potential difference between both sides with time across a 40/60 chitosan/PVA membrane. Initial pH on L side: (O) 13.5; (□) 13.0, (●) 11.0. L side 0.1 M NaBr, NaOH aqueous solution; R side: 0.1 M HBr.

**Figure 20.19** Tentative mechanism of the transport of halogen ions through the chitosan–PVA membrane. $X^-$: halogen ion; $M^+$: metal ion.
BH$_4^-$ ions in the membrane matrix. Since both the species are anions, the Pt NPs thus formed can provide information on the spatial distribution of anion-exchanging molecules (Aliquat-336) in the membrane. The glass transitions in the membrane samples were measured to study the effects of plasticizer on physical structure of the membrane. The self-diffusion coefficients $D$ of the I$^-$ ions and water in these membranes were obtained by analysing the experimentally measured exchange rate profiles of $^{131}$I$^-$ with natI$^-$ and tritiated water with H$_2$O respectively between the membrane and equilibrating solution using an analytical solution of Fick’s second law. The values of $D$ (I$^-$) in membrane samples with a fixed proportion of CTA, plasticizer and Aliquat-336 were found to vary significantly depending upon the nature of the plasticizer used. The comparison of values of $D$ with properties of the plasticizers indicated that both dielectric constant and viscosity of the plasticizer affect the self-diffusion mobility of I$^-$ ions in the membrane. The value of $D$ (I$^-$) in the PIM samples did not vary significantly with concentration of Aliquat-336 up to 0.5 mequiv g$^{-1}$, and thereafter $D$ (I$^-$) increased linearly with Aliquat-336 concentration in the membrane. The self-diffusion coefficients of water $D$ (H$_2$O) in PIM samples were found to be one order of magnitude higher than the value of $D$ (I$^-$) and varied slightly depending upon the plasticizer present in the membrane. It was observed in electrochemical impedance spectroscopic studies of the PIM samples that diffusion mobility of NO$_3^-$ ions was 1.66 times higher than that of I$^-$ ions, and diffusion mobility of SO$_4^{2-}$ ions was half of that for I$^-$ ions. The theoretical interpretation of the experimental counter ions exchange rate profiles in terms of the Nernst–Planck equation for interdiffusion also showed higher diffusion mobility of NO$_3^-$ ions in the PIM than Cl$^-$, I$^-$ and ClO$_4^-$ ions, which have comparable diffusion mobility [70].

20.3.2.3 Transport and Separation of Organic Compounds

Transport of Organic Compounds Cation-exchange membranes having sulfonic acid and carboxylic acid groups as the fixed carrier could also actively transport organic compounds such as aniline, amino acids [16,17], nucleic acid bases [18], phenols [10] and formaldehyde [11], as summarized in Table 20.9.

Ammonium ions were actively concentrated from the alkaline side to the acidic side, as well as alkali metal ions. Phenols and formaldehyde were actively transported from the acidic side to the alkaline side. On the other hand, in the transport of aniline, glycine and adenine, the direction of active transport is shown in Table 20.9.

<table>
<thead>
<tr>
<th>Species</th>
<th>Direction of transport</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal ions</td>
<td></td>
</tr>
<tr>
<td>Ammonium ion</td>
<td></td>
</tr>
<tr>
<td>Aniline</td>
<td></td>
</tr>
<tr>
<td>Amino acids</td>
<td></td>
</tr>
<tr>
<td>Nucleic acid bases</td>
<td></td>
</tr>
<tr>
<td>Phenols</td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td></td>
</tr>
</tbody>
</table>

Table 20.9 Direction of active transport through cation-exchange membrane having sulfonic acid and carboxylic acid as the fixed carrier.
transport was dependent on the initial pH on the acidic side since the alkaline side was kept at a given pH. An example of the active transport of adenine is shown in Figure 20.20 [18]. This figure shows the effect of initial pH on the acidic side on the active transport fraction of adenine through an ISBN–PVA membrane having a carboxyl group. Positive and negative transport fractions represent the transport of adenine from the acidic side to the alkaline side and vice versa respectively. As can be seen from this figure, there is a border on the initial pH 1.2 on the acidic side, and the direction of active transport for adenine is different on this boundary. That is, adenine was actively transported from the alkaline side to the acidic side when the initial pH on the acidic side was lower than pH 1.2, and active transport of adenine occurred as the initial pH on the acidic side became higher than pH 1.2.

Tentative mechanisms for the active transport of adenine are shown in Figure 20.21 [18]. Figure 20.21a shows a tentative mechanism for the symport of adenine and K⁺ ions from the L side to the R side through an ISBN–PVA membrane. As the initial pH on the R side was lower than 1.2 the H⁺ ions on the R side existed in excess compared with the OH⁻ ions on the L side. This excess of H⁺ ions could diffuse easily across the membrane by the proton-jump mechanism, thus neutralizing the OH⁻ ions in the membrane and on the interface of the membrane on the L side. In addition, since the H⁺ ions existed in excess, the surroundings of the interface of the membrane on the L side were changed to weakly acidic. The adenine molecule in this region was positively charged. This positively charged adenine molecule on the L side was incorporated into the membrane by electrostatic interaction with the carboxylate anion on the L side of the membrane. It seemed strange that in spite of the fact that the adenine molecule was positively charged, the carboxyl group on the L side of the membrane changed to a carboxylate anion. However, the fact that the pKₐ value for adenine was 4.15 and the ISBN–PVA membrane used began to swell at about pH 2 [14] could make possible the existence of a positively charged adenine molecule and a carboxylate anion on the L side of the membrane interface. The positively charged form of adenine interacting with the carboxylate anion was exchanged with the H⁺ ion in the boundary region in which H⁺ and OH⁻ ions were competing with each other. Diffusion of a Cl⁻ ion on the R side across the membrane was more difficult than that of the H⁺ ion. Consequently, the electric potential difference caused by electrical inequality between the two sides of

Figure 20.20 Effect of initial pH on the acidic side on the active transport fraction of adenine through a cation-exchange membrane having carboxyl groups [18].
Figure 20.21 Tentative symport (a) and antiport (b) mechanism for adenine and $K^+$ ion from the alkaline side to the acidic side through an ISBN/PVA membrane having carboxyl groups [18].
the membrane occurred in the transport system. The positively charged adenine molecule released by the exchange reaction was transferred to the R side, due to this electric potential gradient, and was then released on the R side by an H⁺ ion. Active transport of the K⁺ ions was understood by a similar mechanism.

As the initial pH on the R side was higher than 1.2, the antiport of adenine and K⁺ ions may be explained by the tentative mechanism shown in Figure 20.21b. The transport mechanism of K⁺ ions was the same as Figure 20.21a. As can be seen from the pH changes on both sides, OH⁻ ions on the L side existed in excess compared with H⁺ ion on the R side, and the excess OH⁻ ions diffused to the R side. On the L side the adenine molecule and ISBN–PVA membrane were negatively charged. The adenine molecule could not be incorporated from the L side into the membrane, due to strong electrostatic repulsion between the negatively charged adenine and the carboxylate anion. On the other hand, since the dissociation of the carboxylic acid in the ISBN–PVA membrane on the R side was depressed in the initial stage of the transport, the membrane on the acidic side contracted. At this moment the adenine molecule was positively charged. Although interaction between the carboxylic acid group and the positively charged adenine was weak, electrostatic repulsion did not occur. After the initial stage, the carboxylic acid group was negatively charged and the adenine molecule on the R side became neutral. There was no electrostatic repulsion between the carboxylate anion and the neutral adenine molecule, similar to the interaction between the carboxylic acid group and the positively charged adenine. Therefore, the positively charged adenine and the neutral adenine molecule could be incorporated by the carboxylic acid and the carboxylate anion into the membrane on the R side and diffused following the electric potential gradient through the membrane. These charged adenine and neutral adenine molecules were transferred by the carboxylate anions through the membrane and released by the OH⁻ ions on the L side. Consequently, the adenine molecule was actively transported from the R side to the L side through the ISBN–PVA membrane.

On the other hand, uracil, which is a nucleic acid base, always was transported actively from the acidic side to the alkaline side [18]. Therefore, when the initial pH on the acidic side was adjusted to less than pH 1.2 and the mixed aqueous solution of adenine and uracil was set, adenine and uracil were antiportively separated. That is, adenine was actively transported from the alkaline side to the acidic side, and vice versa for uracil. These results suggest that adenine and uracil can be separated from each other due to the antiport in the active transport.

An anion-exchange membrane using as the fixed carrier the primary amino group in chitosan could actively transport benzoate ion from the acidic side to the alkaline side, as shown in Figure 20.22 [25]. This chitosan membrane could also actively transport halogen ions [24,26] and benzenesulfonate ions [25] from the acidic side to the alkaline side, and L-phenylalanine [25] from the alkaline side to the acidic side, as summarized in Table 20.10. Therefore, the chitosan membrane could, by active transport, separate and concentrate each member from a mixture of organic acid and amino acid as the transport conditions were well set up. A quaternized chitosan membrane with a quaternary ammonium group could actively transport nucleic acid bases such as adenine, guanine, uracil, thymine and cytosine [71,72]. When the pH on the acidic side was adjusted, the direction of transport for these nucleic acid bases could be controlled. Nucleic acid bases such as adenine, guanine, uracil and cytosine could also be actively transported against their concentration gradients through the chitosan membrane, and the direction of transport for them was significantly dependent on the pH of both sides [73]. Quaternized chitosan membranes cross-linked with ethylene glycol diglycidyl ether were applied to the uphill transport of nucleic acid bases. The transport results are summarized in Table 20.11. Uracil was transported against its concentration gradient from the basic side to the acidic side regardless of the pH on the basic side. Cytosine, adenine and guanine were also transported against their concentration gradients, but the direction of their transport depended upon the pH on the basic side.
Figure 20.22  Active transport of benzoate ion through a chitosan membrane. Initial L side, 0.01 \text{M} sodium benzoate, NaOH aqueous solution; initial R side, 0.01 \text{M} benzoic acid [25].

Table 20.10  Direction of active transport through anion-exchange membrane prepared from chitosan.

<table>
<thead>
<tr>
<th>Species</th>
<th>Direction of transport</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halogen ions</td>
<td></td>
</tr>
<tr>
<td>Benzoate ion</td>
<td></td>
</tr>
<tr>
<td>Benzenesulfonate ion</td>
<td></td>
</tr>
<tr>
<td>l-Phenylalanine</td>
<td></td>
</tr>
</tbody>
</table>

A and B are acidic and basic side respectively. Arrows indicate the transport direction. The initial pH on the A side was kept at 1.0 and the initial pH on the B side was changed.

Table 20.11  Transport direction of uracil, cytosine, adenine, guanine and K\(^+\) ions in the transport against the concentration gradient through a \(q\)-chitosan membrane.

<table>
<thead>
<tr>
<th>Transporting species(^{a)})</th>
<th>Transport direction at initial pH on B side</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11.0</td>
</tr>
<tr>
<td>K(^+)</td>
<td>B → A</td>
</tr>
<tr>
<td>Uracil (9.5)</td>
<td>B ← A</td>
</tr>
<tr>
<td>Cytosine (4.5, 12.2)</td>
<td>B → A</td>
</tr>
<tr>
<td>Adenine (4.15, 9.8)</td>
<td>B → A</td>
</tr>
<tr>
<td>Guanine (3.2, 9.6, 12.4)</td>
<td>B → A</td>
</tr>
</tbody>
</table>

\(a\) Values in parentheses are \(pK_a\) and \(pK_b\) values for nucleic acid bases.
In particular, transport directions for adenine and guanine were switched during identical transport experiments.

**Separation and Concentration of Organic Compounds**  See Uragami et al. [74].

A tentative mechanism of the transport of adenine from the alkaline L side to the acidic R side through the PSA–PVA membrane is shown in Figure 20.23 in which the initial pH on the R side is lower than 1.3; H⁺ ions on the R side exist in excess compared with OH⁻ ions on the L side.

A tentative mechanism of the transport of adenine from the acidic R side to the alkaline L side through the same membrane is also shown in Figure 20.24, in which the initial pH values on the R and the L side are lower than 1.3 and 13.0 respectively.

A tentative mechanism of the transport for uracil through the same membrane is shown in Figure 20.25. On the alkaline L side the uracil molecule is negatively charged and the sulfonic acid group in the PSA–PVA membrane is dissociated. Therefore, since electrostatic repulsion occurs between the negatively charged uracil and the sulfonate anion, the uracil molecule cannot be incorporated into the membrane on the L side. On the other hand, on the acidic R side the uracil molecule exists in the neutral form because the pKᵢ value for uracil is 9.45. Therefore, there are weak interactions between the neutral uracil and the sulfonate anion. The neutral uracil molecule can be incorporated into the membrane on the R side and then released by the OH⁻ ion on the alkaline L side.

The mechanisms in Figures 20.23 and 20.25 suggest that the separation of a mixture of adenine and uracil should be possible. Namely, when a mixed solution of adenine and uracil is provided on both sides of the PSA–PVA membrane, the adenine and uracil molecules can be transported in the antiport and separated from each other because the adenine molecule can be transported against its concentration gradient from the alkaline L side to the acidic R side and the uracil molecule is transported in the opposite direction. The mechanisms in Figures 20.24 and 20.25 show that a mixture of adenine and uracil can be concentrated. Thus, since both adenine and uracil molecules can be transported against
their concentration gradients from the acidic R side to the alkaline L side, these molecules can be transported in the symport mechanism and concentrated on the L side.

20.3.2.4 Transport and Separation of Gas
The facilitated transport of CO$_2$ through ion-exchange membranes containing organic amine counter ions was studied by Way et al. Steady-state CO$_2$ fluxes were measured from pure gas streams and mixtures with CH$_4$. Facilitation factors for CO$_2$ up to 26.7 were calculated from transport data. Transport measurements were binary mixtures of CO$_2$ and CH$_4$ and yielded ratios of CO$_2$ flux to CH$_4$ flux ranging from 29.0 to 264. Conversion of flux ratios to permeabilities yielded separation factors up to 551 for CO$_2$ over CH$_4$, which are compared with literature data for polymeric membranes. The transport data support a mobile, reactive-carrier facilitated transport mechanism with a carbamate zwitterion complex. Effective diffusivities for CO$_2$ and the carrier–gas complex were determined from

Figure 20.24 Tentative mechanism for the antiport of adenine from the acidic side to the alkaline side through a PSA–PVA membrane.

Figure 20.25 Tentative mechanism for the antiport of uracil from the acidic side through a PSA–PVA membrane.
transport data. A reaction equilibrium model predicted facilitation factors that were in very good agreement with experimental values. Potential applications were also discussed [75].

Selective sorption and permeation of molecular oxygen were investigated by Nishide et al. using meso-α,α,α,α-tetakis(o-pivalamidophenyl)porphinatocobalt(II) (CoP) coordinated polymer membrane. Oxygen solubility was augmented ~70 times in comparison with that of nitrogen by the CoP loading in the membrane. Sorption isotherms of oxygen for the membranes were analysed with a dual-mode sorption model to give $C_c$ and $K$. $C_c$ (the saturated amount of oxygen reversibly bound to the CoP sorption site) was independent of temperature and increased with the loaded CoP amount into the membrane. $K$ (the oxygen-affinity constant of CoP) agreed with that determined spectroscopically by monitoring the CoP moiety in the membrane. Oxygen permeation through the membrane was facilitated, and the permeability was in accordance with a dual-mode transport model. Substituting the sorption parameters $C_c$ and $K$ in the model yielded diffusion constants of oxygen in the membranes [76].

The use of a composite membrane for NH$_3$ separation was presented by Shukla and Peinemann. A polyethylene–polyetherimide–carrier composite was shown to permeate NH$_3$ selectively from an NH$_3$–N$_2$ mixture at ambient conditions, attaining a maximum selectivity of 480 at 1% NH$_3$ feed concentration. Experimental data indicated facilitated-transport-mode membrane function [77].

A new type of cation-exchange membrane was prepared by Matsuyama et al. by grafting acrylic acid onto a microporous polyethylene membrane by use of a plasma-grafted polymerization technique. The facilitated transport of CO$_2$ through the plasma-grafted membrane containing ethylenediamine was studied [78]. The membrane obtained showed remarkably high CO$_2$ permeability and selectivity of CO$_2$ over N$_2$. When the CO$_2$ partial pressure in the feed gas was 0.047 atm, the CO$_2$ permeability and the selectivity obtained were 1.0 × 10$^{-4}$ cm$^3$ cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$ and 4700 respectively. These efficiencies were much higher than those of conventional polymer membranes, and were also superior to efficiencies of ion-exchange membranes containing a carrier reported thus far. These excellent results were probably attributable to the high ion-exchange capacity and the high water content. The newly prepared membrane was stable.

A membrane having an amine moiety was prepared by plasma-grafting 2-(N,N-dimethyl)aminoethyl methacrylate (DAMA) onto a microporous polyethylene substrate. Permselectivity of the membrane for CO$_2$ over N$_2$ was achieved in both dry and water-swollen conditions. When the CO$_2$ partial pressure in the feed gas was 0.047 atm, the selectivity of CO$_2$ over N$_2$ reached 130 for the highly swollen water-containing membrane. This value was found to agree with that obtained with a mobile carrier membrane (SLM) using DAMA as the carrier. The effects of several experimental conditions, such as degree of grafting, feed partial pressure and temperature, on the membrane performance were studied. It was suggested that the membrane acted as a fixed carrier membrane for CO$_2$ facilitated transport in the dry condition and acted as a fixed reaction site membrane in the water-swollen condition. The carrier transport mechanism was discussed for dry and aqueous membranes [79].

Molecular oxygen diffusion through CoP complexed with various ligands and fixed in a transparent and rubbery poly(benzyl methacrylate) membrane was studied by Tsuchida et al. The oxygen-binding kinetics and equilibrium constant of CoP complexes in the membrane were determined spectroscopically in situ. The diffusion coefficients of the dissolved oxygen according to Henry’s law and the adsorption or coordinated oxygen to the complex according to the Langmuir isotherm were evaluated by analysing oxygen permeation behaviour through the membrane in terms of the combination of dual-mode transport theory and the spectroscopic data. The oxygen diffusion coefficient via the CoP complex increased with the oxygen-dissociation kinetic constant from the CoP complex [80].

$N,N$-Dimethylformamide (DMF) and $N,N$-dialicylidene ethylene diamine cobalt(II) (CoSalen) were added into the casting solution by Chen et al. to improve both the gas permeability and oxygen/
nitrogen selectivity of polycarbonate (PC) membranes [81]. PC membranes formed by a simple dry method are known to have high oxygen/nitrogen selectivity but low gas permeability. The nonsolvent DMF was added into the casting solution to improve the membrane permeability, and the oxygen carrier CoSalen was added to improve the oxygen/nitrogen selectivity. The addition of DMF increased the membrane permeability but reduced the oxygen/nitrogen selectivity. On the contrary, the addition of CoSalen raised the selectivity but suppressed the permeability. To make a membrane of selectivity near to the value of a native PC membrane but with a higher gas permeation rate by adjusting the DMF and CoSalen contents in the casting solution, the highest oxygen permeation flux of CoSalen complexed porous PC membranes was 0.61 GPU (10^{-6} \times \text{cm}^3 \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}) at an O_2/N_2 selectivity of 4.7 at 35 °C. This membrane was obtained when 19 vol.% of DMF and 4.8 wt% of CoSalen were added into the PC casting solution. This specific membrane, after a long period of storage (400 days), had a higher oxygen flux (0.88 GPU), which was obtained without any loss in selectivity. At a lower temperature, 5 °C, an even higher oxygen selectivity of 7.9 was obtained.

A new membrane material having two kinds of CO_2 carriers was obtained by Zhang et al. Composite membranes were prepared with the material and support membranes. The facilitated transport of CO_2 through these membranes was performed with pure CH_4 and CO_2 as well as CH_4–CO_2 mixtures containing 50 vol.% CO_2. The results showed that the membranes possessed better CO_2 permeance than that of other fixed carrier membranes reported in the literature. In the measurements with pure gases, at 26 °C, 0.013 atm of CO_2 pressure, the membrane with polysulfone support displayed a CO_2 permeance of 7.93 \times 10^{-4} \text{cm}^3 \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1} and CO_2/CH_4 ideal selectivity of 212.1. In the measurements with mixed gases, at 26 °C, 0.016 atm of CO_2 partial pressure, the membrane displayed a CO_2 permeance of 1.69 \times 10^{-4} \text{cm}^3 \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1} and CO_2/CH_4 selectivity of 48.1 [82].

A membrane of a cobalt tetraazaporphyrin polymer complex was prepared by Shinohara et al. with a nanometre thickness and used as an oxygen-facilitated transport membrane. Rapid and reversible oxygen binding to the cobalt tetraazaporphyrin complex with a polymeric imidazole ligand was observed at low temperature. Oxygen transport through the membrane was facilitated, and a high (oxygen/ nitrogen) permselectivity of 28 was obtained [83].

Bao and Trachtenberg [84] compared the efficiency of facilitated transport of CO_2 across a liquid membrane by different facilitators as tested in either an SLM or a hollow fibre contained liquid membrane configuration. Permeance and selectivity were evaluated by both experimental test and numerical simulation. These comparisons were used to define the best liquid membrane composition to maximize separation performance. They also considered other factors that affect the choice of the facilitator (e.g. operation temperature and cost). Under ambient operating conditions, carbonic anhydrase combined with an alkaline carbonate gave a better performance than diethanolamine does.

A water-soluble copolymeric membrane material containing tertiary amine and carboxyl groups for CO_2 facilitated transport was synthesized by radical polymerization of DMAEMA (2-N,N-dimethyl aminoethyl methacrylate)–AA (acrylic acid) by Shen et al. The composite membranes were prepared with copolymer of DMAEMA–AA as separation layer and polysulfone ultrafiltration membrane as support. The permeation rates of the membranes for pure CO_2 and CH_4 were investigated. The results showed that the copolymeric membrane possesses a higher permeance of CO_2. The membrane displays a CO_2 permeance of 6.12 \times 10^{-7} \text{cm}^3 (\text{STP}) \text{cm}^{-2} \text{s}^{-1} \text{Pa}^{-1}, and a CH_4 permeance of 2.4 \times 10^{-9} \text{cm}^3 (\text{STP}) \text{cm}^{-2} \text{s}^{-1} \text{Pa}^{-1} at 299 K, 1.140 kPa of gas pressure. The results with the mixed gas were not as good as those obtained with pure gas because of the coupling effects between CO_2 and CH_4 [85].

A defect-free ultrathin polyvinyl amine (PVAm)–PVA blend facilitated transport membrane cast on a porous polysulfone support was developed by Deng et al. [86]. The target membrane was prepared from commercial PVAm and PVA. The effects of experimental conditions were investigated for a CO_2–N_2 mixed gas. A CO_2/N_2 separation factor of up to 174 and a CO_2 permeance up to 0.58 m^3
(STP) m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) were documented. Experimental results suggest that CO\(_2\) was being transported according to the facilitated transport mechanism through this membrane. The fixed amino groups in the PVAm matrix functioned as CO\(_2\) carriers to facilitate the transport, whereas the PVA added mechanical strength to the blend by entanglement of the polymeric chains, hence creating a supporting network. The good mechanical properties obtained from the blend of PVA with PVAm enabled an ultrathin selective layer (down to 0.3 \(\mu\)m) to be formed on polysulfone support (with molecular weight cut-off of 50 000), resulted in both high selectivity and permeance. The PVAm–PVA blend membrane also exhibited a good stability during a 400 h test.

Saedi \textit{et al.} [87] prepared a novel water-insoluble amino-starch (AS) derivative using the Williamson ether synthesis method. The AS was used as a polymeric additive for the preparation of an integrally skinned asymmetric polyethersulfone (PES) membrane. The PES–AS membranes were combined with a facilitated transport mechanism and solution-diffusion mechanism in an integrally skinned asymmetric membrane for the separation of CO\(_2\) from CH\(_4\) for the first time. The miscibility of PES and the synthesized AS was confirmed by differential scanning calorimetry. The change in the membrane morphology was investigated using scanning electron microscopy. The sorption isotherms were obtained to investigate the effect of the AS on the membrane gas sorption capacity. Introducing the AS into the PES membranes led to a denser sublayer and a higher CO\(_2\) sorption capacity of the prepared membranes. A higher CO\(_2\) permeation, a lower CH\(_4\) permeation and a higher CO\(_2\)/CH\(_4\) selectivity are the most important changes in the performance of the PES membranes caused by the incorporation of a facilitated transport in CO\(_2\) permeation and a denser sublayer of the prepared membranes. Furthermore, the glass transition temperature and the nonequilibrium free volume of the PES membranes was decreased and the plasticization pressure of the PES membranes was improved by introducing the AS into the PES membranes. The incorporation of the facilitated transport mechanism in the PES–AS membranes altered the membrane behaviour against the change in the feed pressure and the feed temperature.

Kasahara \textit{et al.} prepared SLMs incorporating amino acid ionic liquids which remarkably facilitated CO\(_2\) permeation under dry and low humid conditions [88].

Hydroxide-exchange membranes were developed by Xiong \textit{et al.} for facilitated transport of CO\(_2\) in post-combustion flue-gas feed [89]. First, a correlation between the basicity of fixed-site functional groups and CO\(_2\) separation performance was discovered. This relationship was used to identify phosphonium as a promising candidate to achieve high CO\(_2\) separation performance. Consequently, quaternary phosphonium-based hydroxide-exchange membranes were demonstrated to have a separation performance that is above the Robeson upper bound. Specifically, a CO\(_2\) permeability as high as 1090 Barrer and a CO\(_2\)/N\(_2\) selectivity as high as 275 was achieved. The high performance observed in the membranes was attributed to the quaternary phosphonium moiety.

At present, liquid membranes, ion-exchange membranes and fixed carrier membranes are the three popular facilitated transport membranes for CO\(_2\) separation. They possess their own advantages, as well as their respective deficiencies. In view of the characters of these three types of facilitated transport membrane, Liao \textit{et al.} [90] reported a method to combine their advantages and overcome their deficiencies. A new membrane was fabricated by establishing high-speed facilitated transport channels in the fixed carrier membrane. This membrane displayed excellent CO\(_2\) separation performance and good stability. The results suggested that this was an effective way to fabricate high-performance and high-stability CO\(_2\) separation membranes. Furthermore, establishing high-speed facilitated transport channels in fixed carrier membranes will be a universal route to improve the performance of gas separation membranes.

The facilitated transport membranes AgClO\(_4\)–cellulose acetate (CA) and AgBF\(_4\)–CA were prepared and tested for the separation of isoprene–pentane mixtures. The maximum selectivities for isoprene
over pentane were found to be 53 and 83 for AgClO₄–CA and AgBF₄–CA membranes respectively. FTIR and UV–visible spectroscopy studies showed that the silver ions in the membranes were coordinated by the carbonyl groups of CA. Reversible diene coordination to silver ions was observed by FTIR and UV–visible spectroscopy studies. Treatment of the AgBF₄–CA membrane placed in a gas cell with isoprene produced an isoprene-coordinated membrane in which the coordinated isoprene was easily replaced by other diene compounds, such as trans-piperylene and 1,3-butadiene [91].

Zwitterionic silver nitrate salts of 1-(1-methyl-3-imidazolio) propane-3-sulfonate, 1-(1-methyl-1-pyrrolidinio) propane-3-sulfonate and 1-(4-methyl-4-morpholio) propane-3-sulfonate were prepared and tested by Kim et al. as carriers for facilitated olefin transport membranes in the separation of ethylene–ethane, propylene–propane and C₄ mixtures. The interactions of olefins with silver ions bound to sulfonate groups were investigated by FTIR spectroscopy as well as the correlation between the binding affinity of olefins and facilitated transport [92].

As already noted earlier, Fallanza et al. [52] proposed the use of novel PVDF–HFP–BMImBF₄–Ag⁺ facilitated transport membranes to carry out the separation of olefin–paraffin gas mixtures. These membranes exhibited good thermal, chemical and mechanical stability, good separation properties and ease of manufacture. The effect of membrane composition was evaluated, concluding that the membrane with 80% polymer–20% ionic liquid (w/w) showed the best compromise between separation properties and mechanical resistance. The separation performance of membranes containing different concentrations of Ag⁺ in the range 0–80% w/w at temperatures between 293 and 323 K and different operational conditions was evaluated. The facilitated transport membranes they prepared provided very promising results when tested with 50/50% (v/v) C₃H₆/C₃H₈ mixtures, obtaining C₃H₆ permeabilities up to 6630 Barrer and C₃H₈/C₃H₆ selectivities over 700, placing these membranes well above the Robeson upper bound for polymeric and inorganic membranes. Moreover, these membranes showed excellent stability during long-term experiments carried out for 10 days.

20.3.2.5 Transport of Radioactive Ions
The transport behaviour of ¹³⁷Cs from nitric acid feed was investigated by Mohapatra et al. using CTA plasticized-PIMs containing several crown ether carriers, viz. di-benzo-18-crown-6, di-benzo-21-crown-7 and di-tert-butylbenzo-18-crown-6 (DTBB18C6). The PIMs were prepared from CTA with various crown ethers and plasticizers. DTBB18C6 and TBP were found to give higher transport rate for ¹³⁷Cs compared with other carriers and plasticizers. The effects of crown ether concentration, nitric acid concentration, plasticizer and CTA concentration on the transport rate of Cs were also studied. The Cs selectivity with respect to various fission products obtained from an irradiated natural uranium target was found to be heavily dependent on the nature of the plasticizer. Their study showed that, by choosing a proper plasticizer, one can get either good transport efficiency or selectivity. Though TBP-plasticized membranes showed good transport efficiency, they displayed poor selectivities. On the other hand, an entirely opposite separation behaviour was observed with NPOE-plasticized membranes, suggesting the possible application of the latter membranes for the removal of bulk ¹³⁷Cs from nuclear waste. The stability of the membrane was tested by carrying out transport runs for nearly 25 days [93].

The selective separation of radio-strontium from acidic feeds using a highly efficient novel SLM method suggesting possible applications in radioactive waste remediation was investigated by Raut et al. [94]. This method was the first ever report on near-quantitative (~99%) strontium transport with crown ether carrier from acidic feeds (~3 M HNO₃) using an SLM method. The SLM consisted of a solution of di-tert-butyl-dicyclohexano-18-crown-6 dissolved in a mixture of 2-nitrophyenyl ether and n-dodecane absorbed into a microporous polytetrafluoroethylene film. A mixture of 80% 2-nitrophyenyl ether and 20% n-dodecane was found to be the most suitable diluent system and
was evaluated in their study. The transport rates were correlated with the carrier extractant concentration, strontium concentration as well as the feed acid concentration. Transport of strontium from pressurized heavy water reactor simulated high level waste was also studied with encouraging results. Selective transport of Sr(II) was observed from a feed solution constituting a mixture of fission products spiked individually. Radiation stability of the carrier solvent with respect to the efficiency and selectivity was also investigated. The stability of the membrane was remarkably good when tested over 20 days of continuous operation.

Chaudhury et al. [95] reported a novel and cleaner approach of electrodriven selective transport of caesium from simulated nuclear waste solutions through a CTA–PVC-based PIM. The electrodriven cation transport together with the use of highly Cs⁺ selective hexachlorinated derivative of cobalt bis dicarbolide allowed selective separation of Cs⁺ from a high concentration of Na⁺ and other fission products in nuclear waste solutions to be achieved. The transport selectivity was studied using a radio-tracer technique and atomic emission spectroscopy. Transport studies using CTA-based membrane were carried out from neutral solution as well as 0.4 M HNO₃, while that with PVC-based membrane was carried out from 3 M HNO₃. High decontamination factor for Cs⁺ over Na⁺ was obtained in all cases. Experiments with simulated high-level waste solution showed selective transport of Cs⁺ from most other fission products also. Significantly fast Cs⁺ transport rate along with high selectivity are interesting features observed in this membrane. The current efficiency for Cs⁺ transport was found to be similar to 100%. The promising results showed the possibility of using this kind of electrodriven membrane transport method for nuclear waste treatment.

20.3.3 Improvement of Transport Efficiency in Carrier Transport

When it is necessary to improve the efficiency of transport through a membrane with a carrier, improvement in carrier function is a very important factor. In a mobile carrier membrane the improvement of probability of complex formation between the carrier and the transporting species with increased carrier concentration in the membrane is one factor. But as the concentration of carrier becomes too high, the viscosity of the liquid membrane increases. This increase in viscosity leads to a lowering of diffusivity of the complex in the membrane and consequently lowers the transport rate of the species. The efficiency of transport of the material is influenced remarkably by the feed concentration, carrier concentration in the liquid membrane, viscosity of the liquid membrane, pH on the concentrated side of the transported material, stirring of the solution on both sides of the membrane, and so on. Therefore, optimum conditions must be selected for the transport of material.

In the improvement of transport efficiency, design of a membrane structure in which the transported species can easily transfer on the fixed carrier is one of the important factors. There is a continuous fixation of the carrier in the membrane, producing an anisotropy in the density of the carrier in the membrane in the direction of the membrane thickness, the formation of thin membrane, and so on, as a design of the membrane structure. In a carrier membrane of the fixed type, such as an ion-exchange membrane, however, as the concentration of fixed carrier in the membrane is increased, swelling of the membrane with the solution becomes remarkable; consequently, efficiency of transport is lowered because the actively transported species is reversely diffused due to the remarkable swelling of the membrane [14].

On the other hand, a membrane structure must be constructed in which the selectivity function appears easily. In the preparation of such a membrane, it is very important to produce a dense membrane that does not permit reverse diffusion of the species transported actively and the passive transport of carrier from the feed side to the concentrated side [9]. When the efficiency of transport is not sufficiently improved by the increase in carrier concentration and the formation of a dense membrane, providing an electrochemical potential gradient to the transport system is effective.
Figure 20.26 Active transport of $K^+$ ions through a PSA–PVA membrane having sulfonic acid groups and a PVA membrane without a fixed carrier. (○, ◦) PSA–PVA membrane; (■, □) PVA membrane.

Figure 20.27 Schematic diagram of the diaphragm cell with pH controllers [97].
Active transport of $K^+$ ions through PSA–PVA and PVA membranes is shown in Figure 20.26. As can be seen, even a PVA membrane without a fixed functional carrier could actively transport $K^+$ ions [96]. This transport of $K^+$ ions was dependent on the difference in electrical potential between the two sides of the PVA membrane. Of course, the transport rate, transport fraction and selectivity of the PSA–PVA membrane were greater than those for the PVA membrane. However, the improvement in transport efficiency observed in the PVA membrane based on the electrochemical potential gradient was very significant. The transport fraction decreased remarkably, particularly in the transport of material due to the driving force of pH differences across the membrane as neutralization proceeded. Therefore, if an irreversible process is introduced in the process of transport through the membrane, an electrochemical potential gradient occurs, and consequently an improvement in transport efficiency can be expected. The results of the active transport of $Na^+$ ions in Figures 20.13 and 20.14 support the foregoing discussion; in particular, the transport rate, transport fraction, and transport period were improved significantly when a polymer electrolyte was applied to the reagent for pH control of solution. If the diffusivity of the cations is disturbed, the active transport of anions was improved through the occurrence of a higher electrochemical potential gradient [25,28].

From the foregoing discussions, it is expected that if a carrier membrane of the fixed type with a carrier gradient in the thin membrane is applied to the transport of material through the membrane and an electrochemical potential gradient is provided in the membrane, the material will be transported selectively, actively and efficiently.

On the other hand, the control of transport conditions of the acid and alkaline side across the membrane is also very important. For example, when the pH controllers as shown in Figure 20.27 are applied to the acid and alkaline side across the membrane, uphill transport of ammonium ions with pH controllers was more efficient than without, thus keeping the pH difference between both sides of the membrane constant, which is a driving force for the uphill transport [97].

References


21

Membrane Reactor

21.1 Concept of Membrane Reactors

In a conventional catalysis reaction process, the refinement of the reactant, the separation and purification of the product, and unit operations such as heating and cooling other than a reaction are treated separately. The characteristic of a membrane reactor is that it can carry out both the reaction and separation simultaneously. This is a very convenient system. In a separation reaction that couples separation with a reaction, the improvement of the one-pass reaction rate by liberation from the limitation for thermodynamic equilibration, the control of the supply method of the reactant and synergistic effects such as the improvement in selectivity by the removal from the reaction ground of the intermediate which becomes a factor of the side reaction synergistic effect is expected. The combination of various kinds of methods, such as distillation, extraction, adsorption, crystallization and membrane separation, is possible. In membrane separation, the membrane in particular can be incorporated as a partition of the reactor relatively easily. Therefore, this is an energy-saving separation operation without a phase conversion. A reactor that incorporates such a permeable membrane is called a membrane reactor and is interesting from the viewpoint of membrane science and technology.

The membrane reactor can be classified roughly into two types: one that uses only a membrane’s original separation function and one that uses both the functions of the separation and catalyst (see Figure 21.1 [1]). When they use only a membrane’s original separation function, a solid catalyst is usually filled around the separation membrane, and both functions of a separation membrane and a catalyst are utilized. These are called packed-bed membrane reactors (PBMRs) and they have an extractor function that removes the product from the reaction field.

On the other hand, in the type with both functions of separation and catalysis, the separation membrane has a catalysis activity and is called a catalytic membrane reactor (CMR). In addition, it is called itself contactor by the function.

21.2 Membranes for Membrane Reactors

The membranes used for a membrane reactor are classified roughly into inorganic membranes and polymer membranes.

21.2.1 Inorganic Membranes

See the review article by Gallucci et al. [2].

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Inorganic membranes are commonly constituted by different materials, such as ceramic, carbon, silica, zeolite, oxides (alumina, titania, zirconia) as well as metals such as palladium and silver and their alloys. They can be applied at high temperatures. In fact, they are stable at temperatures ranging from 300 to 800 °C and in some cases (ceramic membranes) usable over 1000 °C [3]. They also present high resistance to chemical degradation. As previously said, the main drawback of these inorganic membranes is their high cost. However, although inorganic membranes are more expensive than polymeric ones, they possess advantages such as resistance towards solvents, a well-defined stable pore structure.

Figure 21.1 Classification of membrane reactors.
Hsieh has provided a technical overview of inorganic membranes in his book [4], in which inorganic membranes are divided into two major categories based on structure: porous inorganic membranes and dense (nonporous) inorganic membranes, as shown in Figure 21.2. Moreover, porous inorganic membranes have two different structures: asymmetric and symmetric. Porous inorganic membranes with pores more than 0.3 μm usually work as sieves for large molecules and particles. Glass, metal, alumina, zirconia, zeolite and carbon membranes are the porous inorganic membranes used commercially. However, other inorganic materials, such as cordierite, silicon carbide, silicon nitride, titania, mullite, tin oxide and mica, can also be used to produce porous inorganic membranes. These membranes vary greatly in pore size, support material and configuration. Alternatively, dense membranes made of palladium and its alloys, silver, nickel and stabilized zirconia have been used or evaluated mostly for separating gaseous components. Applications of dense membranes are primarily for highly selective separation of hydrogen and oxygen and the transport occurs via charged particles. However, the dense membranes have found only very limited usage in industrial application, primarily due to their low permeability compared with that of porous inorganic membranes. Therefore, today’s market for commercial inorganic membranes is dominated by porous membranes [5].

### 21.2.1.1 Metal Membranes

Conventionally, dense metal membranes are used for hydrogen separation from gas mixtures and in the membrane reactor area. Palladium and its alloys are the dominant materials for preparing these kinds of membranes due to their high solubility and permeability of hydrogen. Unfortunately, they are very expensive because of the low availability of palladium in the nature. Recently, supported thin metallic membranes have been realized by coating a thin layer of palladium (showing thickness ranging from submicron metre to few micrometres) on a ceramic support. In this case, the advantages include reduced material costs, improved resistance to mechanical strength and higher permeating flux. Otherwise, dense membranes selectively permeable only to hydrogen based on tantalum [6], vanadium [7], nickel [8,9] and titanium [10] are considered valid and less expensive alternatives with respect to the palladium and its alloys.

A problem associated with metal membranes is surface poisoning, which can be more significant for thin metal membranes. The influence of poisons such as H₂S or CO on palladium-based membranes is a serious problem. These gases are adsorbed on the palladium surface, blocking available dissociation sites for hydrogen. The effect of small amounts of H₂S may be minimized by operating at higher
temperature or by using a protective layer of platinum. CO can easily desorb at operating temperatures above 300 °C [11].

A particularly sophisticated technique of hydrogen purification makes use of thin dense metal membranes. Many metals are capable of reacting with hydrogen at moderately elevated temperatures, forming metal hydrides. Atomic hydrogen moves fairly easily around the metal lattice, thus allowing hydrogen to pass between the two surfaces of dense metal layers while other substances are held back completely. Usually, palladium alloys are preferred for this gas separation application since thin layers of most other metals cannot withstand aggressive atmospheres long enough. Palladium, however, is very expensive, and the industrial installation of such membranes stipulates layers of less than 10 μm thickness [12].

On the other hand, the mechanical strength of palladium membranes as thin as 10 μm is not sufficient for practical purposes. The solution to this problem is the deposition of palladium layers on porous supports. At operating temperatures of several hundred degrees Celsius inorganic materials are suitable as mechanical backbones. At Fraunhofer IGB, a new process technology for production of ceramic hollow-fibre membranes has been implemented. With diameters of less than 1 mm and walls as thin as 100 μm these membranes have several advantages over conventional ceramic membranes. Their crossflow resistance is much smaller, as is their weight, and they provide very large surface-to-volume ratios. Thus, compact gas separation modules with large membrane areas become feasible. Naturally, these hollow fibres are very attractive supports for the aforementioned palladium membranes, and very thin metal coatings are developed for them at the Fraunhofer IGB. Palladium coatings of 4 μm thickness have been deposited on asymmetric hollow-fibre membranes by the electroless plating technique. These metal coatings are dense and their adhesion to the ceramic support is very good. The hydrogen transport across the membrane is activated and fluxes become technically acceptable only at elevated temperatures. For instance, at 430 °C an H₂ flux of over 10 m³ m⁻² h⁻¹ bar⁻¹ has been measured. The corresponding N₂ permeation rate was 10 L m⁻² h⁻¹ bar⁻¹, yielding an H₂/N₂ separation factor of 1000 [13,14].

21.2.1.2 Ceramic Membranes

The most useful characteristics of ceramic membranes are their chemical and thermal stability and their high mechanical strength [1,15].

**Dense Ceramic Membranes** Dense ceramic membranes can be fabricated in three configurations: disc/flat-sheet membrane, tubular membrane and hollow-fibre membrane [16].

Dense ceramic membranes are made from composite oxides usually having a perovskite or fluorite crystalline structure [17,18]. A large number of oxygen vacancies are present in the membrane, mostly generated by doping strategy, leading to ionic conductivity. Depending on the mediator of the electronic flux, the ceramic membranes may be divided into three different classes [19]:

1) A single material membrane based on a material exhibiting both ionic and electronic conductivity (MIEC membrane).
2) A dual-phase composite consisting of percolating phases of an ion conductor and an electron conductor (dual-phase membrane).
3) A pure ionic electrolyte conductor, with suitable electrodes connected to an external circuit for the electronic current (electrolyte membrane).
**Porous Ceramic Membranes**  These membranes are used for a variety of commercial applications, and their use in liquid filtration techniques such as ultrafiltration and microfiltration helps to keep costs low.

In order to increase their selectivity, ceramic porous membranes are usually asymmetric. They usually have a multilayered structure, consisting of a support with large pores and a top made of one or more thin layers with small pores. The support could be produced by slip casting or extrusion, while the intermediate and top layers can be produced using one of several techniques [20].

### 21.2.1.3 Zeolite Membranes

Zeolites are microporous crystalline alumina silicate with a uniform pore size. Zeolites are used as catalysts or adsorbents in the form of micrometre- or submicrometre-sized crystallites embedded in millimetre-sized granules. Zeolite membranes have relatively low gas fluxes compared with other inorganic membranes and exhibit negative thermal expansion; that is, in the high-temperature region the zeolite layer shrinks, but the support continuously expands, resulting in thermal stress problems for the attachment of the zeolite layer to the support as well as for the connection of the individual microcrystals within the zeolite layer [21]. Apart from the weak points of the zeolite membrane, it is necessary to think about a method to make use of the good points of zeolite membranes.

### 21.2.1.4 Carbon Membranes

Carbon membrane is one type of porous inorganic membrane. Although the concept of carbon membrane for gas separation dates from the early 1970s, interest in developing carbon membrane only increased after Koresh and Soffer successfully prepared apparently crack-free molecular sieving hollow-fibre carbon membranes. Since then, many researchers have used different polymeric materials, including polyimides, to prepare carbon membranes by using pyrolysis. In general, carbon membranes can be divided into four major configurations: flat sheet, membrane supported on tube, capillary and hollow fibre. The permeation properties of carbon membranes have been improved greatly since those early days. Carbon membranes offer advantages over polymeric membranes, especially in terms of selectivity, as well as in thermal and chemical stability. More attention will be paid to carbon membranes in this century. Ismail and David’s paper reviews the development of carbon membranes and gives a clear future direction in research for carbon membrane [22].

### 21.2.2 Polymer Membranes

See the review article by Gallucci et al. [2].

Basically, all polymers can be used as membrane material, but owing to relevant differences in terms of their chemical and physical properties, only a limited number of them are utilized practically. In fact, the choice of a given polymer as a membrane material is not arbitrary, but based on specific properties, originating from structural factors. Drioli and co-workers [23] give an overview of the commercial polymers used as membranes as well as of other polymers having high potential for application as a membrane material. However, many industrial processes involve operations at high temperatures. In this case, polymeric membranes are not suitable and, therefore, inorganic ones are preferred.
21.3 Technology of Membrane Reactors

A membrane reactor is a device for simultaneously performing a reaction and a membrane-based separation in the same physical device. Therefore, the membrane not only plays the role of a separator, but also accelerates the reaction itself. They can apply to a wide range of various fields, such as in the production of enantiopure amino acids and L-methionine, the acceleration of esterification reactions by removing water or alcohols, the production of methanol by the catalytic conversion of methane in natural gas and oxygen in air, and the production of highly purified hydrogen from stream reforming of gases. In the membrane reactor, a membrane, which can be either organic (polymeric) or inorganic (ceramic, metal) plays the leading role.

21.3.1 Catalytic Membrane Reactors

21.3.1.1 Biocatalyst-Immobilized Polymer Membranes

Types of Biocatalyst-Immobilized Polymer Membranes The preparation of biocatalyst-immobilized polymer membranes is carried out by following essentially the same process as the preparation of immobilized enzyme. To retain sufficient catalytic activity in the immobilized state, the enzyme has to be immobilized under conditions in which the residual groups of the amino acids that comprise the active centre of the protein and their higher order structure are not changed.

A number of methods for immobilizing biocatalysts have been reported and they can be divided into covalent binding onto supports, cross-linking and entrapment. Biocatalyst-immobilized polymer membranes are prepared by methods similar to immobilized enzymes and are summarized in Figure 21.3 [24]; that is: (a) physical adsorption of the biocatalysts onto a polymer support membrane; (b) cross-linking between biocatalysts on (a); (c) covalent binding between the biocatalysts and the polymer membrane; (d) ion complex formation between the biocatalysts and the polymer membrane; (e) entrapment of the biocatalysts in a polymer gel membrane; (f) entrapment and adsorption of biocatalysts in a polymer gel membrane; (g) entrapment and covalent binding between the biocatalysts and the polymer; (h) entrapment and ion complex formation between the biocatalysts and the polymer membrane; (i) entrapment of the biocatalyst in a pore of an ultrafiltration membrane; (j) entrapment of the biocatalyst in a hollow-fibre membrane; (k) entrapment of biocatalysts in microcapsules; and (l) entrapment of the biocatalyst in a liposome.

21.3.1.2 Technology of Biocatalyst-Immobilized Polymer Membranes in Membrane Reactors

Lipase-immobilized membranes were prepared by both non-covalent and covalent immobilization methods using (i) lipase adsorption onto the membranes, (ii) inclusion of the enzyme into the membrane structure by filtration and (iii) covalent attachment of lipase to the membrane. The catalytic properties of these membranes have been studied for the reaction of butyloleate synthesis through the esterification of oleic acid with n-butanol in isooctane. Ultrafiltration membranes composed of regenerated cellulose were used for lipase immobilization. Lipase inclusion into the wide porous supporting layer of the membrane was the most efficient method for preparing highly effective biocatalytic membranes. The percentage of oleic acid conversion using these membranes was about 70.0–72.7 % (with a reaction time of 8 h). It was shown that the distribution profile of the lipase in the membrane was important for the effective enzyme utilization. The profile imaging atomic force microscopy (AFM) technique was used to visualize the surfaces of the lipase-immobilized biocatalytic membranes. AFM has also been used to directly quantify interactions between the lipase-coated tip
and the membrane surface. It was concluded that the direct measurements of the interaction force between the enzyme-coated tip and the membrane surface would be a useful and practical approach for the choice of membranes as porous polymeric support for lipase immobilization through adsorption [25].

Enzyme-membrane reactors (EMRs) were prepared by Hicke et al. using covalent immobilization of fructosyltransferase (FTF) onto amino-functionalized track-etched poly(ethylene terephthalate) membranes with nominal pore diameters of 400, 1000 or 3000 nm, and in all cases the loss of enzyme activity was fast, and the extent of pore blocking increased with decreasing pore diameter. Experiments at varied crossflow velocity with the FTF covalently immobilized on the surface of an epoxy-reactive nonporous film suggested that the rate of FTF deactivation could be much reduced by increasing mass transfer efficiency. Consequently, an FTF-EMR with pore diameters of 1000 nm

Figure 21.3 Type of biocatalysis immobilized polymer membranes.
had been operated using regular backpulsing during flow-through or with dispersed inert nanoparticles (diameter 110 nm) in the feed solution flowing through the pores. For both variants, a significant performance improvement was obtained. Finally, a novel nanoparticle composite membrane was prepared via the covalent immobilization of epoxy-reactive nanoparticles (diameter 200–230 nm) on the pore walls of the track-etched membranes. Spacing between the particles was achieved by using a mixture of reactive and inert nanoparticles and suitable reaction and washing conditions. The FTF-EMR based on the novel nanoparticle composite membranes had a much higher productivity (prolongation of EMR operation time and more formation of inulin) as compared with all the other membranes or variants investigated in this study. Also, a much lower pore-blocking tendency was observed. This improved performance was explained by the two functions of the nanoparticles in the membrane: turbulence promotion and support providing increased surface area for covalent enzyme immobilization [26].

For applications as artificial kidneys, the ultrafiltration, hydrolysis and adsorption characteristics of semipermeable cellulose nitrate membranes containing urease, styelite and activated charcoal, which were prepared by the use of mixed solvents of n-propyl alcohol and N,N-dimethyl formamide, were investigated under various conditions. The optimum composition of the casting solution was found to be a ratio of cellulose nitrate : n-propyl alcohol : N,N-dimethyl formamide, of 13.00 : 21.75 : 65.25 (wt%), containing 3 g of urease, 1.5 g of stylite and 5 g of activated charcoal per 100 g of the casting solution. It was observed that the ultrafiltration rate, the hydrolysis and the adsorption characteristics using aqueous solutions of urea and disodium phenoltetramphthalein sulfonate (BSP) as a feed solution were significantly influenced by the solvent composition in the casting solution, the evaporation period, the additional amount of activated charcoal, and the operating temperature and pressure. When a mixture of albumin, sodium chloride, urea, creatinine, BSP and vitamin B₁₂ was used as a model for blood, the ultrafiltration rate was high (2.5 × 10⁻⁵ g cm⁻² s⁻¹) and urea, creatinine, BSP and vitamin B₁₂ were removed, and also albumin was completely rejected [27].

Figure 11.13 shows the effects of the ultrafiltration period on the ultrafiltration rate, the hydrolysis of urea, the ion-exchange capability, the adsorption and the rejection fraction. As can be seen from Figure 11.13, the ultrafiltration rate decreased. This result can be attributed to the combined factors of the blockage of pores in the membrane, namely the compaction of membrane, and the concentration polarization of albumin molecules. The hydrolysis fraction of urea was always 100% and the ammonium ion was completely adsorbed throughout this ultrafiltration period. The hydrolysis fraction of the adsorbed sodium ion approaches a constant value, and the albumin was perfectly rejected. These results can be interpreted as the membrane being able to function as an artificial kidney [27].

A new method of enzyme immobilization in a polyion complex has been proposed. An enzyme-immobilized polyion complex membrane was prepared by ultrafiltrating a mixture consisting of quaternized chitosan, sodium polyacrylate and invertase [28] or urease [29] in an aqueous NaBr solution. The permeation and hydrolysis characteristics of aqueous sucrose or urea solutions through these enzyme-immobilized membranes were studied under various conditions. A hydrolytic Michaelis–Menten-type reaction for urease-immobilized membrane was postulated [30].

Figure 21.4 is a Lineweaver–Burk plot of the hydrolysis reaction of urea through the urease-immobilized membrane. This relationship shows a good linearity. Therefore, this supports the idea that the hydrolysis reaction of urea through the urease-immobilized polyion complex membrane can be interpreted as the Michaelis–Menten type of reaction.

The kinetic data determined from the intercepts of the axis in Figure 21.4 are summarized in Table 21.1, which also includes those for the batch reaction of the hydrolysis of urea by a native urease. The value of maximum decomposition rate \( V_{\text{max}} \) of urea for the urease-immobilized polyion complex membrane was about 700-fold that of the native enzyme.
This is mainly caused by the fact that the existence amount of the enzyme per unit volume is higher in the enzyme-immobilized polymer membrane. The reciprocal of the Michaelis constant, 1/$K_m$, which is used to evaluate the affinity constant between the substrate and the enzyme molecules, was slightly larger in the system of enzyme-immobilized polymer membrane. A polymer matrix constructed from a polyion complex membrane becomes a barrier for the approach of a substrate molecule to the immobilized enzyme molecule. But once the substrate molecule has contacted the immobilized enzyme molecule, these molecules can interact in the limited space in the polymer matrix.

If some enzymes can be immobilized by the method reported in this study, a composite enzyme-immobilized polymer membrane of the laminate type can be easily prepared, as shown in Figure 21.5, in which $E_1$, $E_2$, $E_3$ and $E_4$ represent different enzymes. When such a composite enzyme-immobilized polymer membrane is applied to chemical reactions and the resulting product is permeated through the $E_1$-immobilized layer and becomes a substrate for the next enzyme ($E_2$)-immobilized layer, then the synthesis of materials due to multistage reactions becomes possible [29].

Table 21.1 Kinetic data for the hydrolysis of urea by the native urease and through the urease-immobilized polyion complex membrane.

<table>
<thead>
<tr>
<th>Enzyme</th>
<th>$K_m$ (mol L$^{-1}$)</th>
<th>$V_{max}$ (mol L$^{-1}$ s$^{-1}$)</th>
<th>$1/K_m$ (L mol$^{-1}$)</th>
<th>$k_c$ (L s$^{-1}$)</th>
<th>$k_1$ (mol L$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>$5.9 \times 10^{-2}$</td>
<td>$1.4 \times 10^{-5}$</td>
<td>16.9</td>
<td>72.9</td>
<td>$1.23 \times 10^3$</td>
</tr>
<tr>
<td>Immobilized</td>
<td>$4.3 \times 10^{-2}$</td>
<td>$9.5 \times 10^{-3}$</td>
<td>23.3</td>
<td>5.49</td>
<td>$1.27 \times 10^3$</td>
</tr>
</tbody>
</table>

Figure 21.4 Lineweaver–Burk plot for the hydrolysis of urea through the urease immobilizing membrane. Operating conditions: 50 °C, 3 kg cm$^{-2}$ and pH 7.0.

Figure 21.5 Model of some enzyme-immobilized polyion complex membranes.
A new combined method has been reported to localize the sites of enzyme immobilization and to determine its catalytic activity on a polymeric capillary membrane reactor. The useful new method resulted from the merging of the classic in situ enzyme activity assay and Western blotting technique, and both results are easily detectable by either low or high magnification in light microscopy. β-Glucosidase from olive fruit was selected as an enzyme model because of its suitable relevance in the industrial processing of foods, in biotechnology and in pharmaceuticals and for its activity against the synthetic substrate 5-bromo-4-chloro-3-indolyl-β-D-glucopyranoside which develops an insoluble dyed product. The enzyme was physically immobilized within 30 kDa cut-off capillary polysulfone membranes and the results were obtained by means of a polyclonal antibody against β-glucosidase and the synthetic substrate clearly showed the coherent localization of the immobilization enzyme sites and its activity [31].

The transport properties of the phase transfer reaction components through a multiphase enzyme-loaded membrane system were then identified. The multiphase system is of interest for the preparation of a two-separate-phase enzyme membrane reactor used for the enantioselective conversion of the racemic ester of naproxen into the corresponding S-naproxen acid. The transport properties of the system have been measured in the absence of biochemical reaction. Therefore, the overall mass transfer coefficients of the reactant (naproxen ester) and product (S-naproxen acid) through the two-separate-phase membrane system have been measured using a deactivated enzyme-loaded membrane. The multiphase system of interest is composed of an organic and an aqueous phase separated by a polymeric membrane containing the immobilized enzyme. The enzyme was immobilized alone or in the presence of an oil–water emulsion, in order to either improve enzyme distribution at the oil–water interface or to enhance the transport of reaction components through the membrane. This mass transfer rate through the membrane as a function of the axial velocity was evaluated. The transport performance through the membrane itself, the membrane loaded with enzyme, and the membrane loaded with the enzyme in the presence of emulsion were studied [32].

A biphasic enzymatic membrane reactor was made by immobilizing Candida rugosa lipase onto the dense surface of polysulfone ultrafiltration membrane by filtration and then crosslinking it with a glutaraldehyde solution. The reactor was further applied to the hydrolysis of olive oil, the performance of which was evaluated with respect of apparent reaction rate based on the amount of fatty acids extracted into the aqueous phase per minute and per membrane surface. The ultrafiltration and cross-linking processes greatly improved the reaction rate per unit membrane area and the enzyme lifetime. The highest reaction rate reached 0.089 μmol FFA min⁻¹ cm⁻² when the enzyme loading density was 0.098 mg cm⁻². These results also indicated that the performance of lipase immobilized onto a membrane surface was superior to that immobilized in the pores, and the apparent reaction rate and stability of the immobilized lipases were greatly improved greatly after cross-linking. It is suggested that the immobilization of the enzymes by filtration and then cross-linking the enzymes onto the membrane surface is a simple and convenient method to prepare a high-activity immobilized enzyme membrane [33].

In order to immobilize enzymes in the polymer matrix by copolymerization, vinylized urease (VU) was synthesized using the method reported by Hoffman and co-workers (1) [34]; that is, N-succinimidylacylate (NSA;10 mg) was added to a phosphate buffer solution of 20 mM (pH 7.4) containing urease (120 mg), and the reaction was performed at 36 °C for 1 h to introduce vinyl groups into the urease molecule. Afterwards, the resulting VU (I) was purified by gel filtration. The degree of vinyl group introduction was 15.9%, which was determined by the trinitrobenzene sulfonate method [35].
Urease-immobilized poly(VU–AAm–HEMA) membranes were prepared by the copolymerization of VU with acrylamide (AAm) and 2-hydroxethyl methacrylate (HEMA) using \(N,N'\)-methylenebiamcrylamide as a cross-linker, plus aqueous solutions of ammonium persulfate and \(N,N,N',N'\)-tetramethylenediamine as redox initiators, in a moulded plate between two glass plates at 25 °C for 3 h, as shown in Figure 21.6 [36].

Uragami et al. [36] prepared two kinds of urease-immobilized polymer membranes. One was prepared by bulk-copolymerizing a mixture consisting of VU, AAm, HEMA and a cross-linker (urease-immobilized poly(VU–AAm–HEMA) membrane) and another was prepared by ultrafiltrating a mixture composed of urease, quaternized chitosan and sodium carboxymethyl cellulose in an aqueous sodium bromide solution (urease-immobilized polion complex membrane). The permeation and hydrolytic characteristics of aqueous urea solutions were kinetically investigated under various conditions through urease-immobilized membranes. The hydrolysis of urea through urease-immobilized membranes followed Michaelis–Menten kinetics and was discussed.

When comparing kinetic data for the hydrolysis of urea through these membranes, the enzymatic activities of the urease-immobilized poly(VU–AAm–HEMA) membranes were lower than those of urease-immobilized polion complex membranes, but the stabilities of the former were higher than those of the latter. An illustration of these membrane performances is shown in Figure 21.7. These differences could be significantly attributed to differences in the higher order structure of urease molecules obtained during immobilization. Although the enzyme activity in conventional and membrane reactors cannot be discussed in a similar way, the membrane reactor has advantages such as (i) maintaining enzyme stability, (ii) easing the separation of enzyme and product and (iii) enzyme recovery. Therefore, in the near future, if the immobilization amount of enzyme immobilized in polyner membranes can be increased, then the performance of these enzyme-immobilized membrane reactors will be improved [36].

A multiphase/extractive enzyme membrane reactor for production of diltiazem chiral intermediate in industrial applications has been reported by Lopez and Matson [37]. Enzyme membrane reactors can be used to enhance the productivity and practicality of certain biotransformations by improving
substrate–enzyme contact, by providing a simple and reversible means of enzyme ‘immobilization’ and by effecting the removal of inhibitory reaction products. Lopez and Matson describe the development and eventual scale-up of a multiphase/extractive membrane reactor designed to manage reaction problems encountered in a biphasic reaction system characterized by the formation of an inhibitory reaction product. In particular, the application of this membrane reactor to an enzyme-mediated resolution of a racemic mixture is described – namely, the optical resolution of a chiral intermediate used in the production of diltiazem, a drug used in the treatment of hypertension and angina. The development process is traced from bench-scale studies of process feasibility through optimization, process reliability, and pilot-plant studies – a process that ultimately culminated in the operation of a commercial-scale membrane reactor facility that currently produces over 751 t year\(^{-1}\) of diltiazem intermediate [37].

Active concentration transport of glucose was carried out with plural enzyme immobilized membranes [38]. In other words, a membrane which immobilized both of adenosine triphosphate (ATP) and hexokinase is composited with a membrane-immobilized glucose-6 phosphate (phosphatase). As shown in Figure 21.8, when anion-selective membranes are laminated on both sides of this composited membrane, glucose is oxidized with the ATP–hexokinase-immobilized membrane and consequently glucose-6-phosphate (G6P) is produced. Because this G6P is a charged anion, G6P cannot be permeated through anion-selective membranes. Therefore, G6P diffused in the phosphatase-immobilized membrane, changed glucose by dephosphorylation and actively concentrated against its concentration gradient.

21.3.1.3 Polymer–Metal Complex Membranes

It is well known that a polymer–metal complex can become the catalyst of various kinds of reactions. However, a lot of polymer–metal complexes are homogeneous solution systems. Therefore, one of the things which enables a polymer–metal complex catalyst in a heterogeneous system is the
polymer–metal complex separation membrane. The high polymer–metal complex separation membrane has both separated transportation functions at the same time to become the catalyst of the reaction. Decomposition of hydrogen peroxide catalysed by alginate–Cu(II) complex membranes was investigated under various conditions [39]. The complex membranes were prepared at various temperatures. As can be seen from Table 21.2, the content of Cu(II) in the complex membrane prepared at a lower temperature was lower than that at a higher temperature, but the ability for the decomposition reaction of hydrogen peroxide of the former complex membrane was higher. This result was interpreted in terms of the difference in a contacting probability of a hydrogen peroxide molecule with coordinated Cu(II) in the complex membrane (see Figure 21.9). A membrane with a very rough physical structure showed no measurable catalytic activity (see Figure 21.10). The decomposition reaction of hydrogen peroxide through the alginate–Cu(II) complex membrane, without uncatalysed decomposition of hydrogen peroxide, obeyed the Michaelis–Menten equation, showing an enzyme-like catalytic function of the membrane. The decomposition reaction of hydrogen peroxide catalysed by the complex membrane was significantly influenced by the physical and chemical structure of the complex membrane.

In the decomposition of hydrogen peroxide through an alginate–Cu(II) complex membrane and a poly(vinyl alcohol) (PVA)–Cu(II) complex membrane, in spite of the fact that Cu(II) content in the latter membrane was approximately a quarter that of the former membrane, the latter membrane showed a higher catalyst activity. This depends on the degree of binding power of the hydrogen peroxide molecule with the ligand Cu(II) ions. In the former membrane, a copper ion interacts with a

**Table 21.2** Kinetic data for decomposition reaction of hydrogen peroxide through some alginate–Cu(II) complex membranes.a)

<table>
<thead>
<tr>
<th>Membrane preparation temperature (°C)</th>
<th>$T_{Cu}/T_{H}$</th>
<th>$K_m$ (mol L$^{-1}$) $\times 10^2$</th>
<th>$V_{max}$ (mol L$^{-1}$ s$^{-1}$) $\times 10^7$</th>
<th>$k_3$ (L s$^{-1}$)</th>
<th>$k_1$ (mol L$^{-1}$ s$^{-1}$)</th>
<th>$1/K_m$ (L mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.680</td>
<td>1.16</td>
<td>7.64</td>
<td>4.29</td>
<td>3.871</td>
<td>86.2</td>
</tr>
<tr>
<td>60</td>
<td>0.708</td>
<td>1.92</td>
<td>7.64</td>
<td>4.22</td>
<td>2.198</td>
<td>52.1</td>
</tr>
<tr>
<td>60</td>
<td>0.680</td>
<td>3.30</td>
<td>7.64</td>
<td>4.36</td>
<td>1.321</td>
<td>30.3</td>
</tr>
</tbody>
</table>

a) $\text{Alg} – \text{Cu} + S \xrightleftharpoons_{k_1}^{k_2} \text{Alg} – \text{Cu} S \rightarrow \text{Alg} – \text{Cu} + P$. $K_m = (k_2 + k_3)/k_3k_2 << k_3K_m = k_3/k_1 V_{max} = k_3[\text{Alg} – \text{Cu}]$. $P$ is product.
carboxyl group, but a copper ion interacts with a hydroxyl group in the latter membrane. As the binding power of the latter membrane is weak, the electronic absorption effect of an axis coordination seat working as a catalytic active point grows big. Consequently, complex formation between a complex catalyst and the hydrogen peroxide molecule as a substrate becomes easy and the catalytic activity is raised. These factors heighten catalytic activity. Also, the latter complex membranes can be used repetitively in permeation and decomposition testing, and a catalytic activity drop is uncommon too. Alginate–Cu(II) complex membranes have a catalytic activity which oxidizes hydroquinone in p-benzoquinone [40]. This oxidation reaction is not caused at the membrane surface and progresses only in the complex membrane.

In addition, the catalytic activity of the complex membrane in this oxidation reaction is increased with increasing Cu(II) content in the complex membrane for the same membrane formation
temperature, namely the same physical structure of the membrane. On the other hand, when the Cu(II) contents in the complex membranes are the same, a complex membrane with a rougher physical structure has a higher catalytic activity. In the oxidation reaction of hydroquinone, this reaction also obeys a Michaelis–Menten-type equation and resembles an enzyme reaction. Uragami et al. [41] also reported that alginate–Cu(II) complex membranes have a catalytic activity for the hydrolysis of dinitrophenylester.

A case study using macromolecular metal complexes is described by Molinari et al. The results of a process named polymer-assisted ultrafiltration for ion removal from various types of waters is reported. Water-soluble polymers such as polyethyleneimine, polyacrylic acid, polyacrylic acid sodium salt and poly(dimethylamine-co-epichlorohydrin-co-ethylene diamine) as chelating agents, the Cu^{2+} as model ion and five ultrafiltration membranes were used. The complexing agents were previously tested to establish the binding capacity and the best operating conditions for the process. Among the polymers tested the polyethyleneimine appeared the most interesting one because its binding mechanism does not involve a counter ion release. It was tested in the simulation of wastewaters treatment containing the Cu^{2+} ion chelated with citric acid; this is a problem of interest in the recycling of water from soil washing operations. The polyethyleneimine quantitatively bound the copper–citrate chelate at pH 5.5 and the three-component complex was separated by ultrafiltration membranes, producing a permeate with very low metal concentration. The polymer regeneration was carried out with good results by operating with the diafiltration method. The copper ion present in the diafiltration permeate in a form chelated with citric acid was recovered by oxidizing the citrate in a membrane photoreactor. The positive results of the case study described show that macromolecule–metal complexes play a key role for running effectively and selectively the polymer-assisted ultrafiltration process for removing metal ions from various type of waters [42].

21.3.1.4 Polymer Catalysis Membranes

A membrane reactor–separator, in which an anion-exchange membrane and a urease-immobilized PVA membrane were clamped together to separate the feed solution and the stripping solution of a dialysis cell, was constructed by Chen et al. [43]. The urea in the feed solution passed through the anion-exchange membrane and water film, and then was hydrolysed to ammonium carbamate in the urease-immobilized PVA membrane. The experimental results showed that no ammonium ion was found in the feed solution under either phosphate or citrate buffer systems at 0.05–0.2 mol dm^{-3} and pH 6–9, and various initial concentrations of urea in the feed solution (20–200 mmol dm^{-3}). This indicates that the water film between the two membranes allows the carbamate ions to decompose into ammonium and carbonate ions completely before entering the anion-exchange membrane. The device therefore can be used for the removal of urea from feed solution, while preventing the backflow of ammonium ions from the stripping solution or water film into the feed solution. It has significant potential in the development of a wearable or portable artificial kidney. The properties of the urease-immobilized PVA membrane were examined. A kinetic model describing the transport–reaction behaviour of urea in the membrane reactor–separator was developed, and the optimum values of the reactor parameters were obtained.

Cation-exchange membranes prepared from poly(styrene sulfonic acid) (PSA) and PVA were cross-linked by both glyoxal and glutaraldehyde and, furthermore, cross-linked membranes were annealed. The ion-exchange capacity of the resulting PSA–PVA membranes increased, and the water content and degree of swelling of PSA–PVA membrane decreased with increasing annealing time. The syntheses of esters from alcohol and acetic acid through various PSA–PVA membranes were carried out in a diaphragm type cell consisting of two detachable parts in which the membrane was set in the middle of the two parts of the cell. When an aqueous solution of alcohol and acetic acid in one part of cell and


*p*-chlorobenzene in another part were set, esters formed by the catalytic action of PSA–PVA membrane increased on the *p*-chlorobenzene phase with time. These results support that the PSA–PVA membrane could perform both the reaction and separation. The formation of esters in this membrane reactor was a secondary reaction as well as the general esterifications between alcohols and acids. The catalytic action in the esterification of the PSA–PVA membranes prepared by changing the ratio of PSA–PVA and the amount of casting solution was also investigated. The rate of esterification reaction was significantly dependent on the number of sulfonic acid groups in the effective membrane volume. The rate of reaction per milliequivalent of $\text{SO}_3\text{H}$ increased with an increase of the degree of swelling of the membrane and decreasing membrane thickness. In the esterification of methanol, ethanol and *n*-propanol with acetic acid, the reactivity through the PSA–PVA membrane was higher than that with HCl as catalyst. In that of *n*-butanol with acetic acid, however, it was the reverse [44].

Wu and Fu [45] prepared four types of anion-exchange membranes with different amine functional groups (trimethylamine, triethylamine, tri-*n*-propylamine and tri-*n*-butylamine) and investigated phenol allylation in a membrane reactor. They concluded that gravity and pressure are important factors in reactor design. The catalytic reactivity in the H2 reactor, the design of which was better than in the V1 reactor, was used to recover phenol from simulated wastewater. The respond surface methodology could be used to obtain the optimal turnover number and reaction rate to verify the reactivity of the catalyst in the membrane. For phase-transfer catalytic membrane systems to perform well, the membrane structure for reactants and solvents must be studied to obtain optimal conditions.

21.3.1.5 Ion-Exchange Resins and Ion-Exchange Membranes in Membrane Reactor

Flores and Cabassud [46] proposed a new process for the removal of metallic (Cu(II)) compounds in the treatment of industrial wastewaters: a membrane reactor with a moving bed of porous ion-exchange resins. After a comparison of various cationic resins, IRP 69, with its small particle diameter and high exchange rate, was chosen for the rest of the study. For these particles, the influence of stirring velocity and temperature on the apparent reaction rate was analysed in a closed, stirred reactor. The conditions for obtaining the kinetic regime and rate constant were determined. A particle filterability study defined the operating conditions (circulation velocity and pressure) needed for a satisfactory compromise between power consumption and the number of modules to be set up. The first elements for a comparison between a conventional packed-bed reactor and a membrane moving particle-bed reactor are given. For the same flow rate and a conversion of 95%, the membrane reactor running under optimum conditions provides reductions by factors of 2.9 for the volume of adsorbing particles, 26 for the pressure loss, and 4.75 for the power supplied to the system. The process thus shows promise but its performance remains to be validated by a pilot study.

The mechanism of anionic pollutant removal in an ion-exchange membrane bioreactor (IEMB) was studied for drinking water denitrification [47]. This hybrid process combined continuous ion-exchange transport (Donnan dialysis) of nitrate and its simultaneous bioreduction to gaseous nitrogen. A nonporous mono-anion permselective membrane precluded direct contact between the polluted water and the denitrifying culture and prevented secondary pollution of the treated water with dissolved nutrients and metabolic products. Complete denitrification may be achieved without accumulation of $\text{NO}_3^−$ and $\text{NO}_2^−$ ions in the biocompartment. Focus was given to the effect of the concentration of co-ions, counter ions and ethanol on the IEMB performance. The nitrate overall mass transfer coefficient in this hybrid process was found to be 2.8 times higher than that in a pure Donnan dialysis process without denitrification. Furthermore, by adjusting the ratio of co-ions between the biocompartment and the polluted water compartment, the magnitude and direction of each individual anion flux could be easily regulated, allowing for flexible process operation and control. Synthetic groundwater containing $135–350 \text{ mg NO}_3^− \text{ L}^{−1}$ was treated in the IEMB system.
A surface denitrification rate of 33 g NO₃⁻ per square metre of membrane per day was obtained at a nitrate loading rate of 360 g m⁻³ day⁻¹, resulting in a nitrate removal efficiency of 85%. Membranes in bioreactors were essentially regarded as micro-/ultra-porous barriers to promote high cell concentrations for process intensification and to avoid contamination of the treated water with the biocatalyst. Crespo and co-workers [48] discussed in particular the use of membrane bioreactors for treatment of water supplies contaminated with micro polluting ions. The contamination of drinking water sources with inorganic compounds is a matter of concern, because of their harmful effect on human health. Some of these compounds are highly soluble in water and dissociate completely, resulting in ions that are chemically stable under normal water conditions. Examples of polluting ions include nitrate, nitrite, perchlorate, bromate, arsenate and ionic mercury, for which the proposed guideline values for drinking water quality are quite low (in the range of micrograms per litre to a few milligrams per litre) owing to their carcinogenic effects or other risk factors to public health.

21.3.1.6 Metal Membranes

A membrane reactor was studied by Tosti et al. for separating the hydrogen produced by the dissociation of hydroiodic acid in the thermochemical-sulfur iodine process. A dense metal membrane tube of wall thickness 0.250 mm was considered in this analysis for hosting a fixed-bed catalyst: the selective separation of hydrogen from an azeotropic H₂O–HI mixture was studied in the temperature range 700–800 K. The materials considered for the construction of the membrane tube were niobium and tantalum; as a matter of fact, the most commonly used Pd–Ag membranes cannot withstand the corrosive environment generated by the hydroiodic acid. Damköhler–Peclet analysis was used for designing the membrane reactor, while a finite-element method simulated its behaviour; the effect of the temperature and pressure on the HI conversion and hydrogen yield was evaluated [49].

Hydrogen as a high-quality and clean energy carrier has attracted renewed and ever-increasing attention around the world in recent years, mainly due to developments in fuel cells and environmental pressures, including climate change issues [50]. In thermochemical processes for hydrogen production from fossil fuels, separation and purification is a critical technology. Where water-gas shift reaction is involved for converting the carbon monoxide to hydrogen, membrane reactors show great promises for shifting the equilibrium. Membranes are also important to the subsequent purification of hydrogen. For hydrogen production and purification, there are generally two classes of membranes, both being inorganic: dense phase metal and metal alloys, and porous ceramic membranes. Porous ceramic membranes are normally prepared by sol–gel or hydrothermal methods, and have high stability and durability in high-temperature, harsh impurity and hydrothermal environments. In particular, microporous membranes show promises in water-gas shift reaction at higher temperatures. Lu et al. reviewed the recent advances in both dense phase metal and porous ceramic membranes, and compared their separation properties and performance in membrane reactor systems. The preparation, characterization and permeation of the various membranes was presented and discussed. They also aimed to examine the critical issues in these membranes with respect to the technical and economic advantages and disadvantages. The relevance and importance of membrane technology to the new generation of zero-emission power technologies was also discussed.

A hydrogen-permeable composite-metal membrane for facilitating the thermal decomposition of H₂S was studied by Edlund and Pledger [51]. The membrane contained a platinum coating layer on the feed side of the membrane. The platinum layer resists irreversible chemical attack by H₂S at 700 °C and partial pressures of up to 115 psia. This membrane was used in a laboratory-scale membrane reactor to drive the decomposition of H₂S to greater than 99.4% of complete conversion. The by-products were sulfur and hydrogen; no sulfur oxides were formed. The thermal decomposition of H₂S within the membrane reactor was accurately described by a simple model that considered the
The initial composition of the feed gas, the equilibrium expression for $\text{H}_2\text{S}$ decomposition, and the hydrogen flux for the membrane.

Xie et al. studied a submerged flat metal membrane bioreactor used to treat synthetic domestic sewage [52]. The experiment was continued for 270 days and ran under two modes – as an aerobic membrane bioreactor (AMBR) and anoxic/aerobic membrane bioreactor (A/O-MBR) – at a permeate flux of $0.4–1 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$. PVA gel beads were added to the aeration tank with a volume ratio of 10% at the end of the A/O-MBR mode. The mean chemical oxygen demand and total nitrogen removal efficiencies achieved 96.69% and 32.12% respectively under the AMBR mode, and were 92.17% and 72.44% respectively under the A/O-MBR mode. Simultaneous nitrification and denitrification occurred at high mixed liquor suspended solids concentration. The metal membranes reduced effluent chemical oxygen demand during filtration. The system ran stably for 115 days at a permeate flux of $0.8–1 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ without changing membranes under the AMBR mode, but the membrane filterability decreased gradually under high mixed liquor suspended solids or A/O-MBR mode, and the addition of PVA worsened the membrane filterability on the contrary. Particle size distribution and sludge fractions had an evident influence on membrane fouling. The main fouling mechanism was cake formation under the AMBR mode and pore blocking under the A/O-MBR mode.

Thin palladium and palladium alloy membrane tubes with thickness up to $50 \mu\text{m}$ were produced by Tosti et al. These metal membranes, used as tube permeators in CMRs for the water-gas shift reaction, were thinner than the commercial ones ($100–150 \mu\text{m}$) and had both complete selectivity to hydrogen and good durability. A manufacturing procedure consisting of several steps of cold rolling and annealing the metal foils coupled with a simple welding technique of the tubes was carried out in order to produce the prototype thin palladium permeators. The procedure of rolling and annealing the palladium and palladium alloy foils was described in detail: the work hardening upon rolling of the palladium and palladium alloy foils was controlled by means of hardness measurements. Model studies and tests on the membranes and the CMRs for the water-gas shift reaction demonstrated the possibility to separate and recover highly pure hydrogen in energy applications such as a nuclear fusion fuel cycle and fuel cells fuelling [53].

Hydrogen permeation through a palladium membrane was measured in the presence of several gases, such as CO, $\text{N}_2$, $\text{CO}_2$, and Ar, both in the feed side and in the shell side of the (membrane) module by Gallucci et al. [54]. It was found that CO molecules remarkably inhibit hydrogen permeation. In particular, in the presence of CO the permeation decreases with two different slopes: (i) for low CO concentrations, the hydrogen permeation decreases quickly (surface effects), whereas (ii) for higher ones it decreases smoothly (dilute effect). Permeation of hydrogen, in the presence of the other gases (i.e. $\text{N}_2$, $\text{CO}_2$ and Ar) always decreases with the same slope (dilute effect). In order to describe the CO inhibition, a theoretical investigation was proposed. In particular, the framework of the density functional theory was used. CO and $\text{N}_2$ density functional full optimizations on palladium clusters show that CO and $\text{N}_2$ molecules present two minima on the cluster surfaces with bond lengths of $2.0 \text{ Å}$ and $3.8 \text{ Å}$ respectively. The CO minima are much stable than $\text{N}_2$ minima, resulting in a surface effect on the hydrogen permeation through the membrane.

Ethanol steam reforming was carried out by Tosti et al. in a membrane reactor consisting of an Ru-based catalyst bed packed into a thin-wall Pd–Ag permeator tube produced via cold rolling and diffusion welding of metal foils [55]. The experimental tests were performed in the temperature range $400–450 ^\circ\text{C}$ with the aim of studying the performances of the membrane reactor in terms of hydrogen yields. The main operating parameters investigated concerned the water/ethanol feed molar ratio ($8.4–13.0$), the pressure inside the membrane ($150–200 \text{ kPa}$), the sweep gas mode (co-current and counter-current) and the spatial velocity. In all the tests, ultrapure hydrogen was separated through the Pd–Ag membrane; in particular, when operated at $450 ^\circ\text{C}$ and $200 \text{ kPa}$, a hydrogen yield
higher than 80% was produced, thus demonstrating the membrane ability of promoting the reaction conversion (shift effect).

The methanol steam reforming reaction was studied by Basile et al. using both a dense Pd–Ag membrane reactor and a fixed-bed reactor [56]. Both the fixed-bed reactor and the membrane reactor were packed with a new catalyst based on CuOAl2O3ZnOMgO, having an upper temperature limit of around 350 °C. A constant sweep gas flow rate in counter-current mode was used in the membrane reactor and the experiments were carried out by varying the water/methanol feed molar ratio in the range 3/1 to 9/1 and the reaction temperature in the range 250–300 °C. The catalyst showed high activity and selectivity towards the CO2 and the H2 formation in the temperature range investigated. Under the same operating conditions, the membrane reactor showed higher conversions than a fixed-bed reactor and, in particular, at 300 °C and H2O/CH3OH molar ratio higher than 5/1 the membrane reactor showed complete methanol conversion.

Auto-thermal ethanol reforming was carried out by Tosti et al. at 200 kPa by a two-step process consisting of a traditional reformer operating at high temperature (700–740 °C) and a Pd–Ag multi-tube membrane module where the separation of hydrogen took place at 350–380 °C [57]. The membrane module was a bundle of 11 thin-walled Pd–Ag tubes of wall thickness 50–60 μm, diameter 10 mm, and length 270 mm; permeation tests were performed at 300–395 °C with lumen pressure of 150–200 kPa, and nitrogen sweep flow rates in the shell side ranged from 10 to 30 L min⁻¹ at atmospheric pressure. A hydrogen permeance of \(1.317 \times 10^{-2} \exp(-3.622 \times 10^{3}/T(K))\) mol m⁻² s⁻¹ Pa⁻⁰·⁵ was measured and complete hydrogen selectivity was verified. A water/ethanol mixture of molar ratio 2.50/1.00 was used as feed stream for carrying out ethanol reforming in the traditional fixed-bed reactor filled with a nickel on alumina catalyst. As a second step, the water-gas shift membrane reaction was carried out in the multitube membrane reactor; the Pd–Ag alloy of the membrane tubes worked for both catalysing the reaction and for separating all the hydrogen produced in the reformer and in the membrane reactor itself. The hydrogen separated through the membrane was collected in the shell side of the membrane module; by operating with a water–ethanol feed flow rate of 200 g h⁻¹, up to 1.2 L min⁻¹ of pure hydrogen was produced.

A hydrogen-permeable composite-metal membrane for facilitating the thermal decomposition of H2S was studied by Edlund and Pledger [58]. The membrane contained a platinum coating layer on the feed side of the membrane. The platinum layer resists irreversible chemical attack by H2S at 700 °C and partial pressures of up to 115 psia. This membrane was used in a laboratory-scale membrane reactor to drive the decomposition of H2S to greater than 99.4% of complete conversion. The by-products were sulfur and hydrogen; no sulfur oxides were formed. The thermal decomposition of H2S within the membrane reactor was accurately described by a simple model that considered the initial composition of the feed gas, the equilibrium expression for H2S decomposition and the hydrogen flux for the membrane.

The performance of a pilot-scale fluidized-bed membrane reactor (FLBMR) was studied experimentally by Ahchieva et al. in comparison with the conventional operation as a fluidized bed reactor for the catalytic oxidative dehydrogenation of ethane using a γ-alumina-supported vanadium oxide catalyst [59]. For both reactor configurations, the influence of process parameters such as temperature and contact time was investigated. Further, the experimental data obtained were compared with previous experiments with a fixed-bed reactor and a PBMR operated with a similar catalyst. For identical overall feed rates, the distributed oxidant feeding in the FLBMR improved the selectivity to ethylene significantly. The beneficial effect of oxidant dosing over the membrane is most pronounced at high temperatures and long contact times. Under limiting oxidant supply the FLBMR and the PBMR showed a similar performance, but under moderate oxygen excess the FLBMR outperformed the PBMR significantly. The maximum ethylene yield observed in the FLBMR was 37% compared with 35% for the
PBMR. Beside a high productivity, for the FLBMR a broader favourable operation range with respect to the oxygen/hydrocarbon ratio was observed, which indicates a lower sensitivity against oscillations and disturbances in the reactant feed, corresponding to a higher safety of operation. Because of the excellent heat transfer characteristics, the FLBMR concept is very promising for maximizing the yield of the desired intermediates also in large-scale plants, especially for strongly exothermic reactions.

21.3.1.7 Ceramic Membranes

Water-selective alumina–silica composite membranes were developed as a dehydration membrane reactor for dimethylether synthesis from methanol by Lee et al. [60]. The membranes were modified on a porous stainless steel support by the sol–gel method accompanied by a suction process. The improved membrane modification process was effective in increasing the vapour permselectivity by removal of defects and pinholes. The optimized composite membrane exhibited a water permeance of $1.14 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ and a water/methanol selectivity of 8.4 at a permeation temperature of 250 °C. The catalytic reaction for dimethylether synthesis from methanol using the membrane was performed at 230 °C, and the methanol conversion was compared with that of the conventional fixed-bed reactor. The methanol conversion of the membrane reactor was much higher than that of the conventional fixed-bed reactor. The methanol conversion of the membrane reactor and the conventional fixed-bed reactor was 82.5% and 68.0% respectively. This improvement of reaction efficiency can last if the water vapour produced in the reaction zone is continuously removed.

The dehydrogenation of methylcyclohexane (MCH) in CMRs for hydrogen production (see Figure 21.11) was studied experimentally and theoretically by Li et al. The membrane reactor was composed of a Pt–$\gamma$-Al$_2$O$_3$–$\alpha$-Al$_2$O$_3$ catalytic support and an H$_2$-selective silica separation layer, showing H$_2$ permeances of $(1.51–2.83) \times 10^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ with H$_2$/SF$_6$ permeance ratios of 290–1000 at 473 K. The MCH conversion was markedly increased after hydrogen extraction from the membrane reactor, which agreed very well with the results obtained by simulation using a proposed mathematical model. The effects of the catalytic activity and hydrogen extraction rate on membrane reactor performance were investigated during the simulations. A system combining a fixed-bed

![Figure 21.11](image-url)
prereactor and a membrane reactor was proposed for MCH dehydrogenation, which further improved the MCH conversion as a result of the enhanced driving force for hydrogen extraction from the membrane reactor [63].

Six different types of experiments were used by Hussain et al. in order to identify and validate the heat and mass transfer parameters of a tubular membrane. The respective configuration is similar to that of a membrane reactor, though without particulate catalyst or catalytic coating. The membrane is made of various layers of $\alpha$- and $\gamma$-Al$_2$O$_3$ and has dimensions (inner diameter of 21 mm) close to those relevant for practical applications. Mass transfer parameters of every single layer were derived separately by means of a dusty gas model, pointing out unexpected effects of asymmetry. Experiments of steady-state heat transfer, dynamic heat transfer and combined heat and mass transfer were introduced; thermal influences on mass transfer were discussed. Four of the six conducted types of experiments were free of fitting, providing a successful test of accuracy and consistency of the identified transport parameters, and a basis for a reliable simulation of membrane reactors [62].

21.3.1.8 Polymer–Metal Composite Membranes

Metal nanoparticles are known as highly effective catalysts, although their immobilization on solid supports is frequently required to prevent aggregation and to facilitate the catalyst application, recovery and reuse. The paper by Domènech et al. reports the intermatrix synthesis of Pd$^0$ nanoparticles in sulfonated polyethersulfone with Cardo group membranes and their use as nanocomposite CMRs. The synthesized polymer and the corresponding nanocomposite were characterized by spectroscopic and microscopic techniques. The catalytic efficiency of catalytic membranes was evaluated by following the reduction of $p$-nitrophenol in the presence of NaBH$_4$ [63].

Layer-by-layer deposition of polyelectrolyte–metal nanoparticle films in porous alumina, track-etched polycarbonate and nylon substrates yields catalytic membranes. With all three substrates, scanning electron microscopy images demonstrate a high density of well-separated nanoparticles in the membrane pores. These nanoparticles catalyse the reduction of nitroaromatic compounds by sodium borohydride with rate constants that are the same as those for nanoparticles immobilized on alumina powder. Moreover, the membranes selectively catalyse the reduction of nitro groups in compounds containing other reducible functionalities, such as cyano, chloro and styrenyl moieties. With nitrophenols and nitroanilines, the only reduction product is the corresponding amine. In contrast, nitrobenzene, nitrotoluene, nitrobenzonitrile, chloronitrobenzenes and $m$-nitrostyrene also form a nitroso product. Membrane catalysts are particularly attractive for controlling product distributions through variation of solution fluxes, as demonstrated by the formation of increased levels of nitroso compounds at high flux [64].

A new polymer–metal nanocomposite containing catalytic metal nanoparticles and useful for the preparation of catalytic membranes was developed by Domènech et al. [67]. Palladium nanoparticles were grown by intermatrix synthesis methodology on polymeric membranes made of either sulfonated and nonsulfonated polyethersulfone with Cardo group or Nafion membranes. The synthesized polymer, the membranes developed and the corresponding nanocomposites were characterized by chemical and microscopic techniques and their catalytic efficiency was tested following a model reaction: the reduction of $p$-nitrophenol to $p$-aminophenol.

21.3.2 Membrane Reactor with Pervaporation and Evaporation

21.3.2.1 Membrane Reactor with Pervaporation

The use of water-permeable membranes for pervaporation in the esterification of carboxylic acid with ethanol was studied by Kita et al. [68]. The perfect conversion due to the equilibrium shift was
obtained by using an asymmetric polyetherimide membrane for removal of water generated by the esterification.

Esterification of oleic acid with ethanol in the presence of p-toluenesulfonic acid was carried out at temperatures up to 383 K and initial molar ratios of ethanol to oleic acid \( m_0 \) up to 6. A kinetic equation having both a term of rate reduction due to water and an \( m_0 \)-dependent rate constant were presented. The esterification, aided with pervaporation through asymmetric polyimide membranes, was carried out at 348 K and 371 K under atmospheric and elevated pressures respectively. Almost complete conversion was attained for \( m_0 \) of 2 in a short time with a low concentration of the catalyst at 371 K. Only water and ethanol permeated through the membranes. The permeation flux was expressed by the product of the permeability constant \( P \) and the permeant concentration of the liquid. \( P \) depended on the concentration of oleic acid and ethyl oleate at 371 K, but not at 348 K. A model in which the kinetic equation was combined with the permeation flux equation taking both volume change and sampling loss of the reaction mixture into consideration represented the experimental time course of the reaction sufficiently well. The influence of operating parameters on the reaction time required for a conversion of 98% and on the productivity was investigated by simulation from the model [67].

Nafion tubes that function both as a reaction catalyst and a pervaporation membrane were used by Bagnell et al. to increase the yield in the esterification of acetic acid with methanol and \( n \)-butanol by selectively removing products, mainly water, from the reaction mixture [68]. The experiments were performed at room temperature in a batchwise reactor using acidic protons in Nafion pellets and the Nafion membrane as the reaction catalyst. In some experiments the acidic protons in the membrane were partially or fully exchanged with caesium ions, which increased the intrinsic selectivity of the membrane for water but lowered its permeability. In the methanol reaction, the yield of methyl acetate was increased from the usual equilibrium value of 73% to a maximum of 77%. In the \( n \)-butanol reaction, the yield of \( n \)-butyl acetate increased from 70% to a maximum of 95%. The effect of the membrane’s catalytic activity on its permselectivity was investigated. The catalytically active membranes showed significantly higher permselectivities for water at the same or higher flux, compared with when no reaction was taking place within the membrane phase.

The kinetic parameters have been established for the esterification of tartaric acid with ethanol. Both concentration-based and activity-based reaction rate constants and equilibrium constants were determined by Keurentjes et al. [71]. The activity-based data were determined using UNIFAC activity coefficient estimations. It was concluded that reaction rate constants determined in dilute solutions are capable of describing the reaction in a concentrated environment. This applied both for the activity-based description and for the concentration-based description. Although the activity coefficients involved differ significantly from unity, the effects of the individual activity coefficients were mutually compensated. Therefore, it was also possible to predict the reaction correctly when the concentration-based parameters were used. When pervaporation was used to remove the water produced in this reaction, the equilibrium composition could be shifted significantly towards the formation of the final product diethyltartrate. The membrane surface area to be installed had a clear optimum: the water removal is too slow when \( A/V \) is chosen too low, and too much of the ethanol is also removed when \( A/V \) is chosen too high.

Esterification of oleic acid with \( n \)-butanol in the presence of Lipozyme® was carried out at 25 °C in isooctane with various initial water activities by Kwon et al. [70]. Initial reaction rate as well as equilibrium conversion decreased at high initial water activity. Therefore, removal of water present in the reaction mixtures was essential. A pervaporation process was applied to the lipase-catalysed synthesis of \( n \)-butyloleate to remove water. Pervaporation selectively separated water from the reaction mixture using the nonporous polymeric membrane cellulose acetate. Therefore, pervaporation is potentially
Pervaporation-facilitated esterification was investigated by Feng and Huang [71]. A parametric study was carried out to provide a fundamental understanding of the reactor behaviour. A batch reactor integrated with a pervaporation unit was selected as the model system. It was shown by simulation that conversions exceeding equilibrium limits can be achieved by using pervaporation to remove water from the reaction mixtures, and that complete conversion of one reactant is obtainable when the other is in excess. The membrane reactor tolerated the presence of water, which can be either in the reaction medium or as impurity of the reacting reagent. There are upper and lower limits in the performance of reactor facilitation by pervaporation. Membrane permeability, membrane area and the volume of the reaction mixtures to be treated were important operating parameters influencing the reactor behaviour. Operating temperature influences reactor performance through its influences on reaction rate and membrane permeability.

A composite catalytic membrane with a cross-linked PVA dense active layer coated on a porous ceramic plate support was prepared by Zhu and Chen using a novel method and evaluated with a pervaporation set-up for the separation of several organic aqueous mixtures. Several key problems occurred during the preparation procedure are discussed. Scanning electron microscopy, infrared attenuated total refraction and X-ray photoelectron spectrometry were used to characterize the catalytic membrane natures. N-Butyl alcohol–acetic acid esterification was used as a model system for investigating the coupling of reaction with pervaporation in a batch reactor. Different reaction parameters, temperatures, catalyst concentrations and initial reactant molar ratios were studied experimentally [72].

Modelling of esterification of acetic acid with n-butanol in the presence of Zr(SO₄)₂·4H₂O coupled pervaporation was studied by Liu and Chen [73]. The influence of several process variables, such as process temperature, initial mole ratio of acetic acid over n-butanol, the ratio of the effective membrane area over the volume of reacting mixture and catalyst content, on the esterification was discussed. The calculated results for the conversion of n-butanol to water and permeation flux were consistence with the experimental data. The permselectivity and water content can be roughly estimated by the model equations.

PVA-based nanocomposite membranes were prepared by Sairam et al. by coprecipitation of different amounts of Fe(II) and Fe(III) taken in an alkaline medium and their pervaporation performances were investigated to dehydrate isopropanol, 1,4-dioxane and tetrahydrofuran (THF) from aqueous feeds containing 10–20 wt% of water in isopropanol and 1,4-dioxane, 5–15 wt% of water in THF [74]. The freestanding membranes were characterized by a dynamic mechanical thermal analyser, which showed a shift in glass transition temperature toward higher range along with an increase in storage modulus with increasing amount of iron oxide in the PVA matrix. Furthermore, thin layered membranes were cast on polyester fabric cloths as support layers to improve their pervaporation separation performances for all three mixtures over that of the pristine cross-linked PVA membrane. In particular, the composite membrane prepared by taking 4.5 wt% of iron oxide showed an improved selectivity with a slight sacrifice in flux compared with membranes containing lower contents of iron oxide as well as the pristine cross-linked PVA membrane. Flux decreased with increasing content of iron in the PVA matrix, while selectivity increased systematically.

A pervaporative CMR can afford chemical reaction and separation or concentration of the products in one step. The hydrogenation of acetophenone in diluted aqueous solution was investigated applying catalytically reactive polydimethylsiloxane and polyether-b-amide membranes in the pervaporative membrane reactor. A quadrupole mass spectrometer (QMS) was employed to follow online the hydrogenation reaction. Homogeneously distributed palladium clusters inside the polymeric
membranes catalyse the hydrogenation of acetophenone to 2-phenylethanol and the consecutive product ethyl benzene at low temperatures (30–70 °C). The reaction depends strongly on the disposability of H₂ inside the membrane. Only by means of the online QMS analyser could the availability of stoichiometric or excess amounts of H₂ at the catalyst with adjusted parameters such as temperature, hydrogen pressure, solute concentrations and membrane permeability be detected. It could be shown that the hydrogen level by bubbling at ambient pressure was not sufficient; however, at 4 × 10⁵ Pa (4 bar) H₂ pressure and 50 °C conversions up to 83% in 6 h were obtained. Efforts to quantify the measured intensities of the QMS were not successful; however, the relation of the organic compounds and the presence of excess H₂ were detected precisely with this method [75].

Mixed matrix membranes of sodium alginate (NaAlg) and PVA containing 5 and 10 wt% silicalite-1 particles were fabricated by the solution casting method and the cured membranes were cross-linked with glutaraldehyde. These membranes were used in pervaporation dehydration of isopropanol at 30, 40, 50 and 60 °C [76]. Membrane morphology was studied by scanning electron microscopy, and a universal testing machine was used to assess the membrane mechanical strengths. Swelling results of the pristine and mixed matrix membranes were correlated with their pervaporation performances. Selectivities of the mixed matrix membranes of NaAlg were 11 241 and 17 991 with fluxes of 0.039 kg m⁻² h⁻¹ and 0.027 kg m⁻² h⁻¹ respectively for 5 and 10 wt% silicalite-1 loadings. Corresponding values for mixed matrix membranes of PVA were 1295 and 2241, and 0.084 kg m⁻² h⁻¹ and 0.069 kg m⁻² h⁻¹ respectively for 10 wt% water-containing feed at 30 °C. Pristine membranes of NaAlg and PVA exhibited lower selectivities of 653 and 77 with increased fluxes of 0.067 kg m⁻² h⁻¹ and 0.095 kg m⁻² h⁻¹ respectively. From the temperature dependence of flux and diffusivity data with 10 wt% water-containing feed, Arrhenius plots were constructed to compute heat of sorption values. Mixed matrix membranes of NaAlg were better than PVA mixed matrix membranes at all compositions (10–40 wt%) of water. Molecular dynamics simulation was employed to compute the interfacial interaction energies of NaAlg and PVA polymers with silicalite-1 filler; also, sorption of liquid molecules was computed. Simulated diffusivities compared well with the experimental data. Thermodynamic treatment of sorption, diffusion and permeation processes was attempted based on the Flory–Huggins theory to explain the pervaporation performances of the membranes.

Filled mixed matrix membranes of NaAlg were prepared by the solution casting method and were filled with 4A zeolite particles in varying compositions from 0 to 10 wt% with respect to weight of NaAlg polymer. Membranes were cross-linked with glutaraldehyde and tested for pervaporation dehydration of acetic acid and ethanol in the temperature range from 30 to 70 °C [77]. Flux and selectivity data increased simultaneously for both feed mixtures at higher loadings of 4A zeolite, due to its high hydrophilic nature as well as molecular sieving effect in addition to its favourable interaction with hydrophilic NaAlg. At increasing temperature, flux increased, but selectivity decreased. Arrhenius activation parameters for permeation process were dependent upon the extent of filler content. Pervaporation-aided catalytic esterification of acetic acid with ethanol was attempted at 70 °C, resulting in considerable increase of ethyl acetate conversion at reduced reaction time due to continuous removal of water by the membrane.

Pervaporation in recent years has received strong attention from industry as a novel, energy-efficient and environmental-friendly separation technology. Pervaporation reactor is a new technology to enhance conversion in reversible esterification reactions. In the work by Rathod et al., PVA–polyethersulfone composite hydrophilic membrane was used for pervaporation-assisted esterification of lactic acid with isopropanol. Experimental work of esterification of lactic acid with isopropanol coupled with pervaporation was carried out. The effect of various parameters, such as initial mole ratio of isopropanol over lactic acid, the ratio of the effective membrane area over the volume of reacting mixture, process temperature and catalyst concentration, on the performance of the pervaporation
reactor were discussed. The data presented can be extended for study and design of pervaporation reactor for similar kinds of reactions [78].

With increasing cost of raw materials and energy, there is an increasing inclination of chemical process industries toward new processes that result in lesser waste generation, greater efficiency and substantial yield of the desired products. Esterification is a chemical reaction in which two reactants, carboxylic acid and alcohol, react to form an ester and water. This reaction is a reversible reaction, and the equilibrium conversion can be altered by varying the process parameters. A pervaporation reactor can enhance the conversion by shifting the equilibrium of reversible esterification reactions. PVA–polyethersulfone composite hydrophilic membrane was used for pervaporation-assisted esterification of propionic acid with isopropyl alcohol. The experiments were carried out in the presence of sulfuric acid as a catalyst at 50–80 °C with various reactants ratios. The esterification was carried out for catalyst loadings of 0.089–0.447 kmol m⁻³. The molar ratios of isopropyl alcohol to propionic acid used for the experiment were 1 to 1.5. Maximum conversion was obtained for a ratio of 1.4. The effect of other parameters, such as process temperature and catalyst concentration, was also discussed. It was found that the use of pervaporation reactor increased the conversion of the propionic acid considerably [79].

Figure 21.12 shows a pervaporation membrane bioreactor system with a silicone rubber hollow-fibre membrane, which is used as an alcohol permselective membrane for simultaneous product recovery in the butanol–isopropanol batch fermentation [80]. In this system the fermentation liquid flows inside of the hollow-fibre membrane and the permeated vapour is carried to the condenser by N₂ gas and taken out as a condensate. In a continuous fermentation of glucose to butanol and isopropanol by immobilized Clostridium beyerinckii cells the products were removed continuously by pervaporation. Both the glucose conversion and the reactor productivity were 65–70% higher than in a continuous fermentation without product removal [81].

![Figure 21.12 Membrane bioreactor system of the pervaporation type.](image-url)
Figure 21.13 Membrane reactor system with a porous hydrophobic polymer membrane in a TDEV-type system.
21.3.2.2 Membrane Reactor with Evapomeation

When the evapomeation method shown in Figure 16.2 is applied to the esterification reaction of \( n \)-butyl alcohol and acetic acid, a hydrophilic PVA membrane can selectively permeate water, and this esterification reaction can be accelerated by the nonequilibrium state of the reaction similar to the pervaporation method as can be seen in Figure 24.2 [82]. In an application of a hydrophilic membrane to pervaporation and evapomeation, however, stopping of the reaction necessitates the production of esters. When the hydrophobic membranes which can selectively permeate esters which is a product from the reaction system are applied to these reaction systems, reaction products can be taken out and the esterification reaction can be carried out continuously. Poly(dimethylsiloxane) and tetraethoxy-silane hybrid membranes could be applied to these reactions (Uragami, T., unpublished data).

21.3.2.3 Combination of Fermentation Tank and Temperature-Difference Controlled Evapomeation

A novel bench plant has been developed consisting of a fermentation tank (in which glucose is fermented by a yeast) is connected to a temperature-difference controlled evapomeation (TDEV) system with a porous hydrophilic membrane (Figure 21.13) [83]. The following reaction occurs in the fermentation tank:

\[
2nC_6H_{12}O_6 \xrightarrow{\text{Zymase}} 4nC_2H_5OH + 4nCO_2
\]

A porous hydrophobic membrane in the TDEV system can easily permeate ethanol (product) and carbon dioxide (by product) and reject aggregated water molecules. Consequently, since ethanol is removed gradually during operation of the TDEV system, the yeast in the fermentation tank is protected from ethanol and the hydrolysis reaction of glucose is accelerated because both ethanol and carbon dioxide are carried out. This system, which makes possible both the fermentation of glucose and the concentration of ethanol by TDEV system, in addition to a saccharification tank which saccharizes cellulose or starch, can be connected to the fermentation tank. This series system can reduce the cost for the production of bioethanol.

References


22

Membrane Contactors

22.1 Principle and Fundamentals of Membrane Contactors

Membrane contactors provide a novel approach to the solution of many problems (especially of the second and third kind) of contacting two different phases, one of which must be a fluid. Essentially, a porous membrane, most often in hollow fibre form, is the basic element in such a device. Any membrane in flat or spiral wound or hollow fibre or any other form has two interfaces since it has two sides. However, conventional separation processes involve usually one interface in a two-phase system; for example, gas–liquid, vapour–liquid, liquid–liquid, liquid–supercritical fluid, gas–solid, liquid–solid, and so on. Membrane contactors allow the creation of one immobilized phase interface between two phases participating in separation via the porous membrane. Three types of immobilized phase interfaces in two-phase configurations are relevant.

- Two fluid phases in contact: gas–liquid, liquid–liquid, vapour–liquid, supercritical fluid–fluid (fluid phase membrane contactors) (Figure 22.1a).
- One fluid phase in contact with one solid phase: liquid–solid; gas/vapour–solid; supercritical fluid–solid (solid–fluid phase membrane contactors) (Figure 22.2).
- The membrane system has two immobilized phase interfaces; each interface is between two immiscible fluid phases. For example, gas–liquid (1) and liquid–gas (2), liquid–liquid (1) and liquid–liquid (2) (multiple-phase-interface-based membrane contactor) (Figure 22.3).

In each of these two-phase configurations identified, phase interfaces are not created by dispersing one phase as drops or bubbles or particles into the other phase. One form of membrane contactor, however, helps in creating a dispersion through the membrane structure and then the two phases continue to contact each other as they flow through the membrane device flow channels. This fourth form of membrane contactor has been utilized in liquid–liquid systems via emulsion formation and in gas–liquid systems via bubble generation (Figure 22.4). Although this configuration is a radical departure from the practice of membrane contactors in the first three categories and is more in line with conventional chemical engineering contactor devices, it has its own utility.

The membrane contactors in all four categories were primarily developed for separation and purification. However, they are being increasingly exploited for the purposes of reaction–separation, separation–reaction, and so forth. Membrane contactors can therefore function as separator–reactors as well as reactor–separators [1].

Membrane contactors are considered as a technology in membrane processes for water purification in various industries. Membrane contactor technology is applicable to removal of $\text{NH}_3/\text{NH}_4^+$ in
wastewater treatment, removal of dissolved oxygen and carbon dioxide from aqueous solutions, volatile organic carbon removal from waste gas, uranium removal, pharmaceuticals, fermentation, semiconductor manufacturing, protein extraction, carbonation of beverages, olefin/paraffin separation, and so on.

Figure 22.1 Membrane contactor allowing two fluid phases to contact each other.

Figure 22.2 Membrane contactor for solid–fluid phase contacting.
Membranes in the membrane contactor are designed to form an interface between two components (liquid–liquid, liquid–gas and gas–gas). The membrane contactors are devices that achieve gas–liquid or liquid–liquid mass transfer without dispersion of one phase within the other. The membrane is used to accomplish a particular separation and transport of one component more easily than another because of differences in physical and/or chemical properties between the membrane and the permeating components. There are a few advantages to using membrane contactors in contrast to conventional methods. Some of them are no flooding at high flow rates, no unloading at low flow rates, absence of emulsions, no density difference between fluids required and high interfacial area [2].

### 22.2 Membranes for Membrane Contactors

#### 22.2.1 Inorganic Membranes

In previous studies [6] on gas/vapour separations using polymeric membranes, which range from conventional polymers to more advanced ones such as polyimide and copolyimides, contactors have always been accompanied by a membrane stability issue: either a wetting phenomenon or a membrane degradation concern because of extensive contact with the solvent. To possibly overcome these conventional challenges and provide extended stability, the use of a ceramic hollow-fibre membrane contactor was proposed by Faiz et al. [7], where propylene/propane separation using silver nitrate as a carrier was investigated for a continuous period of 6 months. Alumina hollow fibres with asymmetric structures consisting of a sponge-like outer layer and a finger-like inner layer were successfully fabricated, modified, characterized and finally examined for propylene/propane separation. The modification step using silane solutions was critical in improving the membrane hydrophobicity to ensure that no wetting occurred during contact with the solvent. Initial studies on the separation performance confirmed that the membrane module was able to operate in a nonwetting mode, where the observed overall mass-transfer coefficient was the highest. Moreover, the ceramic membrane module proved to be stable throughout continuous experiments up to a period of 2 months, where no decline in the performance was observed. However, beyond this investigation period, deposition of silver on the membrane surface started to appear significantly where the membrane’s appearance becomes dark. This silver deposition seemed to diminish the membrane’s hydrophobicity as it continued to accumulate on the membrane surface, where a slight decline in the separation performance was finally observed by the end of the 6-month period. By exposing the advantages of ceramic membranes over their polymeric counterparts, a novel regeneration method was demonstrated where the membrane module undergoes treatment with strong nitric acid to remove silver deposits, followed by remodification of the membranes with silane solutions to restore its hydrophobicity. The performance of the membrane modules was regained completely after regeneration. Thus, this technology can be performed for an extended period without the need to replace the membranes whenever a drop in the performance is observed due to deformation of the membranes, an issue commonly found with polymeric materials.

22.2.2 Organic Membranes

Many polymer membranes can be applied to membrane contactors. Flat-sheet nonporous asymmetric poly(vinyltrimethylsilane) membranes and composite membranes comprising a dense layer of polydimethylsiloxane/polyphenylsilsesquioxane block copolymer were prepared by Bessarabov et al. [8] and were applied to a membrane–liquid contactor. Pure poly[1-(trimethylsilyl)-1-propyne] (PTMSP), cross-linked PTMSP and cross-linked nanofilled PTMSP were developed as membrane materials for gas–liquid membrane contactors for CO₂ capture from natural gas [9].

22.2.3 Organic–Inorganic Hybrid Membranes

Organic–inorganic hybrid membranes can be applied to a membrane contactor [10]. Hydrophobic surface can be produced by either lowering the surface free energy or enhancing the surface roughness or a combination of both. Zhang and Wang [11] explored a novel method to form a highly hydrophobic organic–inorganic composite hollow-fibre membrane by incorporating a fluorinated silica (fSiO₂) inorganic layer on the polyetherimide (PEI) organic substrate. The formation of the composite membrane was examined and confirmed by attenuated total reflection Fourier transform infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy. An ultrasonication test was conducted to examine the structural stability of the composite membrane. The experimental results revealed that the fSiO₂ layer was tightly bonded to the PEI substrate through silane chemical reactions.
The incorporation of the fSiO₂ layer on the membrane surface could enhance the surface roughness and greatly reduce the surface free energy due to the hydrophobic compound perfluorodecyltriethoxysilane. The hydrophobicity of the composite membrane surface was dramatically elevated, as evidenced by the dynamic contact angles increment (e.g. from original 66.7° to 124.8° for advancing values, and from 49.5° to 100.6° for receding values). In addition, it was observed that the mechanical properties of the composite membrane were better than some of the conventional polymeric membranes, such as polyethersulfone and polyvinylidene fluoride (PVDF). The composite membrane was also not as brittle as the pure inorganic membrane. Highly hydrophobic membrane is the core element in a gas–liquid membrane contactor, and the newly developed PEI–fSiO₂ composite hollow-fibre membranes were intended for use in such application. The CO₂ absorption flux of the composite membranes was investigated in both physical and chemical absorptions in a gas–liquid membrane contactor system. Moreover, the membrane contactor showed a reasonably stable performance throughout the 31 days’ long-term operation using a 2 M sodium taurinate aqueous solution as the liquid absorbent and pure CO₂ as the feed gas. The chemical compatibility test indicated that, after the long-term constant contact with the sodium taurinate, the hydrophobicity of the PEI–fSiO₂ composite membrane was still maintained and was much higher than that of the original PEI substrate and conventional hydrophobic polymeric membranes such as PVDF. The incorporation of the fSiO₂ inorganic layer not only offered high hydrophobicity, but also would protect the polymeric substrate from attack by chemical absorbents, giving the membrane a longer lifespan.

In a gas–liquid membrane contactor, a larger pore size can result in a lower membrane mass transfer resistance. However, the membrane pore size is usually limited by the concern of pore wetting (e.g. a large pore size means a higher wetting tendency). As a breakthrough, the paper by Zhang and Wang reported a porous PEI hollow-fibre membrane with high surface porosity and large pore size to minimize the membrane mass transfer resistance by using a triple-orifice spinneret in the hollow fibre spinning process, and followed by a novel approach of fSiO₂ nanoparticle incorporation to make the membrane surface highly hydrophobic and chemical resistant to prevent the membrane from wetting caused by the large pore size on the membrane surface. The newly developed composite hollow fibre membranes showed an advancing contact angle value of 123.3°, a receding contact-angle value of 107.2° and contact-angle hysteresis of only 15.9°, indicating a high water resistant property. The composite membrane also exhibited a higher rigidity property compared with the original PEI substrate. The CO₂ absorption flux of the composite membranes was investigated in both physical and chemical absorptions in a gas–liquid membrane contactor system. The membrane contactor showed a stable performance throughout the 60-day long-term operation using a 2 M sodium taurinate aqueous solution as the liquid absorbent. The highly hydrophobic composite hollow-fibre membrane was able to outperform a conventional polymeric hydrophobic membrane in terms of superior gas absorption flux and outstanding long-term stability, suggesting that the formation of organic–inorganic composite membranes is an effective way to enhance the feasibility of membrane contactor processes for practical applications. The results demonstrated the important role of membrane fabrication and modification techniques in facilitating the commercialization of membrane contactor technology [12].

Gas–liquid membrane contactors which integrates the absorption process with membranes is an emerging membrane technology that is also of particular interest in acid gas absorption. Zhang and Wang [13] presented a short review on the recent developments of membrane contactor technology. With the analysis of key challenges being addressed for membrane contactor development, the state of the art of highly hydrophobic microporous membranes, novel liquid absorbents and membrane module design and process simulation are presented. The future opportunities for achieving breakthrough in membrane contactors that can lead to large-scale practical applications are also summarized.
22.3 Technology of Membrane Contactors

22.3.1 Liquid–Liquid Membrane Contactors

The versatility of the phenomenon of dispersion-free solvent extraction through an immobilized aqueous–organic interface in a microporous hydrophobic membrane is demonstrated by Prasad and Sirkar. This technique was used for an organic–organic interface to extract aromatics from a hydrocarbon feedstock by a polar organic solvent. The phenomenon was studied further with microporous hydrophilic and composite hydrophobic–hydrophilic membranes. Operational modes and the influence of the membrane and boundary layer resistances for various solvent–solute–membrane systems was studied for a CELGARE (hydrophobic) and a CUPROPHAN (hydrophilic) membrane. Limited performance data for microporous hydrophobic CELGARE hollow fibres (X-20) were also presented [14].

Ammonia separation from water by a membrane contactor was simulated on transient state and compared with experimental data. An aqueous low concentrated solution of ammonium with high pH was pumped inside a hydrophobic hollow fibre (lumen), and the sulfuric acid solution in the outside part and the feeding solutions were in a closed-loop configuration. In order to simulate the separation process, equations were developed considering radial and axial diffusion and convection in the lumen with a well-developed parabolic velocity profile. The model proposed showed minimal deviations when compared against experimental data. This study by Licon et al. shows that the most important parameters to control during the operation are the flow rate and the pH (mainly the latter), due to high dependence in chemical equilibrium of ammonium reaction to ammonia [15].

Non-dispersive solvent extraction of uranium from nitric acid feed solutions was studied using three dialkyl amides – N,N-di-n-hexylhexanamide, N,N-di-n-hexyloctanamide, N,N-di-n-hexyldecanamide – and their binary mixtures with N,N,N’,N’-tetra-n-octyldiglycolamide (TODGA) (Figure 22.5 –http://jolisfukyuy.sc.jaea.go.jp/fukyuy/mirai/2006/7_3.html) in normal paraffinic hydrocarbon (NPH) as the carrier solvents [16]. The feed solution usually contained 10.6 g L⁻¹ of uranium in 3 M HNO₃ and the extraction

![Figure 22.5](http://jolisfukyuy.sc.jaea.go.jp/fukyuy/mirai/2006/7_3.html) Structure of TODGA. Three molecules of oxygen (O, red) participate in complex formation and have characteristics as three seat ligands. Control of hydrophilicity or hydrophobicity of the DGA compound is when the length of the alkyl group binding to nitrogen (N, blue) is charged.
studies were carried out using a commercial hollow-fibre contactor operating in recirculation mode at a flow rate of 3 L h\(^{-1}\). In a separate set of experiments, the stripping studies were carried out in the non-dispersive solvent extraction mode using the U-loaded organic extract and 0.01 M HNO\(_3\) or 1 M Na\(_2\)CO\(_3\) as the strippant. Use of TODGA along with the amides resulted in faster mass transfer rates though the extraction, and stripping efficiencies of the dialkylamides were reversed in the mixture compared with that observed in the absence of TODGA.

A non-destructive process for recovering valuable aromatic fractions from odorous industry aqueous effluent was investigated by Souchon \textit{et al.} [17]. Non-dispersive extraction often selected aroma compound and was carried out on very diluted model aqueous solutions, using membrane contactors, in two configurations: liquid–liquid and liquid–gas. Mass transfers from water to \(n\)-hexane, from water to miglyol (two solvents widely used in the aromatic industry) and from water to air were studied using a crossflow-designed hollow-fibre membrane contactor. The influence of the physicochemical properties of the aroma compounds and the influence of the solvent viscosity on mass transfer were discussed. Moreover, a resistance-in-series model was applied and allowed to predict the mass transfer intensity in agreement with experimental values whatever the separation principle, be it liquid–liquid or liquid–gas.

Liquid–liquid extraction in a hollow-fibre membrane contactor was examined as a means to remove organic contaminants from an aqueous surfactant stream by Kitiyanan \textit{et al.} The effect of flow rate and the presence of the micellar pseudophase on the liquid–liquid extraction process were determined. Laboratory studies with the model contaminants perchloroethylene and isobutylbenzene in aqueous solutions of Dowfax 8390 or Igepal CO-880 surfactants were discussed. Squalane was utilized as the extracting fluid and a Hoechst-Celanese Corporation membrane module as the contactor. Results showed that (1) higher aqueous flow rates resulted in lower removal efficiencies, (2) high surfactant concentrations lowered the removal efficiencies, (3) hollow-fibre contactors helped prevent emulsion formation, and (4) liquid–liquid extraction is a viable option for the removal of contaminants from aqueous surfactant streams [18].

### 22.3.2 Gas–Liquid Membrane Contactors

Mass transfer between the two phases in a gas–liquid membrane contactor can be obtained without dispersing one phase into the other. Compared with separation by a membrane alone, very high selectivity is obtained in the contactor by the absorption liquid, even at very low acid gas concentration without loss of CH\(_4\). The membrane barrier between the phases gives the advantage of more flexible operation conditions as the two streams can be operated independently at a constant available contact area. Higher gas and liquid flow rates can be used without the danger of entrainment of droplets or flooding, which could be a problem in conventional absorption towers. An essential advantage is the high gas–liquid contacting surface area per unit contactor volume, resulting in a small footprint. In addition, there is the possibility of linear scale up by membrane modules. New nanostructured membrane materials to be applied in a membrane contactor for removal of CO\(_2\) from high-pressure natural gas are to be developed. The reports on high-pressure conditions in membrane contactors are scarce, and there lies the potential for developing new, efficient membrane materials rather than applying commercial ones. Today, mostly microporous polymer membranes are investigated and used in the membrane contactor process, though various asymmetric and composite membranes have also been tested for this application. The CO\(_2\) mass transfer coefficient for the process is highest for a gas-filled membrane, compared with the membrane pores being filled with liquid. Therefore, the membrane material will need to be hydrophobic in order to keep the liquid from entering the membrane pores. Mechanical strength of the membrane will also be an important property. As mentioned previously, the selectivity of the system is obtained by the absorption liquid, so a high CO\(_2\) selectivity
for the membrane material is not needed. Poly(4-methyl-2-pentyne) (PMP) and PTMSP with nanoparticle fillers for mechanical strength were the polymers explored for the membranes to be used in the contactor. An amine solution was used as absorption liquid. PMP and PTMSP are both glassy, high free-volume polymers, with a very high permeability; PTMSP has the highest permeability of all known synthetic polymers. The membrane needs to be characterized with respect to pore size, pore size distribution, porosity, and mechanical strength before testing in the laboratory set-up [19].

The application of olefin-selective membrane materials in gas–liquid membrane contactors for the separation of paraffins and olefins using a silver nitrate solution as the absorption liquid turned out to be very successful, especially with respect to the olefin/paraffin selectivity obtainable. Composite hollow-fibre membranes with a top layer of a highly permeable block copolymer of poly(ethylene oxide) and poly(butylene terephthalate) were prepared by Nymeijer et al. and applied in a gas–liquid membrane contactor for the separation of paraffins and olefins using a silver nitrate solution as the absorption liquid [20]. The water present in the absorption liquid swells the hydrophilic polymer sufficiently. This prevents drying out of the layer and enables the partitioning of silver ions into the polymer matrix, making it olefin selective. Ethylene permeabilities obtained were comparable to the values found for membranes with nonselective, elastomeric top layers (40 – 50 Barrer). Selectivities, however, were more than 20 times higher. Independent of the liquid flow rate, a selectivity of 165 was obtained for poly(ethylene oxide)–poly(butylene terephthalate)-coated membranes. This makes the application of olefin-selective membranes in a membrane contactor for olefin/paraffin separations very attractive.

Wessling and co-workers [21] prepared selective composite membranes containing sulfonated poly(ether ether ketone) (SPEEK) layers on top of a hydrophobic, polypropylene support are applied as absorber and desorber in a gas–liquid membrane contactor system for the separation of paraffins and olefins. The water present in the absorption liquid swells the hydrophilic polymer sufficiently, making the membranes olefin selective. As a result, even at high liquid velocities where the membrane determines the selectivity of the process, high selectivities can be obtained in combination with high productivities. Continuous contact between the absorption silver nitrate solution and the SPEEK layer prevented the layer from drying out and subsequent loss of selectivity. Previously unknown high ethylene/ethane selectivities (>2700) were obtained in combination with reasonable ethylene productivities (7.6 × 10^{-10} cm^3 cm^{-2} s^{-1} Pa^{-1} (1 × 10^{-6} cm^3 cm^{-2} s^{-1} cmHg^{-1})).

In gas–liquid membrane contacting it is important to know the gas permeance of microporous hydrophobic membranes used in such a system. Gas permeance of carbon dioxide from a CO2–N2 mixture having a low CO2 concentration into an aqueous KOH solution through flat microporous (Celgard 2400, Saint-Gobain R128-10)/nonporous PTMSP membranes was therefore studied at zero net total pressure difference. Pure gas permeance data of CO2 through the same membranes for positive ΔP and gas–gas system were extrapolated to zero mean pressure to also find gas permeance. Conventional theoretical estimates of the liquid film resistance for such systems were compared with the experimental results for the liquid film resistance; they were found to be considerably higher than that estimated from the theory based on a liquid film having a fast chemical reaction. The membrane resistance obtained by subtraction of the experimental liquid film resistance from the total resistance of the system appeared to predict the CO2 permeance for the thicker PTMSP film measured under positive ΔP quite well. However, this method led to higher estimates of membrane resistance for thinner PTMSP films, Celgard 2400 and other supposedly highly permeable porous substrates compared with those based on the data obtained by extrapolation to P = 0. There appears to be an upper limit of permeance which may be determined correctly in such experimental measurements based on ΔP = 0. This upper limit is considerably higher than that achieved by earlier investigators. Several factors potentially contributing to this discrepancy were pointed out [22].
The effects of membrane porosity and pore size on CO₂ absorption performance and long-term stability were investigated using asymmetric PVDF hollow-fibre membrane contactors, prepared with differing inner surface structures by thermally induced phase separation. Membranes prepared using nitrogen gas as the bore fluid had lower inner surface porosity than membranes prepared with solvent. Monoethanolamine solutions were used as absorbents on the tube side, while pure CO₂ was supplied to the shell side. Gas absorption performance and long-term stability of the synthesized membranes were compared with those of a commercial poly(tetrafluoroethylene) membrane. The effect of surface properties on gas absorption performance depended on monoethanolamine concentration. A membrane with lower porosity and small pore diameter at the inner surface was stable for 200 h, while a membrane with high porosity and larger pore size was completely wetted within 100 h and flux rate decreased sharply. A mathematical model for pure CO₂ absorption was developed by considering partial wetting of the membrane. The simulation results were discussed in light of the results from long-term stability tests of membranes [23].

22.3.3 Gas–Gas Membrane Contactors

Wettability of nanoporous membrane contactors exposed to different chemical solvents was studied by Hassanlouei et al. [24]. Their work was conducted using computational simulation of CO₂ capture from flue gas in a hollow-fibre membrane module. A computational fluid dynamics method was applied for numerical solution of governing transport equations. Simulations were performed to study CO₂ transport through membrane for complete wetting and nonwetting conditions. Simulation results were validated through comparing with the experimental data for CO₂ capture using amine aqueous solutions. The simulation results were consistent with the experimental data. To investigate the influence of solvent on separation performance, six common chemical absorbents – aqueous solutions of diethanolamine, N-methyldiethanolamine, monoethanolamine, 2-amino-2-methyl-1-propanol, sodium hydroxide and potassium glycinate – were considered in the simulation. The simulation results revealed that the capture of CO₂ using aqueous solution of potassium glycinate was the highest among the absorbents.

With the aggravation of the unprecedented greenhouse effect, the reduction of greenhouse gases, which mainly consist of CO₂, has caught much attention by global scholars. Membrane absorption of CO₂ from flue gas seems to be a promising alternative to conventional absorption methods like chemical absorption. Zhang et al. discussed the principles of the membrane absorption process. The research developments and current status of CO₂ capture in flue gas using a hollow-fibre membrane contactor were reviewed. The affecting factors included the membrane structure and material, module connection form, gas and liquid flow pattern and absorbent. Also, these factors that affected the separation performance of mass transfer processes, as well as the mass transfer coefficients and models for CO₂ absorption, were critically discussed in the tube side, shell side and membrane. Also, an experiment system for CO₂ absorption in a membrane contactor was depicted. The modelling works were validated with experimental results. Additionally, the deficiencies of the present development in membrane gas absorption of acid gases and recommendations for future pilot-scale applications were proposed [25].

Biogas upgrading and utilization is a novel technology to obtain resource-efficient vehicle fuel. Zhang et al. developed a mass transfer model for CO₂ absorption from biogas into potassium arginine solutions [26]. Computational fluid dynamics methods were employed to solve the differential equations in three domains of the membrane contactor. The simulations were focused on the characteristics of both gas and absorbent phases to demonstrate the concentration distributions in axial and radial directions in the module. The simulated results were in excellent
agreement with experimental data when considering the effect of initial CO₂ concentration and gas velocity. Furthermore, the effects of operating pressure, flow pattern, flow condition and modules in series on the membrane performance were investigated. The results showed the purity of CH₄ reached 95% at an operating pressure of 0.9 MPa. It was found that a fluid in the turbulent condition or counter-current configuration had a significant effect on improving the contactor performance. The simulation results also indicated that the use of two modules could increase CO₂ removal and obtain high CH₄ purity. Finally, the results confirmed that the two-dimensional model developed was able to predict the behaviour of CO₂ separation in the membrane contactors.

22.3.4 Membrane Contactors Promoting Chemical Reaction

Ozone mass transport in a flat-sheet membrane contactor with chemical reaction in the liquid phase was investigated by Phattaranawik et al. [27]. The ozone mass transfer coefficients without reaction in the liquid phase were indirectly determined by the oxygen transfer measurement with the steady-state method. The oxidation of nitrite to nitrate was utilized to study mass transfer with ozonation. The ozone fluxes and the enhancement factors were predicted by the facilitation of the resistance-in-series model together with the film and surface renewal models. The performance of the membrane modules designed was assessed by the decolorization of natural organic matter solutions and indigo reagent I. The ozone mass transfer coefficients from oxygen transport experiments were considerably higher than those calculated from the available correlations but provided good predictions for ozone fluxes for pure water. The ozonation accelerated mass transfer in the membrane contactor by 6–100 times in this study. The experimental results validated the proposed methods for the predictions of the ozone fluxes and the enhancement factors. The average discrepancies between the experimental and calculated results were 6% for the ozone flux predictions and 3% for the enhancement factor predictions. The resistances to the ozone mass transfer with and without chemical reaction were controlled by the liquid film. The ozone consumption for the natural organic matter decolorization in the membrane contactor was considerably lower than that in a conventional bubble column.

References


Fuel Cell Membranes

23.1 Principles of the Fuel Cell

There are four kinds of fuel cells: the polymer electrolyte fuel cell (PEFC), the phosphoric acid fuel cell, the molten carbonate fuel cell and the solid oxide fuel cell. In this chapter, the structure and principles of the PEFC are described.

The fuel cell is similar to ‘a battery’, but it is also ‘an electrical generator’. However, unlike a dry cell battery they are not disposable, and if hydrogen (H₂) and oxygen (O₂) are available then electricity can be made continually, as shown in Figure 23.1.

A PEFC generates electricity across an ion-exchange membrane by supplying a reducing agent (fuel) to the cathode with an oxidizer in the anode. When a proton exchange membrane such as Nafion® is used as an ion-exchange membrane it is called proton exchange membrane fuel cell (PEMFC). Start up is rapid, and the driving temperature is low at 80–100 °C too. When hydrogen is used for fuel, expensive platinum is used as a catalyst, and the platinum catalyst deteriorates when carbon monoxide is present in the fuel. The generation efficiency of the fuel cell is relatively low at approximately 30–40%.

Because of their room temperature operation and small size and light weight, their possible application in portable devices and fuel-cell-powered cars is expected.

The fuel cell generates electricity on the principle that is the reverse of the ‘electrolysis of water’ (see Figure 23.2). The electrolysis water generates hydrogen and oxygen through the passage of electricity from an external source through the water. The fuel cell is the reverse, with the electrochemical reaction of hydrogen and oxygen making electricity.

A device that accumulates electricity like a dry cell and a battery is associated with the words fuel cell, but a fuel cell ‘is the generation facilities’ which convert the chemical energy of the reaction of hydrogen and oxygen into electric energy.

The fundamental structure of the solid polymer fuel cell consists of membrane/electrode zygospore (membrane electrode assembly) with a laminated fuel pole (cathode), a solid polymer membrane (electrolyte), and an air pole (anode) and conductive board called a bipolar plate with the supply duct of the reactant gas.

At the fuel pole, fuel such as hydrogen or methanol is supplied and disintegrates to a proton (H⁺) and an electron by the reaction in Equation 23.1 (or the reaction in Equation 23.2 in methanol). After this, the proton moves through the electrolyte membrane and the electron moves through the conducting wire to the air pole.

\[
\begin{align*}
H_2 & \rightarrow 2H^+ + 2e^- & (23.1) \\
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 6\text{H}^+ + 6e^- & (23.2)
\end{align*}
\]
The solid electrolyte macromolecule film has work to move a proton formed at the fuel pole to the air pole. Sulfonic system ion-exchange membranes were used initially, but a fluorine-based polymer membrane with sulfonic acid groups such as Nafion is mainly used now because of the high and stable proton conductivity.

23.2 Good Points of Fuel Cells

1) High efficiency The general energy efficiency can approach approximately more than 80% if the exhaust heat generated is used (this is called a cogeneration system). This is a little less than twice the efficiency of conventional generation methods. Use of this good efficiency enables their use as a power supply in outer space.
2) **Clean**  Only water is formed at the time of generation, and the exhaust contains almost none of the global warming gases and air pollution materials, such as carbon dioxide (CO₂), nitrogen oxides (NOₓ), sulfur oxides (SOₓ) and the particulate matter.

3) **Abundant resources**  The hydrogen necessary for a fuel cell is abundantly available from sources such as LP gas, natural gas, oil, methanol, various raw materials including biomass gas, and hydrogen from iron works or soda factories.

4) **Quiet**  They are extremely quiet in comparison with an engine or a turbine and of low vibration.

### 23.3 Membranes for Fuel Cells

#### 23.3.1 Polymer Membranes

In fluorine-based polymer membranes with sulfonic acid groups, such as Nafion, the proton is hydrated and moves over the sulfonic acid group. Therefore, water in a membrane will move from the fuel pole to the air pole. In this situation it is necessary to soak the fuel pole with water because water is gradually lost from the fuel pole side. Because of this need to use water, the use of these systems below 0 °C or above than 100 °C is very difficult. Therefore, the development of polymer films capable of operating under medium high temperature conditions with no humidification is urgently required.

In addition, when methanol is used as fuel, ‘the crossover phenomenon’ whereby methanol penetrates the electrolyte membrane occurs. As a result of crossover, methanol reacts at the air pole and greatly reduces the electromotive force. In particular, the crossover becomes a big issue when the methanol concentration is increased to improve the output density. Methods using porous polyimide and proton conduction glass have been studied recently to control this crossover.

At the air pole (anode), the electrons supplied by the conducting wire from the electrolyte membrane combine with protons to produce water according to the following reaction in the presence of atmospheric oxygen:

\[ 4H^{+} + O_{2} + 4e^{-} \rightarrow 2H_{2}O \]

#### 23.3.2 Ceramic Membranes

A protonic ceramic fuel cell (PCFC) is a fuel cell based on a ceramic electrolyte material that exhibits high protonic conductivity at elevated temperatures. PCFCs share the thermal and kinetic advantages of high-temperature operation at 700 °C with molten carbonate and solid oxide fuel cells, while exhibiting all of the intrinsic benefits of proton conduction in PEMFCs and phosphoric acid fuel cells. The high operating temperature is necessary to achieve very high electrical fuel efficiency with hydrocarbon fuels. PCFCs can operate at high temperatures and electrochemically oxidize fossil fuels directly to the anode. This eliminates the intermediate step of producing hydrogen through the costly reforming process. Gaseous molecules of the hydrocarbon fuel are absorbed on the surface of the anode in the presence of water vapour, and hydrogen atoms are efficiently stripped off to be absorbed into the electrolyte, with carbon dioxide as the primary reaction product. PCFCs have a solid electrolyte, so that the membrane cannot dry out as with PEMFCs, and liquid cannot leak out as with phosphoric acid fuel cells (see https://en.wikipedia.org/wiki/Protonic_ceramic_fuel_cell).
23.4 Technology of Fuel Cells

23.4.1 Technology of Fuel Cells with Polymer Electrolyte Membranes

Springer et al. [1] presented an isothermal, one-dimensional, steady-state model for a complete PEFC with a 117 Nafton® membrane. In their model they employed water diffusion coefficients, electro-osmotic drag coefficients, water sorption isotherms and membrane conductivities, all measured in their laboratory as functions of membrane water content. The model predicted a net-water-per-proton flux ratio of 0.2 H2O/H+ under typical operating conditions, which is much less than the measured electro-osmotic drag coefficient for a fully hydrated membrane. It also predicted an increase in membrane resistance with increased current density and demonstrated the great advantage of a thinner membrane in alleviating this resistance problem. Both of these predictions were verified experimentally under certain conditions.

Direct methanol fuel cells (DMFCs) using Pt–Ru electrocatalysts and perfluorsulfonic acid membranes provide high performances if operated above 100 °C with optimized catalyst layers [2]. A decal transfer method is used to apply thin-film catalyst/ionomer composite layers to Naftion membranes. A Naftion 112 membrane/electrode assembly operating on 5 atm oxygen at 130 °C yields a current of 670 mA cm−2 at 0.5 V cell voltage. Peak power density is 400 mW cm−2. The same cell operating on 3 atm air at 110 °C yields 370 mA cm−2 at 0.5 V and provides a maximum power density of 250 mW cm−2.

Rikukawa and Sanui [3] provide an overview of the synthesis, chemical and electrochemical properties, and PEFC applications of new proton-conducting polymer electrolyte membranes (PEMs) based on hydrocarbon polymers. Owing to their chemical stability, high degree of proton conductivity and remarkable mechanical properties, perfluorinated polymer electrolytes such as Naftion, Aciplex®, Flemion®, and Dow membranes are some of the most promising electrolyte membranes for PEFCs. A number of reviews on the synthesis, electrochemical properties and fuel cell applications of perfluorinated polymer electrolytes have also appeared during this period. While perfluorinated polymer electrolytes have satisfactory properties for a successful fuel cell electrolyte membrane, the major drawbacks to large-scale commercial use involve cost and low proton conductivities at high temperatures and low humidities. Presently, one of the most promising ways to obtain high-performance proton-conducting PEMs is the use of hydrocarbon polymers for the polymer backbone. They attempted for the first time to summarize the synthesis, chemical and electrochemical properties and fuel cell applications of new proton-conducting polymer electrolytes based on hydrocarbon polymers that had been undertaken during the decade prior to their review.

Jones and Roziere [4] reviewed the progress made in the functionalization of polybenzimidazole (PBI) and polyetherketones with a view to increasing their proton conduction properties without detriment to their thermohydrolytic and chemical stability such that corresponding membranes may be employed in hydrogen–oxygen (air) or DMFCs. The approaches included complexation of PBI with acids, grafting of groups containing sulfonic acid moieties on to PBI by N-substitution, and direct sulfonation of polyetherketones. A further approach concerned the incorporation of inorganic proton-conducting particles in the polymer matrix, and this was developed in detail for the case of hybrid sulfonated polyetheretherketone–metal(IV) phosphate membranes.

The low-temperature direct propane polymer electrolyte membrane fuel cell (DPFC) based on low-cost modified membranes was demonstrated for the first time by Savadogo and Varela [5]. The propane was fed into the fuel cell directly without the need for reforming. A PBI membrane doped with acid and a Naftion 117 membrane modified or non-modified with silicotungstic acid were used as the polymer membranes. The anode was based on Pt, Pt–Ru or Pt–CrO3 electrocatalysts and the cathode...
was based on a Pt electrocatalyst. For non-optimized fuel cells based on H$_2$SO$_4$-doped PBI membranes and Pt–CrO$_3$ anode, the open circuit potential was 1.0 V and the current density at 0.40 V was 118 mA cm$^{-2}$ at 950 °C. For fuel cells based on Nafion 117 membranes modified with silicotungstic acid and on Pt–CrO$_3$, the open-circuit voltage was 0.98 V and the current density at 0.40 V was 108 mA cm$^{-2}$, while fuel cells based on non-modified Nafion 117 membranes exhibited an open-circuit voltage of 0.8 V and the current density at 0.40 V was 42 mA cm$^{-2}$. It was also shown that propane fuel cells using anodes based on Pt–Ru/C anode (42 mW cm$^{-2}$) exhibit a similar maximum power density to that exhibited by fuel cells based on Pt–CrO/C anode (46 mW cm$^{-2}$), while a DPFC using a Pt/C-based anode exhibited lower maximum power density (18 mW cm$^{-2}$) than fuel cells based on the Pt–CrO/C anode (46 mW cm$^{-2}$).

A PEM fuel cell with amorphous hydrated ruthenium dioxide (RuO$_2$·xH$_2$O) supercapacitative sublayers inserted between the electrocatalyst layers and the Nafion membrane was fabricated to enhance the cell’s pulse power output. RuO$_2$·xH$_2$O material showed a high capacitance (~230 F g$^{-1}$) and allowed a much higher pulse power output, which was demonstrated by cyclic voltammetry and millisecond-width pulse voltammetry in a nitrogen atmosphere on both anode and cathode at 50 °C. When the gases were changed to hydrogen and air, the sublayer slightly decreased the steady-state power output of the cell by decreasing both proton conductivity and the rate of oxygen reduction. In spite of this, the presence of the sublayer gave a much higher pulse power output, which is of value for communications applications, for example. This modified fuel cell performed the same functions as those of a more complex fuel cell/supercapacitor hybrid system without significant increase in weight, volume and cost. Moreover, the blocking effect of the thin RuO$_2$ on methanol crossover was advantageous for DMFC applications [6].

Progress in the area of proton conducting PEMs is intimately linked with the development of PEM fuel cells, and is today largely driven by the insufficient properties of humidified Nafion membranes at temperatures above 100 °C [7]. Developments in the field include new ionomers and hybrid membranes containing inorganic nanoparticles to control morphology and enhance water retention, as well as improved systems based on the complexation of basic polymers with oxo-acids. In addition, the molecular design and synthesis of all-polymeric electrolytes that rely entirely on structure diffusion of the protons holds great promise in the long perspective.

To better understand the operation of a new fuel cell design, Hirai and co-workers [8] used magnetic resonance imaging to measure the water content distribution in a PEM under fuel cell operation with and without a supply of liquid water. The supply of liquid water to the membrane improved the cell performance by increasing the water content in the membrane and thus reducing the electrical resistance of the membrane. The study also showed that magnetic resonance imaging is a promising method to investigate the distribution of water in the membrane of a fuel cell under operating conditions.

Wang et al. [9] reported progress and research trends in the area of alkaline PEM development in terms of material selection, synthesis, characterization and theoretical approach, as well as their fabrication into alkaline PEM-based membrane electrode assemblies and the corresponding performance/durability in alkaline PEMFCs. The various advantages and challenges are also reviewed. To overcome challenges hindering alkaline PEM technology advancement and commercialization, several research directions were then proposed.

PEM fuel cells, which convert the chemical energy stored in hydrogen fuel directly and efficiently to electrical energy with water as the only by-product, have the potential to reduce our energy use, pollutant emissions and dependence on fossil fuels. A great deal of effort has been made in the past, particularly during the last couple of decades or so, to advance PEM fuel cell technology and fundamental research. Factors such as durability and cost still remain as the major barriers to fuel cell
commercialization. In their 2011 paper, Wang et al. noted that more than 35% cost reduction had been achieved in fuel cell fabrication but that the $61/kW (as of 2009) for a transportation fuel cell was still over 50% higher than US Department of Energy’s (DOE’s) target of $30/kW by 2015, in order to compete with the conventional technology of internal-combustion engines. In addition, a lifetime of ~2500 h (for transportation PEM fuel cells) was achieved in 2009, yet this still needed to be doubled to meet the DOE’s target of 5000 h. Breakthroughs were urgently needed to overcome these barriers. In this regard, fundamental studies play an important and indeed critical role. Issues such as water and heat management, and new material development remain the focus of fuel-cell performance improvement and cost reduction. Previous reviews mostly focused on one aspect, either a specific fuel cell application or a particular area of fuel cell research. The objective of the Wang et al. review was three-fold: (1) to present the latest status of PEM fuel cell technology development and applications in the transportation, stationary and portable/micro power generation sectors through an overview of the state of the art and most recent technical progress; (2) to describe the need for fundamental research in this field and fill the gap of addressing the role of fundamental research in fuel cell technology; and (3) to outline major challenges in fuel cell technology development and the needs for fundamental research for the near future and prior to fuel cell commercialization [10].

The performance of high-temperature PEM fuel cells is critically dependent on the selection of materials and optimization of individual components. A conventional high-temperature membrane electrode assembly primarily consists of a PBI-type membrane containing phosphoric acid and two gas diffusion electrodes, the anode and the cathode, attached to the two surfaces of the membrane. Zeis [11] provides a survey on the materials implemented in state-of-the-art high-temperature membrane electrode assemblies. These materials must meet extremely demanding requirements because of the severe operating conditions of high-temperature PEM fuel cells. They need to be electrochemically and thermally stable in a highly acidic environment. The polymer membranes should exhibit high proton conductivity in low-hydration and even anhydrous states. Of special concern for phosphoric-acid-doped PBI-type membranes is the acid loss and management during operation. The slow oxygen reduction reaction in high-temperature PEM fuel cells remains a challenge. Phosphoric acid tends to adsorb onto the surface of the platinum catalyst and therefore hamper the reaction kinetics. Additionally, the binder material plays a key role in regulating the hydrophobicity and hydrophilicity of the catalyst layer. Subsequently, the binder controls the electrode–membrane interface that establishes the triple phase boundary between proton-conductive electrolyte, electron-conductive catalyst and reactant gases. Moreover, the elevated operating temperatures promote carbon corrosion and therefore degrade the integrity of the catalyst support. These are only some examples how materials properties affect the stability and performance of high-temperature PEM fuel cells. For this reason, materials characterization techniques for high-temperature PEM fuel cells, either in situ or ex situ, are highly beneficial. Significant progress has recently been made in this field, which enables us to gain a better understanding of underlying processes occurring during fuel cell operation. Various novel tools for characterizing and diagnosing high-temperature PEM fuel cells and key components are presented in this review, including Fourier transform infrared (FTIR) and Raman spectroscopy, confocal Raman microscopy, synchrotron X-ray imaging, X-ray microtomography and atomic force microscopy.

Anion-exchange membranes were synthesized from different compositions of glycidyl methacrylate (GMA) and vinylbenzyl chloride, with constant content of divinylbenzene by radical polymerization using benzoyl peroxide on non-woven polyethylene terephthalate substrate [12]. Polymerized membranes were then quaternized by soaking in trimethylamine, triethylamine, tripropylamine (TPA), and 1,4-diazabicyclo[2.2.2]octane (DABCO). Characteristics of membranes were confirmed by FTIR spectroscopy, water uptake, ion-exchange capacity, ion conductivity, and thermal and alkaline stability.
The results revealed that membranes quaternized by TPA and DABCO showed high affinity when GMA content was 15 wt% and 75 wt% respectively. Ion-exchange capacity and ion conductivity of membranes quaternized by TPA were 1.34 meq g\(^{-1}\) and 0.022 S cm\(^{-1}\) (at 60 °C) respectively, and ion-exchange capacity and ion conductivity of membranes quaternized by DABCO were 1.34 meq g\(^{-1}\) and 0.021 S cm\(^{-1}\) (at 60 °C) respectively. The results indicated that the membrane containing 15 wt% GMA quaternized by TPA showed the highest thermal stability among membranes and exhibited high ion conductivity compared with existing researches using GMA, vinylbenzyl chloride and divinylbenzene monomers.

The gas diffusion medium is a crucial component in PEMFCs. Being composed of a gas diffusion layer with a micro-porous layer coated onto it, it ensures a proper water management due to the highly hydrophobic materials employed in cell assembly. In current commercial applications, the desired water-repellent behaviour is usually obtained by using polytetrafluoroethylene (PTFE). Fluorolink\textsuperscript{®} P56 (Solvay Specialty Polymers, Milan, Italy), a commercially available anionic, segmented high molecular weight polyfluorourethane with perfluoropolyether groups, was extensively evaluated as an alternative to PTFE for micro-porous layer hydrophobization. A change in polymer used is desirable in order to simplify the production process, both in terms of ink formulation and thermal treatment, as well as to get a higher hydrophobicity and, consequently, more efficient water management. Innovative prepared samples were compared with a PTFE-based gas diffusion medium in order to assess differences from both morphological and electrochemical points of view [13].

### 23.4.2 Technology of Fuel Cells with Inorganic Electrolyte Membranes

Changes in proton conductivities of phosphosilicate gels derived from tetraethoxysilane and phosphoric acid or triethylphosphate were discussed by Matsuda \textit{et al.} on the basis of the structural changes in the gels with heat treatment. Proton conductivities of both phosphosilicate gels increased with an increase in relative humidity, indicating that continuous paths suitable for fast proton conduction were formed in the gels due to the adsorption of water. Phosphoric-acid-derived phosphosilicate gels showed higher proton conductivities than triethylphosphate-derived ones at a given heat treatment temperature in a range from 50 to 600 °C. The decrease in the amount of isolated phosphoric acid and the formation of crystalline phases in the phosphosilicate gels lowered the proton conductivity. Phosphoric acid was found to be a preferred starting material to triethylphosphate in order to introduce larger amounts of phosphorus atoms into silica networks without crystallization for the fabrication of highly proton-conductive solid electrolytes [14].

Highly proton-conducting glass films were prepared by Li and Nogami by controlling the pore size of the silica film. The conductivity of films with pores perpendicular to the substrate surface was high, whereby the conductivity increased with increasing water content. The high conductivity was retained at relatively low humidity due to the restriction of water movement in the pores. These porous proton-conducting materials are of interest for use in small fuel cell systems [15].

Kasuga and co-workers [16] investigated the proton conductivities of the sol–gel-derived P\(_2\)O\(_5\)–SiO\(_2\) glass at −50 to +120 °C. The glass obtained was porous, where the surface area, pore volume and pore diameter were 740 m\(^2\) g\(^{-1}\), 0.5 cm\(^3\) g\(^{-1}\) and <5 nm respectively. The freezing temperature of water molecules adsorbed in the pores was −20 °C, which is much lower than that of free liquid water due to the quantum size effect of the water confined in the pores. The electrical conductivities followed the Arrhenius equation in the temperatures between −20 and +120 °C. Below −20 °C the adsorbed water molecules were frozen, resulting in a rapid decrease of the proton conductivity. Considering the high conductivity, and chemical and thermal stability, these oxide glass membranes have potential for fuel cell membranes.
A new nanostructured and fully inorganic composite zirconium phosphate proton-conducting material was synthesized by support impregnation with zirconium oxide suspensions or sols and subsequent phosphorization by Vaivars et al. [17]. The composite inorganic zirconium phosphate membranes prepared using the zirconium oxide suspension were found to give rise to high proton conductivity. The proton conductivity obtained was in the order of $10^{-2}$ S cm$^{-1}$ at room temperature (relative humidity of 100%), which is comparable to Nafion proton conductivity. An inorganic membrane based DMFC was tested and an efficiency equivalent to more than 50% of the Nafion efficiency was obtained when using standard platinum catalyst inks.

A porous glass membrane modified with sulfonic acid groups was evaluated by Ioroi et al. as a proton-conducting electrolyte in DMFCs, and the performance was examined [18]. The cell performance was characterized by voltage versus current measurements, electrochemical impedance spectroscopy and methanol permeation (crossover) measurements. When diluted methanol ($3\, M$) was supplied to the cell, the porous glass membrane showed inferior performance compared with Nafion due to lower conductivity of the porous glass membrane. However, the porous glass membrane showed better performance with a $17.5\, M$ methanol solution than the Nafion membrane did. This better performance of the porous glass membrane is due to the lower methanol permeation in concentrated methanol solutions.

Proton-conducting organic–inorganic hybrid membranes containing sulfonic acid groups as proton donor were prepared by Yazawa et al. from porous glasses and an organosilane [19]. They found that silanol groups on pore surfaces react one-to-one with organosilane molecules and that the pore surface was covered by sulfonic acid groups. Proton conductivity of the hybrid membranes was $1.25 \times 10^{-1}$ S cm$^{-1}$ at 140 °C under 100% relative humidity. The conductivity was dependent upon the pore size because of the capillary condensation of water and the friction of water molecules. The membranes were thermally stable up to 140 °C. They were chemically stable in methanol because the framework structure of these membranes consisted of porous inorganic glass.

The synthesis and characterization of a novel inorganic glass composite membrane consisting of a mixture of phosphotungstic acid and phosphomolybdic acid are reported by Uma and Nogami [20]. Phosphosilicate gels doped with these two proton-conducting donor components were derived by a sol–gel method. The influence of the textural properties of the glass composites could be interpreted from N$_2$ adsorption–desorption isotherms. The pore size was less than 6 nm for all glass membranes. These glass membranes were found to be stable up to 400 °C. FTIR spectroscopy indicated that the characteristic Keggin anions $\text{PW}_{12}\text{O}_{40}^{3-}$ and $\text{PMo}_{12}\text{O}_{40}^{3-}$ were present in the glass composite membrane. The highest proton conductivity was measured as $1.01 \times 10^{-1}$ S cm$^{-1}$ at 85 °C with 85% relative humidity. Membrane electrode assemblies were prepared and showed good performance, with a maximum power density value of 35 mW cm$^{-2}$ at 93 mA cm$^{-2}$ as well as a current density of 137 mA cm$^{-2}$ when utilized in an H$_2$/O$_2$ fuel cell at 28 °C and 30% relative humidity.

Uma and Nogami also prepared phosphosilicate glass membranes doped with a mixture of titanium oxide (TiO$_2$) and zirconium oxide (ZrO$_2$). FTIR spectroscopy, thermal gravimetric and differential thermal analysis, pore, impedance and permeability studies as well as electrochemical analysis were carried out. The specific surface area and pore distributions were described by the Brunauer–Emmett–Teller method, and the average pore size was found to be approximately 2.2 nm for all composite glass membranes. The FTIR analysis displayed a maximum intensity in the range 1000–1200 cm$^{-1}$, indicating the presence of Si–O–Si bonds in the glass composites. A high proton conductivity of $5.8 \times 10^{-3}$ S cm$^{-1}$ was obtained for one of the membranes at 80 °C and 50% relative humidity. The permeability was measured for a hydrogen flow background and was found to decrease from $1.41 \times 10^{-11}$ to $3.83 \times 10^{-12}$ mol cm$^{-1}$ s$^{-1}$ Pa$^{-1}$ as the temperature changed from 30 to 110 °C [21].
Phosphotungstic-acid-based inorganic ion-exchange membrane was prepared on graphite support using a simple synthesis protocol [22]. The top layer of membrane was obtained by immobilizing phosphotungstic acid in silica derived from tetraethylorthosilicate precursor. After casting, the top layer was heat treated at 150 °C. Membrane surface morphology was observed by using a scanning electron microscope, and the top layer was found to be about 30 μm thick. FTIR spectroscopy was used to determine the functional groups, and X-ray diffraction was used to study the crystallinity of the top layer. The membrane was found to be thermally stable up to 250 °C, as obtained from thermogravimetric analysis. Static transport number for cation \((t^+)\) was determined in the pH range of 2–11 using membrane potential measurements. It was found to be above 0.95 in the pH range 4–9. Ohmic resistance of the membrane was determined from impedance measurement and was found to be 12 Ω cm², which is lower than the reported value for inorganic ion-exchange membranes and comparable to some of the organic ion-exchange membranes. The membrane surface was hydrophilic, with a water contact angle of 9°; this hydrophilic nature might be useful for its use as electrolyte-filled separators for batteries and super-capacitors.

Goddard and co-workers [23] developed a novel proton exchange membrane for fuel cells using inorganic phosphotungstic acid as proton carrier and mesoporous silica as matrix (phosphotungstic acid–meso-silica). The proton conductivity measured by electrochemical impedance spectroscopy was 0.11 S cm⁻¹ at 90 °C and 100% relative humidity with a low activation energy of −14 kJ mol⁻¹. In order to determine the energetics associated with proton migration within the phosphotungstic acid–meso-silica proton exchange membrane and to determine the mechanism of proton hopping, they report density functional theory calculations using the generalized gradient approximation. These density functional theory calculations revealed that the proton transfer process involves both intramolecular and intermolecular proton transfer pathways. When the adjacent phosphotungstic acid molecules are close (less than 17.0 Å apart), the calculated activation energy for intramolecular proton transfer within a phosphotungstic acid molecule is higher (29.1–18.8 kJ mol⁻¹) than the barrier for intermolecular proton transfer along the hydrogen bond. They found that the overall barrier for proton movement within the phosphotungstic acid–meso-silica membranes is determined by the intramolecular proton transfer pathway, which explains why the proton conductivity remains unchanged when the weight percentage of phosphotungstic acid on meso-silica is above 67 wt%. In contrast, the activation energy of proton transfer on a clean SiO₂ (111) surface is computed to be as high as −40 kJ mol⁻¹, confirming the very low proton conductivity on clean silica surfaces observed experimentally.

23.4.3 Technology of Fuel Cells with Nanocomposite and Organic–Inorganic Composite Electrolyte Membranes

Composite membranes that exhibit fast proton transport at elevated temperatures are needed for PEMFCs and other electrochemical devices operating in the 100–200 °C range. Traditional water-swollen proton-conducting membranes such as the Nafion membrane suffer from the volatility of water in this temperature range, leading to a subsequent drop in conductivity. Doyle et al. demonstrate that perfluorinated ionomer membranes such as the Nafion membrane can be swollen with ionic liquids to give composite free-standing membranes with excellent stability and proton conductivity in this temperature range while retaining the low volatility of the ionic liquid [24]. Ionic conductivities in excess of 0.1 S cm⁻¹ at 180 °C were demonstrated using the ionic liquid 1-butyl-3-methyl imidazolium trifluoromethane sulfonate. Comparisons between the ionic-liquid-swollen membrane and the neat liquid itself indicate substantial proton mobility in these composites.
Layered zirconium sulfoarylphosphonates of the α- and the γ-type are proton conductors thermally stable up to at least 180 °C. In these materials, the sulfoaryl groups are bonded through the phosphorus atoms to an α- or a γ-inorganic framework made of oxygen and zirconium atoms. Compounds where the sulfonic function is attached to a phenyl, benzyl or to a fluorinated benzyl group were characterized by Alberti et al. for their conductivity as a function of temperature and relative humidity. Independent of the layer type, the highest conductivities were found for the sulfoarylphosphonates. The conductivity was strongly affected by the relative humidity, reaching values of $5 \times 10^{-2}$ S cm$^{-1}$ at 100 °C (100% relative humidity) and $2 \times 10^{-2}$ S cm$^{-1}$ at 150 °C (80% relative humidity). Owing to their ability to undergo infinite swelling in appropriate solvents, these materials can be incorporated into polymeric proton-conducting membranes. The possible advantages of these membranes for increasing the efficiency of indirect or direct methanol fuel cells working at medium temperature are discussed [25].

PEM fuel cells have recently been investigated extensively as a key technology for solving global energy and environmental problems by their higher energy conversion efficiency compared with internal combustion engines [26]. The electrolyte membrane is a basic element in PEM fuel cells; however, the PEM, typically such as Nafion, usually suffers from degradation at higher temperature, resulting in narrow operational temperature windows below 100 °C. If there were an alternative polymer membrane with high stability and sufficient protonic conductivity in the temperature range above 100 °C, an intermediate-temperature-operated PEM fuel cells could be realized which can potentially overcome major problems in the current system, such as CO poisoning on the Pt surfaces, large amounts of Pt metals at both electrodes and heat management. Additionally, DMFCs could be feasible for intermediate temperature operation. In their work, Nakajima et al. used sol–gel processes to synthesize a new family of PEMs consisting of organic–inorganic nanohybrid macromolecules. The flexible, homogeneous and large-sized hybrid polymer membrane was found to be thermally stable up to 250 °C and to have protonic conductivities of approximately $10^{-3}$ to $10^{-2}$ S cm$^{-1}$ from room temperature to 140 °C under a humidified condition. The current membrane is potentially useful in an intermediate-temperature-operated advanced fuel cell system.

Nafion–silica composite membranes were fabricated by Sahu et al. by embedding silica particles as inorganic fillers in perfluorosulfonic acid ionomer by a novel water hydrolysis process [27]. The process precluded the use of an added acid but exploits the acidic characteristic of Nafion facilitating an in-situ polymerization reaction through a sol–gel route. The use of Nafion as acid helps in forming silica/siloxane polymer within the membrane. The inorganic filler materials have high affinity to water and assist proton transport across the electrolyte membrane of the PEFC even under low relative humidity conditions. In this study, composite membranes were tested in hydrogen–oxygen PEFCs at varying relative humidities between 100 and 18% at elevated temperatures. Attenuated total reflectance FTIR spectroscopy and scanning electron microscopy studies suggested an evenly distributed siloxane polymer with Si–OH and Si–O–Si network structures in the composite membrane. At the operational cell voltage of 0.4 V, the PEFC with an optimized silica–Nafion composite membrane delivered a peak power density value five times higher than that achievable with a PEFC with conventional Nafion-1135 membrane electrolyte while operating at a relative humidity of 18% at atmospheric pressures.

An organic–inorganic hybrid ionic conductive material was prepared through oxidation of thiol groups in a surface-modified porous glass. Surface-modified pores in the hybrid materials acted as permeation paths for protons. Proton conductivity of the hybrid material was $4.2 \times 10^{-2}$ S cm$^{-1}$ at 120 °C under 100% relative humidity. This hybrid material was thermally stable at high temperature (above 100 °C) due to the temperature-tolerant inorganic frameworks [28].

Inorganic–organic composite electrolytes were fabricated by Oh et al. from partially Cs$^+$-substituted heteropoly acids (Cs-HPAs) and PBI for application in medium-temperature fuel cells [29].
PBI was synthesized using diaminobenzidine and isophthalic acid in polyphosphoric acid in the temperature range 170–200 °C under nitrogen atmosphere. Heteropoly acids, such as phosphotungstic acid (H₃PW₁₂O₄₀) and silicotungstic acid (H₄SiW₁₂O₄₀), were mechanochemically treated with caesium hydrogen sulfate (CsHSO₄) to obtain Cs-HPAs with a molar ratio of 50/50. The PBI–Cs-HPAs composite electrolytes were fabricated by solvent casting, and FTIR results showed that the PBI–Cs-HPAs composite formed successfully. High proton conductivity and good fuel cell performance of PBI composite electrolytes were comparable to those of phosphoric-acid-doped pure PBI electrolytes, even though they have lower phosphoric acid doping level (PADL) than that of pure PBI. The high proton conductivities of 1.91 × 10⁻² S cm⁻¹ and 1.71 × 10⁻² S cm⁻¹ were achieved at 160 °C under anhydrous conditions for PBI–50H₃PW₁₂O₄₀ · 50CsHSO₄ with 87 wt% PADL and PBI–50H₄SiW₁₂O₄₀ · 50CsHSO₄ with 82 wt% PADL respectively. These observations implied that the mechanochemically synthesized Cs-HPA composites are promising materials to achieve high electrochemical properties with a low level of PADL for PBI electrolytes.

Organic–inorganic nanocomposite PEM contains nano-sized inorganic building blocks in organic polymer by a molecular level of hybridization. This architecture has opened the possibility to combine in a single solid both the attractive properties of a mechanically and thermally stable inorganic backbone and the specific chemical reactivity, dielectric, ductility, flexibility and processability of organic polymers. The state of the art of PEM fuel cell technology is based on perfluorosulfonic acid membranes, which have some key issues and shortcomings, such as water management, CO poisoning, hydrogen reformate and fuel crossover. Organic–inorganic nanocomposite PEMs show excellent potential for solving these problems and have attracted a lot of attention during the last 10 years [30].

Zwitterionic copolymers (consisting of sulfonic acid and amine groups) with plenty of –Si(OCH)₃ groups similar to stems, branches and fruits of vines from a bionic aspect, were synthesized as a crosslinking agent. Organic–inorganic hybrid zwitterionic membranes (ZIMs), with high flexibility, charge density and conductivity, were prepared using poly(vinyl alcohol) [31]. The ZIMs developed with dual acidic and basic functional groups exhibited high stabilities, water retention ability and cation selectivity. The ZIMs (especially Si–70%) were designed to possess all the required properties (water uptake: 40.6%; ion-exchange capacity: 1.52 equiv g⁻¹; electro-osmotic flux: 2.34 × 10⁻⁵ cm s⁻¹ A⁻¹; and conductivity: 9.67 × 10⁻² S cm⁻¹). ZIMs were designed to possess all of the required properties of a proton-conductive membrane; namely, reasonable swelling, good mechanical, dimensional and oxidative strength, flexibility and low methanol permeability, along with good proton conductivity due to zwitterionic functionality. Moreover, Si–70% and a Nafion117 membrane exhibited comparable DMFC performance. Also, investigation on multi-ionic organic–inorganic hybrid ZIMs as PEMs will give rise to a new developing field in materials and membrane science.

An attempt was made by Kumar et al. [32] to develop a new polyethylene oxide (PEO)-based solid polymer electrolyte membrane (PEO + KHCO₃) by an isothermal immersion technique. Several experimental techniques such as infrared, composition dependence conductivity, temperature dependence conductivity in the temperature range 308–368 K and transport number measurements were employed to characterize this PEM system. The infrared studies confirmed the solvation of K⁺ ion with PEO. The conductivity of the (PEO + KHCO₃) electrolyte was found to be about three times larger than that of pure PEO at room temperature. The transference data indicated that the charge transport in these polymer electrolyte systems was predominantly due to ions. Using this conducting PEM, a PEM fuel cell stack was fabricated with the configuration anode–polymer electrolyte–cathode and its I–V characteristics studied.

Although an increased number of reports in recent years on proton exchange membranes developed from nanocomposites of PBI with inorganic fillers brought hope to end the saga of contradiction between proton conductivity and a variety of stabilities (mechanical, thermal, chemical, etc.), it still
remains a prime challenge to develop a highly conducting proton exchange membrane with superior aforementioned stabilities. In fact, the very limited understanding of the interactions, especially interfacial interaction between PBI and inorganic filler, leads to confusion over the choice of inorganic filler type and their surface functionalities. Taking a clue from their earlier study based on poly(4,4′-diphenylether-5,5′-bibenzimidazole) (OPBI)–silica nanocomposites, where silica nanoparticles modified with short-chain amine showed interfacial interaction-dependent properties, Singha and Jana explored the possibility of enhanced interfacial interaction and control over the interface by optimizing the chemistry of the silica surface. They functionalized the surface of silica nanoparticles with a longer aliphatic chain having multiple amine groups – termed long-chain amine-modified silica (LAMS). FTIR and $^{13}$C solid-state nuclear magnetic resonance provided proof of hydrogen bonding interactions between the amine groups of the modifier and those of OPBI. LAMS nanoparticles yielded a more distinguished self-assembly extending all over the OPBI matrix with increasing concentrations. The crystalline nature of these self-assembled clusters was probed by wide-angle X-ray diffraction studies, and the morphological features were captured by transmission electron microscope. They demonstrated the changes in storage modulus and glass transition temperature of the membranes, the fundamental parameters that are more sensitive to interfacial structure using temperature-dependent dynamic mechanical analysis. All the nanocomposite membranes displayed enhanced mechanical, thermal and chemical stability compared with neat OPBI. The lower water uptake and swelling ratio and volume in both acid and water reflected the more hydrophobic characteristic of the nanocomposites. All the nanocomposite membranes showed phosphoric acid values to be higher than OPBI, but the levels showed a decreasing trend with increasing silica content; the reason was attributed to the interparticle interaction. The self-assembled clusters of LAMS nanoparticles in the matrix created more sites for proton hopping, as a result of which the proton conductivity of all the nanocomposites displayed an increasing trend [33].

Nafion–CaO, Nafion–ZrOH, and Nafion–CaO–ZrOH membranes were fabricated by Mazinani et al. in order to improve proton conductivity, thermal stability and mechanical properties as well as decrease methanol crossover in DMFCs. The ion-exchange method was utilized to incorporate Ca and Zr into Nafion membranes. Prepared membranes were characterized by using absorption transmission reflectance and energy-dispersive X-ray spectroscopy techniques. Methanol crossover decreased significantly for all fabricated membranes. Nafion–CaO and Nafion–CaO–ZrOH membranes respectively exhibited ten- and six-times increases in proton conductivity compared with Nafion (0.08 S cm$^{-1}$), while the proton conductivity of Nafion–ZrOH decreases. The elastic modulus was enhanced from 48 MPa for Nafion to 60 MPa, 78 MPa and 90 MPa for Nafion–CaO, Nafion–ZrOH and Nafion–CaO–ZrOH membranes respectively. In addition, the thermal stability of Nafion (360 °C) increased to 407 °C, 457 °C and 470 °C respectively for the fabricated membranes [34].

Composite membranes consisting of N-ethyl-N-methylpyrrolidinium fluorohydrogenate (EMPyr(FH)$_{1.7}F$) ionic liquid and poly(vinylidene fluoride hexafluoro-propylene) (PVdF-HFP) copolymer were successfully prepared in weight ratios of 5 : 5, 6 : 4 and 7 : 3 using a casting method. The prepared membranes possessed rough surfaces, which potentially enlarged the three-phase boundary area. The EMPyr(FH)$_{1.7}F$/PVdF-HFP (7 : 3 weight ratio) composite membrane had an ionic conductivity of 41 mS cm$^{-1}$ at 120 °C. For a single cell using this membrane, a maximum power density of 103 mW cm$^{-2}$ was observed at 50 °C under non-humidified conditions; this was the highest power output that had ever been reported for fluorohydrogenate fuel cells. However, the cell performance decreased at 80 °C, which was explained by penetration of the softened composite membrane into gas diffusion electrodes to partially plug gas channels in the gas diffusion layers; this was verified by in-situ a.c. impedance analysis and cross-sectional scanning electron microscope images of the membrane electrode assembly [35].
Al–Si was synthesized via a sol–gel process and introduced in poly-2,2′-m-(phenylene)-5,5′-bibenzimidazole (PBBI). As a result, a series of five Al–Si/PBBI composite (ASPBI) membranes (0, 3, 6, 9, and 12 wt%) were developed and characterized for application in high-temperature PEM fuel cells. The chemical and morphological structure of ASPBI membranes were analysed by FTIR spectroscopy, X-ray diffractometry and scanning electron microscopy. According to the doping level test and thermogravimetric analysis, as the concentration of Al–Si increased, the doping level increased up to 475% due to the affinity and interaction between Al and phosphoric acid. Moreover, the proton conductivity, current density at 0.6 V and maximum power density of ASPBI membranes increased up to 0.31 S cm$^{-1}$, 0.320 A cm$^{-2}$, and 0.370 W cm$^{-2}$ respectively because the increased concentration of Al–Si allowed the membranes to hold more phosphoric acid. Alternatively, as the amount of Al–Si increased, the tensile strength of phosphoric-acid-doped and -undoped membranes decreased. This was caused by both excess phosphoric acid and aggregation, which can cause serious degradation of the membrane and induce cracks. Furthermore, the phosphoric-acid-doped and -undoped ASPBI12 had the lowest tensile strength of 11.6 MPa and 77.2 MPa respectively. The improved proton conductivity and single cell performance of ASPBI membranes implied that these membranes are possible candidates for high-temperature PEM fuel cell applications. However, further studies seeking to enhance the compatibility between PBBI and Al–Si and optimize the amount of filler need to be performed [36].

References


Hybrid Systems of the Membrane Separation Process

It is expected that hybridization of the membrane separation process and the chemical, fermentative production step, other separation technology or other membrane technology will provide a performance that is more highly efficient.

24.1 Hybrid Systems of Membrane Technology and Reactive Production Step, Other Separation Technology

Marzouk et al. [1] investigated the assessment of Donnan dialysis coupled to an adsorption process for the removal of chromium from aqueous solutions. This study was conducted in order to benefit from each process, and it was an original and new combination. The coupling was a solution to improve the contact time and the amount of chromium(VI) removed. The coupling was successfully performed with 90% of chromium(VI) removed after 6 h.

The integration of continuous fermentation and membrane separation in the same unit to enhance the performance of a bioreactor was studied by Cho and Hwang [2]. Pervaporation with ethanol-selective silicone rubber hollow fibres was considered. This was called a continuous membrane fermentor separator (CMFS). In order to observe the membrane effects, the continuous fermentation experiments were conducted through cyclic operations of the dead membrane phase (conventional continuous fermentation) and live membrane phase (CMFS) under the same geometrical and physicochemical conditions. Relative to conventional continuous fermentation, the performance of CMFS results in high yeast cell densities, reduction of ethanol inhibition, longer residence time of substrate, more glucose consumption, and recovery of clean and concentrated ethanol; these are called ‘membrane effects’. A 10–20% increase in ethanol productivity was achieved, and pervaporated ethanol concentration was over seven times higher than that in the fermentor. A mathematical model was developed and used to determine the effects of design and operation parameters of the CMFS. Computer simulation results predicted significant improvement in ethanol productivity as well as in glucose utilization when the dimensionless membrane volume was increased.

The kinetic parameters were established by Keurentjes et al. for the esterification of tartaric acid with ethanol. Both concentration-based and activity-based reaction rate constants and equilibrium constants were determined. The activity-based data were determined using UNIFAC activity coefficient estimations. It can be concluded that reaction rate constants determined in dilute solutions are capable of describing the reaction in a concentrated environment. This applies both for the activity-based description and for the concentration-based description. Although the activity coefficients
involved differ significantly from unity, the effects of the individual activity coefficients are mutually compensated. Therefore, it is also possible to predict the reaction correctly when the concentration-based parameters are used. When pervaporation was used to remove the water produced in this reaction, the equilibrium composition was shifted significantly towards the formation of the final product diethyltartrate. The membrane surface area to be installed had a clear optimum: the water removal was too slow when \(A/V\) was chosen too low, and too much of the ethanol was removed when \(A/V\) was chosen too high [3].

Modified polyimide membranes were prepared by Ni et al. using a biatomic acid as a modifier and tested for pervaporation separation of water–ethanol binary mixtures [4]. The modified membranes had the best selectivity and medial hydrophilicity in comparison with the polyimide and poly(amic acid) membranes. The pervaporation-coupled esterification of valeric acid with ethanol was investigated, and it was found that the modified membranes still kept a good water/ethanol selectivity for the multicomponent reacting system. The amount of water generated by esterification was most removed through the membranes, and a high conversion of valeric acid was obtained due to the equilibrium shift.

A composite membrane with a cross-linked poly(vinyl alcohol) (PVA) dense active layer dip-coated on a polyethersulfone support membrane was prepared by Chen and Chen and evaluated with a pervaporation set-up for the separation of a water–ethylene glycol mixture [5]. The effects of preparation conditions, including heat-curing temperature and time, dehydration rate, cooling rate, structure of support and cross-linking density of the cross-linked PVA active layer, on the separation factor and permeate flux were discussed. Optimum results were obtained with cross-linked PVA membranes containing 3.7 wt% crosslinking agent and 0.05 wt% catalyst, giving a separation factor of 231 and a permeation rate of 383 g m\(^{-2}\) h\(^{-1}\) for an 82.5 wt% ethylene glycol aqueous solution at 80 °C.

A tubular zeolite NaA membrane, prepared on a carbon–zirconia support, was tested by Jafar et al. for the removal of water from water–isopropanol and water–ethanol mixtures, in both pervaporation and vapour permeation modes, and shown to give high selectivity. The esterification of lactic acid with ethanol to give ethyl lactate was studied in a batch reactor, without catalyst and with p-toluene sulfonic acid as catalyst. The use of a zeolite A vapour permeation membrane to remove water generated by the reaction gave substantially enhanced yields of product, compared with control experiments carried out without the membrane and with the membrane but without vacuum being applied [6].

Novel PVA–titanium dioxide mixed matrix membranes were prepared by Sairam et al. by incorporating nano-sized titanium dioxide (21 nm) and titanium dioxide surface modified with polyaniline (PANI) into PVA and cross-linked with glutaraldehyde. The developed membranes have been assessed for intermolecular interactions using Fourier transform infrared, X-ray diffraction and differential scanning calorimetry (DSC) techniques to understand their morphological and thermal properties. The suitability of these membranes to dehydrate isopropanol by pervaporation was demonstrated. The effect of feed composition and extent of filler loading on the pervaporation separation performance of these membranes was evaluated. Sorption studies were carried out to evaluate the extent of interaction and degree of swelling of the membranes in pure liquids as well as feed mixtures of water and isopropanol. Additions of small amounts of nano-sized filler particles into the cross-linked PVA membrane matrix were instrumental in increasing the membrane selectivity to infinite values. The non-cross-linked mixed matrix PVA membranes yielded higher swelling properties than those of the cross-linked ones. However, swelling results of the cross-linked (unfilled) PVA membranes were higher than all the mixed matrix membranes. The addition of filler particles decreased the extent of swelling and the flux properties, giving an increase in selectivity [7].

Mixed matrix membranes of PVA loaded with phosphomolybdic heteropolyacid (HPA) and cross-linked with glutaraldehyde were prepared by the solution casting technique by Teli et al. Pervaporation experiments were performed at 30 °C to separate water–isopropanol feed mixtures containing
10–40 wt% of water. The membranes were characterized by DSC and dynamic mechanical thermal analysis to understand their thermal behaviour and mechanical strength properties. At high content (i.e. 7 wt% with respect to weight of PVA) of HPA, the mixed matrix membranes could extract water efficiently on the permeate side with a selectivity of 90 000 and a flux of 0.032 kg m$^{-2}$ h$^{-1}$ for a feed mixture containing 10 wt% of water (the lowest feed composition of water studied). Flux of the mixed matrix membranes decreased with increasing concentrations of HPA; however, a significant improvement in pervaporation performance was observed for HPA-loaded membranes than the pristine PVA. DSC and dynamic mechanical thermal analysis indicated a decrease in melting temperature and an increase in glass transition temperature respectively [8].

Inert membrane reactors have long been a subject of interest, with the two main applications consisting of distributing a reactant to increase selectivity and removing a product to enhance conversion in equilibrium-limited reactions. The paper of De la Iglesia et al. [9] is related to the second option. Inorganic zeolite membranes were selected due to their ability to withstand harsh conditions, and their high separation performance of water over alcohols in pervaporation. Two different zeolite membranes, mordenite and zeolite A, were tested in the esterification of acetic acid with ethanol in a continuous membrane reactor packed with catalyst Amberlyst™ 15. Both membranes were capable of shifting the equilibrium in less than 1 day of experiment. Mordenite membranes showed a great resistance to acidic reaction medium, with conversions of about 90% maintained for 5 days of experiment, with very high separation factors for H$_2$O/ethanol and H$_2$O/acetic acid.

The production of isobutyl acetate by pervaporation–esterification equilibrium reaction in a batch pervaporation membrane reactor (PVMR) using homogeneous (sulfuric acid) and heterogeneous (Dowex 50W-X8) catalysts was investigated by Korkmaz et al. [10]. The effects of catalyst loading, catalyst type, reaction time, membrane thickness, temperature and initial molar ratio of reactants were investigated. A cross-linked polydimethylsiloxane membrane selective to esters was prepared and used in PVMR. Batch reactions were carried out also in a simple batch reactor without pervaporation under the same conditions to compare the conversions for the reactions with and without pervaporation. In conclusion, PVMR experiments showed that the polydimethylsiloxane membrane can be used to remove the isobutyl acetate formed selectively with acceptable conversions and pervaporation fluxes.

In order to treat spent process water from companies of the food and beverage industries up to drinking water quality, a process concept was developed by Noronha et al. consisting of the following two treatment steps: (1) biological chemical oxygen demand (COD) reduction using a membrane bioreactor (MBR) in which the active biomass as well as other particulate matter were completely retained by means of immersed hollow-fibre microfiltration (MF) membranes; (2) subsequent reduction of bacterial germs, residual organics and inorganic constituent compounds by means of downstream two-stage nanofiltration (NF) with integrated ultraviolet (UV) disinfection. This hybrid process was tested by operating a pilot plant (capacity 100 L h$^{-1}$) for 6 months at a fruit juice company in order to treat spent process water (COD: 2500–6500 mg L$^{-1}$; electrical conductivity: 2300–4700 μS cm$^{-1}$) from the on-site mixing and equalizing tank. The process under study proved to be technically feasible and reliable. The treated water was partially desalted and fulfilled both the chemical and bacteriological standards required by the German Drinking Water Act. Therefore, it can be reused, for example, as cooling or boiler make-up water as well as for pasteurization, preparation of conveyor belt lubricants and bottle washing. Based on the results obtained, a preliminary evaluation was conducted to determine the investment and operating costs required for implementation of the hybrid process tested [11].

A novel approach in the treatment of olive mill wastewater was presented by Turano et al. The aim of the proposed process was both the reduction of pollution caused by the wastes and the selective...
separation of some useful products that are present (fats, sugars, polyphenols, etc.). The treatment consisted of a preliminary centrifugation step, in which the suspended solids were removed, and an actual selective separation phase, carried out by ultrafiltration (UF), of the centrifuge supernatant. The combination of centrifugation and UF allowed a COD reduction of about 90%. Moreover, a complete separation of fats, completely rejected by the membrane, from salts, sugars and polyphenols, contained in the permeate, was attained. The experimental study was directed to investigate the fluid-dynamic aspects related to the UF of real olive mill wastewaters. It was based on a preliminary rheological characterization of the waste and on the evaluation of permeation efficiency that was analysed as a function of several parameters, such as the importance of pretreating wastewater, the effects of localized turbulence, promoted by UF module geometry, and of the main operating variables (transmembrane pressure and feed flow rate). UF experimental results, obtained in a lab-scale flat-sheet membrane module, were interpreted using both the cake-filtration and the resistance-in-series models, thus allowing the evaluation of the $R_f$ parameter that represents the effect of fouling on separation efficiency. An estimation of specific cake resistance $\alpha$ was therefore performed on the basis of the feed concentration of total non-water compounds present in the waste, showing that pretreated wastewaters gave a lower $\alpha$ with respect to raw wastewaters by a factor of about 1000. Moreover, it was found that at the same transmembrane pressure, lower values of $\alpha$ correspond to a greater Re and that higher local turbulence implied lower specific cake resistances. The results obtained gave useful indications for a preliminary characterization of pilot and industrial modules utilized for olive mill wastewaters treatment aimed at a significant COD reduction and a selective separation of valuable compounds that are present in the waste [12].

Application of membrane techniques (pervaporation and membrane-based solvent extraction) and adsorption to the removal of phenol from solutions modelling wastewater from phenol production by cumene oxidation process was investigated by Kujawski et al. [13]. The transport and separation properties of composite membranes poly(ether-block amide), PERVAP 1060 and PERVAP 1070 in pervaporation of water-phenol mixtures were determined. It was found that the best removal efficiency of phenol was obtained using the poly(ether-block amide) membrane. Methyl tert-butyl ether (MTBE), cumene and the mixture of hydrocarbons were applied in the membrane-based phenol extraction. An Extra-Flow contactor with Celgard X-30 polypropylene hollow-fibre porous membranes was used in the experiments. MTBE was found the most efficient extractant. Adsorption of phenol on the different Amberlite resins was also investigated. Among the Amberlite resins of various grades used, Amberlite XAD-4 had the best properties in phenol removal from aqueous solutions. It was shown that regeneration of the adsorbent bed could be effectively performed with sodium hydroxide solution.

Bohdziewicz and Sroka’s study aimed to assess the effectiveness of meat industry wastewater treatment by applying two hybrid systems of activated sludge and UF in (1) an aerobic bioreactor in combination with UF and (2) a bioreactor equipped with separate denitrification and nitrification tanks in combination with UF. It was found feasible to treat this wastewater in both systems; however, the aerobic bioreactor necessitated the use of a very low activated sludge loading of 0.017 g COD per gram of total solids per day. Consequently, the bioreactor equipped with separate denitrification and nitrification tanks proved to be more favourable. The substrate loading of 0.15 g COD per gram of total solids per day, aeration intensity of 800 dm$^3$ and constant activated sludge loading of 4 g dm$^{-3}$ were used in this system. The wastewater treated under these conditions satisfied the requirements of the Regulation of the Minister of the Environment of 8 July 2004 and could be discharged into receiving water [14].

Van Hoof et al. performed an economic analysis comparing different processes for the dehydration of isopropanol–water. Traditional azeotropic distillation was compared with a hybrid system consisting of distillation followed by pervaporation and a hybrid system consisting of distillation followed by...
pervaporation followed by a second distillation. In the hybrid combinations, pervaporation with both polymeric (PERVAP® 2510, Sulzer Chemtech GmbH) and ceramic membranes (NaA-type zeolite, Mitsui & Co.) was investigated. Both membranes were tested for the dehydration of isopropanol at 70 and 90 °C. Based on the experimental results, calculations were performed with the pervaporation design calculation program (RWTH Aachen) to obtain economic data on the pervaporation processes.

For the simulations of the distillation processes, Aspen Plus 11.1 was used. It was found that the hybrid system distillation–pervaporation with ceramic membranes was the most interesting process from an economic point of view and could lead to a saving in total costs of 49% compared with azeotropic distillation [15].

A theoretical investigation of an integrated pervaporation and distillation column within a single column is studied by Fontalvo and Keurentjes [16]. The pervaporation section consisted of hollow fibres, with the separation layer on the outer diameter. Vapour and liquid flow faced the separation layer, while the permeate stream was removed from the inside lumen. Several advantages were identified from the process integration. There was no need for interstage heating since the latent heat required for pervaporation was supplied by condensation of the vapour in the pervaporation section. Additionally, vapour induced turbulence in the liquid phase, enhancing the mass and heat transfer between the liquid and the membrane surface. Also, the liquid phase within the column was close to saturated conditions, and thus its components were also close to their maximum driving force for pervaporation at the operation pressure. As a consequence, the membrane area was reduced compared with an externally connected pervaporation–distillation hybrid system. Owing to a higher amount of liquid that was in contact with the membrane than in an externally connected pervaporation–distillation hybrid system, the driving force of the transported component was improved, reducing the required membrane area. It was shown that the hybrid column was able to overcome the distillation boundaries for multicomponent mixtures and, therefore, perform separations that are not possible in a single distillation column. Two case studies of ternary mixtures were analysed. The hybrid system behaviour was studied as a function of the membrane area, position of the pervaporation section and membrane wetting.

Caballero et al. noted that the separation of olefins (ethylene, propylene) from paraffins (ethane, propane) on a commercial scale is performed almost exclusively by cryogenic distillation in petrochemical industries. Since this technology is highly energy intensive, there is a strong economic incentive to explore alternative separation technologies with lower energy consumption [17]. Consequently, they investigated the separation of ethylene and ethane as a representative case, using a mathematical programming approach to optimize and retrofit a hybrid separation system consisting of a distillation column and a parallel membrane separation unit. A two-stage approach was used. First, a shortcut model was introduced that allowed determining whether the hybrid system could be of interest and the order of magnitude of the energy savings that could be expected. Second, a superstructure optimization approach was proposed that used rigorous models for both the column and the membrane using a process simulator and state-of-the-art MINLP solvers. The results presented in the case study show that significant savings in total costs and energy (up to 30%) could be obtained with the hybrid system.

The pervaporation process features a liquid feed and retentate and a vapour permeate. The phase change produces a temperature decrease as the retentate flows through the unit. Since flux rates decrease with decreasing temperature, the conventional pervaporation unit consists of several membrane modules in series with interstage heating. The vapour permeate must be condensed for recovery and recycle, and refrigeration is usually required. Hybrid systems of distillation columns and pervaporation units are frequently used in situations where distillation alone is impossible or very expensive. Despite the many papers dealing with pervaporation, the issue of dynamic control seems to be
almost completely unexplored. Consequently, Luyben studied a hybrid column–pervaporation process that was designed to produce 99.77 wt% ethanol from a feed stream of ethanol–water mixture with composition near the azeotrope. The control objective was to maintain the purity of the ethanol product retentate stream in the face of disturbances in feed flow rate and feed composition. There were two possible manipulated variables: permeate pressure and retentate temperature. Permeate flux was increased by decreasing permeate pressure or increasing retentate temperature. A simplified dynamic pervaporation model was developed that captures the essential features of the process using energy and component balances along with overall pervaporation performance relationships. Dynamic simulations were used to demonstrate the effectiveness of a control structure that uses a cascade composition/temperature structure. A simple process modification was shown to improve controllability [18].

There are four possible configurations hybrid column–pervaporation, as shown in Figure 24.1. Separation of ethanol from solutions with different concentrations in a BIOTRON bioreactor integrated with a direct contact membrane distillation (MD) system was investigated by Tomaszewska and Białorzyk [19]. The experiments were carried out using immersed, capillary polypropylene membranes. The permeability of the membrane at the feed inlet temperatures of 308, 318 and 333 K was determined. The permeate and ethanol flux were strongly affected by the vapour pressure, which increased with the feed temperature and it was also associated with ethanol concentration in the feed. It was found that the MD can be successfully applied for the separation of volatile components such as ethanol.

A PVMR for the synthesis of ethyl tert-butyl ether (ETBE) from a liquid-phase reaction between ethanol and tert-butyl alcohol (TBA) was investigated by Kiatkittipong et al. [20]. Supported β-zeolite and a PVA membrane were used as a catalyst and a membrane in the reactor respectively. The permeation studies of an H₂O–ethanol binary system revealed that the membrane worked effectively for H₂O removal at the mixtures containing H₂O content lower than 62 mol%. The permeation studies of quaternary mixtures (H₂O–ethanol–TBA–ETBE) were performed at three temperatures: 323, 333 and 343 K. It was found that the membrane was preferentially permeable to H₂O. The permeability coefficients were correlated with the Arrhenius equation. In the PVMR studies, both experiment and simulation were carried out. An activity-based model was developed to investigate the performance of the PVMR using parameters obtained from other independent experiments. The simulation results agreed well with experimental results. It was observed that the ratio of the initial mole of ethanol to TBA λ, the ratio of the membrane area to the initial mole of TBA δ, the ratio of the amount of catalyst to the initial mole of TBA ϕ, the operating temperature and the membrane selectivity played important roles in the reactor performance. The analysis of the operating temperature showed an optimum yield due to the competing effect of the rate of reaction and the rate of reactant losses.

To improve conversion of n-butanol to the corresponding ester using acetic acid, the ionic liquid 1-allyl-3-butylimidazolium bis(trifluoromethanesulfonylimide), which does not dissolve in the water by-product, and PVA or PVA–tetraethoxysilane hybrid membranes were employed when using evaporation, along with microwave heating as shown in Figure 24.2. The effect on the conversion of n-butanol of each individual process variable as well as that of all of the variables used in combination was investigated, and the characteristics of each approach were discussed [21].

Ortiz and co-workers [22] reviewed the investigated applications of membrane reactors for in situ water removal during catalytic reactions in the food, pharmaceutical, cosmetics and petrochemical sectors. The global target in the works reported was the design of a compact and more efficient catalytic reactor (process intensification). By applying in situ water removal, two objectives were pursued: (i) overcoming the thermodynamic limitations of the reaction and (ii) avoiding catalyst poisoning. Different solution strategies proposed to overcome the difficulties in operating a membrane reactor in
Figure 24.1 Possible configuration for distillation column–pervaporation hybrid system.

Figure 24.2 Combined system using the ionic water-permselective membrane in an EV cell and microwave heating.
extreme acidic or temperature conditions were addressed, covering various aspects ranging from membrane materials to reactor configuration design using pervaporation or vapour permeation techniques. As a general remark, membrane materials (polymeric and inorganic) still lack the required characteristics or reproducibility necessary for industrial application in the sectors under study. Further investigation is required to accomplish this task.

Biogas upgrading is one piece in the framework of future energy supply. Commonly, absorption and adsorption technology is applied for biogas upgrading where CO₂, H₂S and water vapour have to be removed from CH₄. Gas permeation technology offers an interesting alternative to conventional upgrading techniques. Combining gas permeation membranes and conventional separation equipment in membrane hybrid processes merges the advantages of both technologies. Hence, Scholz et al. analysed seven different membrane hybrid processes for biogas upgrading. A single gas permeation stage was combined with pressurized water scrubbing, amine absorption, cryogenic separation, and a particular process in which the permeate of the gas permeation stage drives a gas engine. Furthermore, they compared the specific upgrading costs with an individual three-stage membrane process as well as with conventional separation processes. Simulation studies were performed in Aspen Plus to rigorously model the different hybrid process configurations. A full cost model determined operational and investment costs. The processes combining membranes and pressurized water scrubbing outperformed the conventional pressurized water scrubbing process in terms of specific upgrading costs. The application of a membrane remarkably reduced the upgrading costs for cryogenic separation. While the conventional process is far from being profitable, the hybrid process can compete with established biogas upgrading techniques. The three-stage gas permeation process and both hybrid processes involving the pressurized water scrubbing technology had the lowest upgrading costs. Ultimately, it is important to note that the results obtained in this study relied on the parameters set therein. A site where heat is provided inexpensively and low grid injection pressures are required might favour the application of amine absorption processes [23].

Tomaszewska and Łapin studied the conversion of KCl with H₂SO₄ into KHSO₄ performed using a chemical reactor coupled with direct-contact MD. The feed temperature at the inlet of the MD module amounted to 333 or 343 K and the permeate temperature was 293 K. The concentration of solutions with various initial molar ratios of KCl to H₂SO₄ in the MD membrane reactor resulted in the formation and periodic precipitation of KHSO₄ in the feed tank. The application of the membrane reactor enabled a continuous removal of HCl from the reaction mixture through the polypropylene membrane to shift the equilibrium of the conversion. Pure hydrochloric acid reaching a concentration of 43 g dm⁻³ was obtained. It was found that higher feed temperature and excess of H₂SO₄ in relation to KCl was profitable. In the case of the conversion at 343 K with the reaction mixture containing KCl and H₂SO₄ in a 1 : 2 molar ratio, the efficiency of KHSO₄ production was high. The potassium conversion coefficient was about 93%. Pure KHSO₄ was precipitated from the concentrated solution [24].

Bioethanol, as a clean and renewable fuel, is gaining increasing attention, mostly through its major environmental benefits. It can be produced from different kinds of renewable feedstock; for example, sugar cane, corn, wheat, cassava (first generation), cellulose biomass (second generation) and algal biomass (third generation). The conversion pathways for the production of bioethanol from disaccharides, from starches, and from lignocellulosic biomass were examined by Baeyens et al. The common processing routes were described, with their mass and energy balances, and assessed by comparing field data and simulations. Improvements through five possible interventions were discussed: (i) an integrated energy-pinch of condensers and reboilers in the bioethanol distillation train; (ii) the use of very high gravity fermentation; (iii) the current development of hybrid processes using pervaporation membranes; (iv) the substitution of current ethanol dewatering processes to >99.5 wt% pure ethanol by membrane technology; and (v) additional developments to improve the plant
operation, such as the use of microfiltration of the fermenter broth to protect heat exchangers and distillation columns against fouling, or novel distillation concepts [25].

Three different combinations of treatment techniques – that is, electrocoagulation combined with microfiltration, MBR, and electrocoagulation integrated with MBR (hybrid MBR (HMBR)) – were analysed and compared for the treatment of tannery wastewater operated for 7 days under the constant transmembrane pressure of 5 kPa by Keerthi et al. [26]. HMBR was found to be most suitable in performance as well as fouling reduction, with 94% of COD removal, 100% chromium removal and 8% improvement in percentage reduction in permeate flux compared with MBR with only 90% COD removal and 67% chromium removal. The effect of mixed liquor suspended solids on fouling was also investigated and was found to be insignificant. Electrocoagulation combined with microfiltration was capable of elevating the flux but was not as efficient as HMBR and MBR in COD removal. Fouling reduction by HMBR was further confirmed by scanning electron microscopy–energy dispersive X-ray analysis and particle size analysis.

Widespread detection of numerous micropollutants, including aromatic pharmaceuticals, in effluents of wastewater treatment plants has prompted much research aimed at efficiently eliminating these contaminants of environmental concern. In the study by Ba et al., a novel hybrid bioreactor of cross-linked enzymes aggregates of laccase (CLEA-Lac) and polysulfone hollow-fibre MF membrane was developed for the elimination of acetaminophen (ACT), mefenamic acid (MFA) and carbamazepine (CBZ) as model aromatic pharmaceuticals. The MF alone showed removals of the three drugs varying approximately from 50 to 90% over the course of 8 h in the filtrate of aqueous solution. Synergistic action of the MF and CLEA-Lac during operation achieved eliminations from aqueous solution of around 99%, nearly 100% and up to 85% for ACT, MFA and CBZ respectively. Under continuous operation, the hybrid bioreactor demonstrated elimination rates of the drugs from filtered wastewater up to 93% after 72 h for CBZ, and near-complete elimination of ACT and MFA was achieved within 24 h of treatment. Concomitantly to the drug eliminations in the wastewater, the CLEA-Lac exhibited 25% residual activity while being continuously recycled with no activity in the filtrate. Meanwhile, the filtrate flow rate showed only minor decline, indicating limited fouling of the membrane [27].

The Toray Group have designed an MBR that combines a membrane separation technique and an activated sludge method to do solid–liquid separation with a membrane that gives stable processing of water with high quality. It is mainly applied to the handling of industrial effluent and domestic drainage. In addition, the MBR is capable of liquid waste treatment with a raised activated sludge density. The polyvinylidene fluoride (PVDF) flat film type element has high permeability and good physical and chemical strength – see http://www.toray-watertreat.com/jigyou/jig_002.html (in Japanese).

Experimental investigations were carried out by Kumar and Pal on continuous and direct production of poly-($\gamma$-glutamic acid) in a hybrid reactor system that integrated a conventional fermentative production step with membrane-based downstream separation and purification [28]. The novelty of the integrated system lies in the high degree of purity, conversion, yield and productivity of poly-($\gamma$-glutamic acid) through elimination of substrate–product inhibitions of a traditional batch production system. This new system is compact, flexible, eco-friendly and largely fouling-free, ensuring steady and continuous production of poly-($\gamma$-glutamic acid) directly from a renewable carbon source at the rate of 0.91 g L$^{-1}$ h$^{-1}$. Crossflow MF membrane modules ensured almost complete separation and recycle of cells without much of a fouling problem. A well-screened UF membrane module helped to concentrate poly-($\gamma$-glutamic acid) while ensuring recovery and recycling of 96% unconverted carbon source resulting in yield of 0.6 g g$^{-1}$ along with high product purity.

Stylianou et al. [29] proposed novel water treatment systems based on ozonation combined with ceramic membranes for the treatment of refractory organic compounds found in natural water
sources such as groundwater. This includes, first, a short review of possible membrane-based hybrid processes for water treatment from various sources. Several practical and theoretical aspects for the application of hybrid membrane–ozonation systems are discussed, along with theoretical background regarding the transformation of target organic pollutants by ozone. Next, a novel ceramic membrane contactor, bringing into contact the gas phase (ozone) and water phase without the creation of bubbles (bubbleless ozonation), is presented. Experimental data showing the membrane contactor efficiency for oxidation of atrazine, endosulfan and MTBE are shown and discussed. Almost complete endosulfan degradation was achieved with the use of the ceramic contactor, whereas atrazine degradation higher than 50% could not be achieved even after 60 min of reaction time. Single ozonation of water containing MTBE could not result in a significant MTBE degradation. MTBE mineralization by \( \text{O}_3/\text{H}_2\text{O}_2 \) combination increased at higher pH values and \( \text{O}_3/\text{H}_2\text{O}_2 \) molar ratio of 0.2, reaching a maximum of around 65%.

A novel ultrasonic-assisted direct contact MD (USDCMD) hybrid process was designed and the effects of feed temperature, feed concentration, feed velocity, ultrasonic power and frequency on mass transfer were investigated by Hou et al. [30]. Under ultrasonic irradiation, changes and damage in membrane structure were found on the PVDF membrane, while the pore size and the stretching strain of polypropylene fibres were also enlarged and declined respectively. PTFE hollow fibre was selected to carry out USDCMD. The results showed that ultrasonic irradiation could effectively enhance mass transfer. Under an ultrasonic irradiation of 20 kHz and 260 W, a maximum permeate flux enhancement of 60% was obtained under conditions of feed temperature of 53 °C, feed velocity of 0.25 m s\(^{-1}\) and feed salt concentration of 140 g L\(^{-1}\). The increment was enlarged with a decrease in feed temperature, feed velocity and ultrasonic frequency as well as with an increase of feed concentration and ultrasonic power. Ultrasonic irradiation had no significant influence on the mechanical strength, pore size and hydrophobicity of the PTFE membrane in a 240 h continuous USDCMD experiment, and the novel MD process exhibited satisfying performance stability, which indicated that ultrasonic irradiation can be applied to MD for mass transfer enhancement.

Environmental and health concerns are driving wastewater treatment to come up with advanced technologies. Current research on possible treatments for waters polluted by bio-recalcitrant and/or toxic compounds is moving towards a coupling of processes, either traditional or more innovative. Membrane processes are under development but should be coupled with techniques for the destruction of pollutants to provide modern hybrid processes. On the other hand, advanced oxidation processes are also investigated, as they generate highly active species, such as hydroxyl radicals. These radicals are able to attack most organic compounds non-selectively with reaction rate constants. However, advanced oxidation processes have proved uneconomical for highly diluted solutions. The coupling of the two is of great interest for science and technology, involving modelling and optimization of both stages. To this end, the French National Research Agency is undertaking the SOFENcoMEM project, which proposes to study a continuous hybrid process for wastewater treatment, coupling a heterogeneous Fenton reaction with activation techniques (ultrasound and/or UV) and membrane filtration (see http://www.agence-nationale-recherche.fr/?Project=ANR-14-CE04-0006).

Among the advanced technologies, Fenton oxidation, which is conventionally based on the use of hydrogen peroxide and \( \text{Fe}^{2+} \) ions in solution, has been successfully applied for the degradation of various pollutants. However, this process is limited by the narrow pH window (2–4), and iron recovery is difficult. To overcome these drawbacks, heterogeneous iron oxide catalysts, either supported on porous materials (e.g. activated carbon, zeolite) or dispersed in the form of nanoparticles, are under development. In the latter case, coupling with membrane filtration (UF or MF) will ensure the retention of the catalyst during continuous water treatment.
The Fenton reaction is also classically operated in the presence of UV–visible irradiation (photo-Fenton). This activation prevents the formation of inactive catalyst species and also promotes the reduction of Fe$^{3+}$ to Fe$^{2+}$ while generating additional radicals.

Similarly, the application of ultrasound (sono-Fenton) should also play several promoting roles in the heterogeneous reaction. In solution, a synergetic effect between Fenton reaction and ultrasound has been proven, in which ultrasound improves Fe$^{2+}$ regeneration and subsequent formation of radicals. Moreover, acoustic cavitation gives rise to extreme conditions inside and around the collapsing bubble, and results in thermal cleavage of volatile compounds, further improving pollutant mineralization. Moreover, low-frequency ultrasound also induces mechanical effects, including particle aggregate disruption and possible surface activation or reactivation. One last interesting point is that zero-valent iron particles can be activated by very short inputs of ultrasound. This results in highly effective catalytic species requiring moderate dosages of H$_2$O$_2$.

Cyclodextrins are cyclic oligosaccharides of wide industrial application, whose synthesis is catalysed by cyclodextrin glycosyltransferase (CGTase) from starch. Rodríguez Gastón et al. produced cyclodextrins using CGTase from Bacillus circulans DF 9R in a continuous process and a UF membrane reactor. The batch process was conducted as a control. This method allowed increasing the yield from 40 to 55.6% and the productivity from 26.1 to 99.5 mg of cyclodextrin per unit of enzyme. The method also allowed the obtaining of a high-purity product. The flow rate remained at 50% of its initial value after 24 h of process, improving the results described in the literature for starch hydrolysis processes. CGTase remained active throughout the process, which could be explained by the protective effect of the substrate and reaction products on CGTase stability. In addition, batch processes were developed using starches from different sources. They concluded that any of the starches studied could be used as substrate for cyclodextrin production with similar yields and product specificity [31].

### 24.2 Hybrid Systems with Plural Membrane Technology

#### 24.2.1 Haemodialysis–Dialysis Hybrid

Despite routine home haemodialysis performed with thrice weekly frequency providing the best clinical results of any dialysis modality, it has been losing competition to centre haemodialysis and home peritoneal dialysis. The main reason for this paradox is a lack of suitable equipment for home haemodialysis. Contrary to peritoneal dialysis, which is easy to learn and perform without need for a helper, home haemodialysis is difficult because the kidney machines are not designed for home therapy. Daily haemodialysis provides even better results than routine home haemodialysis. Several studies showed excellent intradialytic and interdialytic tolerance. In spite of these results the method is used only in a few centres. There are two major reasons for this incongruity: time requirement for the patient and the cost for the provider. With more frequent dialysis, more time is spent on machine set-up, tear down and cleaning. If supplies are not reused, the cost of dialysis increases substantially with increased frequency of dialysis. Daily home haemodialysis may become practical with a new machine. Three components seem crucial for this device: a built-in water treatment system; a simple, small, positive-pressure, single-pass, batch dialysate system; and a reusable extracorporeal circuit, automatically cleaned and disinfected daily. Daily home haemodialysis performed with the new artificial kidney system may be considered as a hybrid of haemodialysis and peritoneal dialysis. High efficiency is taken from haemodialysis; simplicity is taken from peritoneal dialysis [32].
24.2.2 Dialysis–Reverse Osmosis Hybrid

Ion-exchange (IEX) and Donnan dialysis (DD) are techniques that can selectively remove cations, limiting scaling in reverse osmosis (RO). If the RO concentrate could be recycled for regeneration of these pretreatment techniques, RO recovery could be largely increased without the need for chemical addition or additional technologies. In the study by Vanoppen et al., two different RO feed streams (treated industrial wastewater and simple tap water) were tested in the envisioned IEX–RO and DD–RO hybrids, including RO concentrate recycling. The efficiency of multivalent cation removal depends mainly on the ratio of monovalent to multivalent cations in the feed stream, influencing the IEX efficiency in both IEX and DD. Since the mono-to-multivalent ratio was very high in the wastewater, the RO recovery could potentially be increased to 92%. For the tap water, these high RO recoveries could only be reached by adding additional NaCl, because of the low initial monovalent to multivalent ratio in the feed. In both cases, the IEX–RO hybrid proved to be most cost efficient, due to the high current cost of the membranes used in DD. The membrane cost would have to decrease from ~300 €/m² to 10–30 €/m² – comparable to current RO membranes – to achieve a comparable cost. In conclusion, the recycling of RO concentrate to regenerate IEX pretreatment techniques for RO is an interesting option to increase RO recovery without addition of chemicals, but only at high monovalent/multivalent cation ratios in the feed stream [33].

24.2.3 Nanofiltration–Reverse Osmosis Hybrid

Scale formation of soluble salts is one of the major factors limiting the application of NF and RO membranes. The article by Lee and Lee reviews the scale formation mechanisms in membrane systems, methods to retard scale formation, and a new hybrid system consisting of MF/NF–RO. Two distinct mechanisms in NF–RO fouling by scale formation, including surface and bulk crystallization, have been identified and investigated. The hydrodynamic operating conditions and module geometry determine which fouling mechanism is dominant. An increase in solute concentration at the membrane surface by concentration polarization is responsible for surface crystallization. Conventional methods for scale control only retard the rate of scale formation, and their performances are unpredictable. On the other hand, using an MF/NF–RO hybrid system for continuous removal of crystal particles from the retentate stream appears to be effective at high recovery of permeate. When applying the MF/NF–RO hybrid system, substantial improvement in flux is observed in spiral-wound modules, whereas it is negligible in the case of tubular modules. This is because the microfilter could only removes crystals formed in the retentate through the bulk crystallization that is the dominant fouling mechanism in the spiral-wound module [34]. Systems are being designed and operated on high-salinity brackish feed water sources.

An increasing number of brackish water RO (BWRO) and NF systems are being designed and operated on high-salinity feed water sources which can range from 2000 to 12 000 mg L⁻¹ TDS. Increased feed TDS can dramatically impact the design of the RO–NF in terms of hydraulic design, feed pressure requirements, and in permeate quality. Issues discussed include hybrid RO–NF membrane system designs for improved hydraulic flux design, the use of energy recovery devices, and the impact of higher salinities on the rejection of ions. Systems with improved hydraulic flux designs can reduce the rate of fouling and cleaning, be more energy efficient, and improve permeate quality. High TDS feed water systems lend themselves to designing with hybrid RO systems, primarily due to the hydraulic flux imbalance created by the large osmotic pressure differential from the feed end.
to the concentrate end. A hybrid RO–NF system is one which uses a different set of RO–NF membranes from one stage to another stage or can use a different set of membrane types within a stage itself [35].

The hybridized system of RO and NF developed by Aqua Giken Company, Japan, as shown in Figure 24.3, is very effective for the concentration of seawater [36]. This system, which is a low-running-cost and energy-saving technology, can be operated fully automatically, consecutively for 24 h without chemical additives, by only one high-pressure pump (6 MPa).

### 24.2.4 Ultrafiltration–Reverse Osmosis Hybrid

Tomaszewska and Bodzek [37] assessed the potential of reverse osmosis with low-pressure BWRO membranes to reduce TDS and enhance removal of boron and other microelements (such as iron, fluoride and arsenic), so making geothermal waters suitable for discharge into surface waters or reuse for drinking purposes. Preliminary treatment involved an iron removal system (a reduction in iron concentration from a maximum of ~40 mg L\(^{-1}\) to 0.013–0.021 mg L\(^{-1}\) (i.e. a reduction of 99% was obtained) and UF modules (the average silt density index after pretreatment was 2.4). The RO system was equipped with spiral-wound Dow Filmtec BW30HR-440i polyamide thin-film composite membranes. To optimize boron removal the membrane separation performance was assessed in short- and long-term tests at a semi-production scale (production of desalinated water at 1 m\(^3\) h\(^{-1}\)) over an 8-month period.

It was found that the boron removal rate in acidic feed water depended on the boron concentration. The highest removal rate of 56% was obtained in water with 2.5 mg boron per litre, followed by 48% in water containing 8.98 mg boron per litre and a very poor final result of 12% in 96.73 mg boron per litre. High boron removal rates of 96 and 97% were obtained in water with pH 10 and 11 containing ~10 mg boron per litre, regardless of the feed water uptake ratio. Feed waters with a high boron concentration of ~100 mg L\(^{-1}\) and pH 10 yielded a low boron removal rate of 66%. Efficient and stable performance of the BWRO-membrane equipped desalination system was achieved with geothermal waters containing 7 g/L TDS and a boron concentration of up to 10 mg/L. Taking account of the low pressure applied in the reverse osmosis process (1.1 MPa), a relatively high removal rate was obtained following the first stage of RO (at pH of 5 ± 0.4): 96–97% with respect to conductivity, and 94% with respect to \(\text{SiO}_2\), 92% for fluoride and not less than 84% for arsenic.

Tomaszewska and Bodzek [38] then presented the results of membrane scaling studies obtained after 8 months of desalinating geothermal water in an integrated system that combined iron removal, UF and two independent RO systems fitted with low-pressure BWRO membranes connected in series. Scaling prediction conducted using geochemical modelling showed that at a temperature of 30 °C and
for neutral-pH water from the geothermal intake (GT-1 well) there were good conditions for the precipitation of aragonite, barite, calcite, chalcedony, dolomite, hydroxyapatite and quartz on the RO membranes. A theoretically selected phosphonate scaling inhibitor failed to protect the membranes against sediment precipitation. Adjusting the pH of the water to ~5 by treating it with hydrochloric acid had a positive effect on the desalination process. On the basis of a morphological evaluation of sediments in the electron scanning microscope image and through the analysis of the chemical composition of the sediments crystallized on the membrane, silicates (SiO₂) and aluminosilicates (Al₂SiO₅) as well as barite (BaSO₄) and copper sulfate (CuSO₄) crystalline structures were found. Calcium phosphate as well as celestite (SrSO₄) and strontianite (SrCO₃) sediments were also observed, which points to significant concentration polarization. Most grains were a few micrometres to a maximum of 30 μm in size. Sediment clusters were usually heterogeneous in character. Desalination was performed with a high permeate recovery ratio (75–78%) with favourable key indicator retention ratios.

Membrane-based water desalination processes and hybrid technologies are often considered as a technologically and economically viable alternative for desalination of geothermal waters. This has been confirmed by the results of pilot studies concerning the UF-RO desalination of geothermal waters extracted from various geological structures in Poland. The assessment of the feasibility of implementing the water desalination process analysed on an industrial scale is largely dependent on the method and possibility of disposing or utilizing the concentrate. The analyses conducted in this respect have demonstrated that it is possible to use the solution obtained as a balneological product owing to its elevated metasilicic acid, fluorides and iodides ions content. Owing to environmental considerations, injecting the concentrate back into the formation is the preferable solution. The energy efficiency and economic analysis conducted demonstrated that the cost effectiveness of implementing the UF–RO process in a geothermal system on an industrial scale largely depends on the factors related to its operation, including without limitation the amount of geothermal water extracted, water salinity, the absorption parameters of the wells used to inject water back into the formation, the scale of problems related to the disposal of cooled water, local demand for drinking and household water, and so on. The decrease in the pressure required to inject water into the formation as well as the reduction in the stream of the water injected are among the key cost-effectiveness factors. Ensuring favourable desalinated water sale terms (price/quantity) is also a very important consideration owing to the electrical power required to conduct the UF–RO process [39].

24.2.5 Microfiltration–Reverse Osmosis Hybrid

A pilot-scale combination of an MF and an RO membrane system was applied on-site to treat tunnel construction wastewater by Lee et al. [40]. The MF membrane system initially removed contaminants (turbidity of less than 0.3 NTU) in the form of particulate materials in the feed water, thereby allowing the combined MF–RO system to efficiently remove more than 99% of known organic and inorganic contaminants and qualify the reclaimed water for reuse. The MF membrane autopsy analysis using X-ray fluorescence and inductively coupled plasma mass spectrometry revealed that the dominant foulants were inorganic deposits involving Si, Al and Fe, comprising the main components of cement materials, as well as deposits involving heavy metals such as Mn, Cu and Zn in the form of particles. Thus, thick cake contaminants shown by field emission scanning electron microscope images might be induced via suspended solids consisting of cement and clay materials and metals.
24.2.6 Ultrafiltration–Nanofiltration Hybrid

Orange press liquor is a by-product generated by the citrus processing industry containing huge amounts of natural phenolic compounds with recognized antioxidant activity. Cassano et al. investigated an integrated membrane process for the recovery of flavonoids from orange press liquors on a laboratory scale. The liquor was previously clarified by UF in selected operating conditions by using hollow-fibre polysulfone membranes. Then, the clarified liquor with a total soluble solids (TSS) content of 10 g per 100 g was pre-concentrated by NF up to 32 g TSS per 100 g by using a polyethersulfone spiral-wound membrane. A final concentration step, up to 47 g TSS per 100 g, was performed by using an osmotic distillation apparatus equipped with polypropylene hollow-fibre membranes. Suspended solids were completely removed in the UF step, producing a clarified liquor containing the major part of the flavonoids of the original press liquor due to the low rejection of the UF membrane towards these compounds. Flavanones and anthocyanins were highly rejected by the NF membrane, producing a permeate stream with a TSS content of 4.5 g per 100 g. Increasing concentrations of both the flavanones and anthocyanins were observed in the NF retentate by increasing the volume reduction factor. The final concentration of flavonoids by osmotic distillation produced a concentrated solution of interest for nutraceutical and pharmaceutical applications [41].

24.2.7 Ultrafiltration–Membrane Distillation Hybrid

Investigations on the treatment of oily wastewater by a combination of UF and MD as a final purification method were performed by Gryta et al. [42]. A tubular UF module equipped with PVDF membranes and a capillary MD module with polypropylene membranes were tested using a typical bilge water collected from a harbour without pretreatment. The permeate obtained from the UF process generally contained less than 5 ppm of oil. A further purification of the UF permeate by MD resulted in a complete removal of oil from wastewater and a very high reduction of the total organic carbon (99.5%) and TDS (99.9%).

24.2.8 Membrane Distillation–Forward Osmosis Hybrid

In some embodiments, systems and methods are provided for purifying a liquid, such as an impaired water. In some examples, seawater or brackish water is purified, such as to a potable level. Some configurations provide a system which includes an MD unit, such as a vacuum-enhanced direct-contact MD unit. The system also includes a forward osmosis (FO) system, which may include one or more FO units. A concentrated draw stream from the MD unit, such as a concentrated brine solution, serves as a draw solution for an FO unit, which may extract water from a source water, such as an impaired water. In some implementations, the FO system includes a second FO unit which uses the diluted draw solution from the first FO unit as a draw solution to extract water from a source water. The system may include additional components, such as a heater or a buffer tank [43].

Polyelectrolytes have proven their advantages as draw solutes in the FO process in terms of high water flux, minimum reverse flux and ease of recovery. The concept of a polyelectrolyte-promoted FO–MD hybrid system was demonstrated by Ge et al. and applied to recycle the wastewater containing an acid dye, as shown in Figure 24.4. A poly(acrylic acid) sodium (PAA-Na) salt was used as the draw solute of the FO to dehydrate the wastewater, while the MD was employed to reconcentrate the PAA-Na draw solution. With the integration of these two processes, a continuous wastewater treatment process was established. To optimize the FO–MD hybrid process, the effects of PAA-Na concentration, experimental duration and temperature were investigated. Almost a complete rejection of
PAA-Na solute was observed by both FO and MD membranes. Under the conditions of 0.48 g mL\(^{-1}\) PAA-Na and 66 °C, the wastewater was most efficiently dehydrated, yet with a stabilized PAA-Na concentration around 0.48 g mL\(^{-1}\). The practicality of PAA-Na-promoted FO–MD hybrid technology demonstrates not only its suitability in wastewater reclamation, but also its potential in other membrane-based separations, such as protein or pharmaceutical product enrichment. Their study may provide the insights for exploring novel draw solutes and their applications in FO-related processes [44].

The robustness and treatment capacity of an FO–MD hybrid system for small-scale decentralized sewer mining were demonstrated by Xie et al. [45]. A stable water flux was realized using a laboratory-scale FO–MD hybrid system operating continuously with raw sewage as the feed at water recovery up to 80%. The hybrid system also showed an excellent capacity for the removal of trace organic contaminants (TrOCs), with removal rates ranging from 91 to 98%. The results suggest that TrOC transport through the FO membrane is governed by ‘solute–membrane’ interaction, whereas that through the MD membrane is strongly correlated to TrOC volatility. Concentrations of organic matter and TrOCs in the draw solution increased substantially as the water recovery increased. This accumulation of some contaminants in the draw solution was attributed to the difference in their rejection by the FO and MD systems. Xie et al. demonstrated that granular activated carbon adsorption or UV oxidation could be used to prevent contaminant accumulation in the draw solution, resulting in near complete rejection (>99.5%) of TrOCs.

24.2.9 Electrodialysis–Forward Osmosis Hybrid

In isolated locations, remote areas or islands, potable water is precious because of the lack of drinking water treatment facilities and energy supply. Thus, a robust and reliable water treatment system based on natural energy is needed to reuse wastewater or to desalinate groundwater/seawater for provision.
of drinking water. In the study by Zhang et al., a hybrid membrane system combining electrodialysis (ED) and FO, driven by renewable energy (solar energy), was proposed to produce high-quality water (potable) from secondary wastewater effluent or brackish water. In this hybrid membrane system, feed water (secondary wastewater effluent or synthetic brackish water) was drawn to the FO draw solution while the organic and inorganic substances (ions, compounds, colloids and particles) were rejected. The diluted draw solution was then pumped to the solar-energy-driven ED. In the ED unit, the diluted draw solution was desalted and high-quality water was produced; the concentrate was recycled to the FO unit and reused as the draw solution. The results showed that the water produced from this system contained a low concentration of total organic carbon, carbonate and cations derived from the feedwater, had a low conductivity, and met potable water standards. The water production cost considering the investment for membranes and solar panel is €3.32–4.92/m³ (for 300 days of production per year) for a small size potable water production system [46].

24.2.10 Forward Osmosis–Reverse Osmosis Hybrid

FO is an osmotically driven membrane process that uses osmotic pressure of concentrated solutions, including seawater, to extract clean water from low-salinity solutions. In a new approach, FO uses the difference in salinity of seawater and impaired water as the driving force to dilute seawater with reclaimed water through a tight FO membrane. By diluting the seawater feed stream to an RO desalination plant, the energy demand of desalination is reduced, and two tight barriers are in place to enhance rejection of contaminants that might be present in the impaired water feed stream. Cath et al. conducted bench- and pilot-scale osmotic dilution tests with synthetic seawater as a draw solution and with secondary and tertiary effluent from a domestic wastewater treatment plant as feed streams. Impaired surface water from the South Platte River in Colorado was also tested as a feed stream to the osmotic dilution process. Although water flux was generally low, flux decline caused by fouling was minimal during weeks of continuous operation. Multiple membrane barriers provided more than 90% rejection of organic and inorganic solutes. In addition, the hybrid FO–RO process was found to be economically and technically feasible across a broad range of operating conditions [47].

24.2.11 Forward Osmosis–Nanofiltration Hybrid

A hybrid FO–NF process for seawater desalination was proposed by Tan and Ng [48]. Seven potential draw solutions for the FO–NF process were investigated using laboratory-scale FO and NF test cells. Results from both FO and NF tests suggested that the hybrid FO–NF process is a feasible process for seawater desalination. Water fluxes of about 10 L m⁻¹ h⁻¹, for both FO and NF processes could be achieved. Solute rejection of the FO membrane was maintained at over 99.4% for all seven draw solutes tested. Solute rejection of the NF membrane for the four selected draw solutions could achieve a maximum of 97.9%. A hybrid FO–NF process with two-pass NF regeneration was proposed to achieve good quality product water that meets the recommended drinking water TDS guideline, of 500 mg L⁻¹ from the World Health Organization. It is possible to desalinate seawater with this system configuration to obtain product water with TDS of 113.6 mg L⁻¹. Finally, MgSO₄ and Na₂SO₄ were proposed as the most likely draw solution for the hybrid process.

24.2.12 Forward Osmosis–Electrokinetic Hybrid

A direct energy conversion technology based on the electrokinetic (EK) phenomenon has attracted increasing attention during recent years. However, an external driving source (e.g. hydrostatic
pressure) is needed to produce an EK flow in microchannels. Since the required driving pressure becomes significant when the size of channels shrinks, the EK energy conversion efficiency is usually low. Jiao et al. [49] recently developed a novel hybrid energy conversion technique using combined principles of EK and FO. The proposed FO–EK energy conversion technique was demonstrated by using an experimental system comprising two submodules, an FO submodule and an EK submodule (see Figure 24.5). Through the use of a salinity gradient, a suction force is created to induce a hydrodynamic flow in the FO submodule based on the principle of FO. Accordingly, electric energy, in forms of EK streaming potential and streaming current, is generated across a porous glass housed in the EK submodule. This proposed power generation technique converts the salinity gradient energy into the electric energy without need of external pressure input. In this study, thorough experiments were carried out to investigate the FO–EK energy conversion processes. The results showed that the generated power density decays with an increase of the pore size of the porous glass and monotonically increases with increasing salinity difference between the draw and the feed solutions. It was also demonstrated that a maximum power density of 0.165 W m$^{-3}$ can be achieved by using the porous glass with an average pore size 6 $\mu$m at 4 M salinity difference. Two kinds of theoretical mathematical models were presented; namely, a uniform-capillary model and a heterogeneous-capillary model. Compared with the uniform-capillary model, the heterogeneous-capillary model proposed by Jiao et al. has better agreement with the experimental data.

24.2.13 Nanofiltration–Forward Osmosis–Reverse Osmosis Hybrid

Brackish water desalination is a common method for fresh water supply in arid areas. Concentrated brine is the major waste stream generated from the desalination process. The study by Altaee and Hilal proposed a multistage NF–FO–BWRO system to increase the recovery rate of brackish water. The simulation results showed that the NF–FO–BWRO system was able to achieve >90% recovery rate for a number of feed salinities varied from 1 to 2.4 g L$^{-1}$. High-permeability NF membrane was used in the first stage to produce the first permeate flow at relatively low power consumption. Concentrated brine from the NF was fed to an FO membrane for power for additional fresh water extraction before disposal, and 0.25–0.5 M NaCl was used as the draw solution in the FO membrane. The results showed that system recovery rate increased with increasing concentration of the draw solution. The NF
process was responsible of 75% of the total recovery rate, while the BWRO process contribution was up to 20%. Almost 80% of the total power consumption for desalination was due to the BWRO process. The NF and FO processes accounted for the remaining 20% power consumption. The BWRO system also required two to three times more membranes than the FO and NF processes. NF–FO–BWRO is flexible and can generate different proportions of permeate flows through controlling the recovery rates of each component [50].

### 24.2.14 Ultrafiltration–Reverse Osmosis–Electrodialysis Reversal Hybrid

A pilot plant was built by Montaña et al. to test the behaviour of UF, RO and ED reversal (EDR) in order to improve the quality of the water supplied to the Barcelona metropolitan area from the Llobregat River [51]. Montaña et al. presented results from two studies to reduce natural radioactivity. The results from the pilot plant with four different scenarios were used to design the full-scale treatment plant built (Sant Joan Despí Water Treatment Plant). The samples taken at different steps of the treatment were analysed to determine gross alpha, gross beta and uranium activity. The results obtained revealed a significant improvement in the radiological water quality provided by both membrane techniques (RO and EDR showed removal rates higher than 60%). However, UF did not show any significant removal capacity for gross alpha, gross beta or uranium activities. RO was better at reducing the radiological parameters studied, and this treatment was selected and applied at the full-scale treatment plant. The RO treatment used at the Sant Joan Despí Water Treatment Plant reduced the concentration of both gross alpha and gross beta activities and also produced water of high quality with an average removal of 95% for gross alpha activity and almost 93% for gross beta activity at the treatment plant.

### References


25

Optical Resolution by Membranes

The α-amino acids, which are protein components, are all known to have enantiomers except glycine. The chemical and physical properties of enantiomers are the same, and distinction between them is difficult under normal conditions. However, many of the amino acids utilized by organisms are predominantly of the L-form, so it is important to distinguish the enantiomer closely. For example, D-sodium glutamate, which is enantiomer of the famous L-sodium glutamate, has a bitterness when used as a taste seasoning. Because the effects on organisms of a particular enantiomeric form are totally different, the optically active material used for pharmaceutical products, pesticides, cosmetics, food additives and those raw materials must be a compound having a fixed optical isomerism. However, an operation to isolate the optically active material is necessary because if attention is not paid to the three-dimensional structure an optically inert equivalent enantiomeric mixture (racemic body) is obtained. This is called optical resolution. Nowadays, membrane-based separation techniques constitute well-established process methods for industrial treatments of fluids. Like the simulated moving bed technique, these techniques can be performed in continuous mode.

25.1 Present Conditions and Problem of Optical Resolution with Membranes

Methods for directly performing optical resolution that are put to practical use include a chemical method with an optical resolution agent, a method using the biological molecules such as enzymes, and the high-performance liquid chromatography (HPLC) method. However, there are some bad points as follows:

1) A stoichiometric quantity of optical resolution agent is required to resolve an object or further resolution agent is necessary for the resolution.
2) Except for HPLC, the effective resolution object of a resolution agent and an enzyme is limited.
3) These are basically batch processes and, other than HPLC, are inefficient because they are not continuous methods.
4) Including HPLC, the methods are unsuitable for processing in large quantities.

When membranes for effective optical resolution can be developed, these bad points can be solved [1].
The conditions that are required by an effective optical resolution membrane are as follows:

1) The membrane should be a self-supportive solid membrane and have superior membrane strength.
2) The membrane should have high permselectivity; namely, high-resolution performance.
3) The membrane should have a high permeation rate or have a permeation rate that can be raised by pressurization.
4) Permeation performance should be stable for a long time.
5) The membrane should be able to resolve a broad range of compounds.
6) The membrane should be able to permeate the desired enantiomer selectively.

Condition (1) is regarded as the most basic requirement. The moulding to various forms is easy for a self-supportive solid membrane, and incorporation into various practical processes is possible because the durability is high in a membrane with a high strength; furthermore, the permeation rate can be increased by pressurization.

However, optical resolution membranes having a high optical resolution ability realized in the past have been limited to liquid membranes [2,3], which included a host compound recognizing an optical isomer as a movement carrier. High-resolution performance is provided with the liquid membrane, but it is difficult to prevent a loss of liquid and carrier, and the durability is low. In addition, the kinds of guest molecules that a certain carrier can recognize is limited. Naturally, conditions (2) and (3) are important for a separation membrane. Generally, when one of these increases in the membrane separation, the other shows a decreasing tendency, and it is a problem if neither can be met at the same time. Condition (4) is also important: if resolution ability is seen only in the early stages of permeation, the advantage of the membrane is not made use of. Furthermore, if condition (5) is met the value of the membrane increases, and still more so if condition (6) can be met.

Many researchers have made efforts to solve the problems of conditions (1)–(6), and the big hope is that the possibility of obtaining optical resolution using membranes is in near now.

### 25.2 Membranes for Optical Resolution

For the separation of racemic mixtures, two basic types of membrane processes can be distinguished: a direct separation using an enantioselective membrane, or separation in which a nonselective membrane assists an enantioselective process [4]. The most direct method is to apply enantioselective membranes, thus allowing selective transport of one of the enantiomers of a racemic mixture. These membranes can either be a dense polymer or a liquid. In the latter case, the membrane liquid can be chiral, or may contain a chiral additive (carrier). Nonselective membranes can also provide essential nonchiral separation characteristics in combination with chirality outside the membrane. The required enantioselectivity can stem either from a selective physical interaction or from a selective (bio)conversion [5].

#### 25.2.1 Liquid Membranes

See Kennere and Keurentjes [5].

As shown in Figure 25.1, a liquid membrane for optical resolution contains an enantiospecific carrier which selectively forms a complex with one of the enantiomers of a racemic mixture at the feed side and transports it across the membrane, where it is released into the receptor phase.
The carrier should not dissolve in the feed liquid or receptor phase in order to avoid leakage from the liquid membrane. In order to achieve sufficient selectivity, minimization of nonselective transport through the bulk of the membrane liquid is required. Liquid membranes are divided into three basic types, as shown in Figure 25.2: emulsion, bulk and supported liquid membranes (SLMs).
25.2.1.1 Emulsion Liquid Membrane
See Kennere and Keurentjes [5].

The application of an emulsion liquid membrane system involves three consecutive steps. First, two immiscible phases are stirred with a surfactant to generate an emulsion. Subsequently, the emulsion is mixed with another liquid containing the material to be extracted. The phases are then separated, and the emulsifying agents are recovered in a de-emulsification step.

25.2.1.2 Bulk Liquid Membrane
See Kennere and Keurentjes [5].

In the classical set-up of bulk liquid membranes, the membrane phase is a well-mixed bulk phase instead of an immobilized phase within a pore or film. The principle comprises enantioselective extraction from the feed phase to the carrier phase, and subsequently the carrier releases the enantiomer into the receiving phase. As formation and dissociation of the chiral complex occur at different locations, suitable conditions for absorption and desorption can be established. In order to allow for effective mass transport between the different liquid phases involved, hollow-fibre membranes can be used.

25.2.1.3 Supported Liquid Membrane
See Kennere and Keurentjes [5].

In SLMs, a chiral liquid is immobilized in the pores of a membrane by capillary and interfacial tension forces. The immobilized film can keep apart two miscible liquids that do not wet the porous membrane. Vaidya et al. [6] reported the effects of membrane type (structure and wettability) on the stability of solvents in the pores of the membrane.

25.2.2 Polymer Membranes
See Kennere and Keurentjes [5].

As the main disadvantage of liquid membrane systems is the instability over a longer period of time, another approach would be to perform separation through a solid membrane [9]. Enantioselective polymer membranes typically consist of a nonselective porous support coated with a thin layer of an enantioselective polymer. This type of polymer membrane requires a high specific surface, low mass transfer resistance, good mechanical strength and enantio recognition ability. The separation mechanism involves enantiospecific interactions (solution and diffusion) between the isomers to be separated and the top layer polymer matrix. In case the required optical purity cannot be obtained in one single step, a cascade of membrane units can easily be applied to achieve the desired purity. Both the permeability $P$ (flux) and enantioselectivity $\alpha$ determine the performance of an enantioselective membrane, for which $\alpha$ is defined as the ratio of the permeabilities of the L- and D-enantiomers:

$$\alpha = \frac{P_L}{P_D}$$

(25.1)

Enantiospecific polymers commonly used as stationary phases in chromatography are potentially applicable for chiral membrane separation; for example, polysaccharides, acrylic polymers, poly ($\alpha$-amino acids) and polycetylene-derived polymers [8]. Additionally, chiral separations have been reported at high resolution and high rate by a bovine serum albumin multilayer-adsorbed porous hollow-fibre membrane as stationary phase [9]. In general, interest has been mainly focused on the separation of racemic amino acids by enantioselective polymer membranes [10–18]. Although almost complete resolution can be obtained in a dialysis configuration, the flux through this type of
membranes is extremely low. Aoki and co-workers [19–24] reported the preparation of membranes completely made of chiral polymer in order to improve the permeability.

A different approach is the use of an ultrafiltration membrane with an immobilized chiral component [18]. The transport mechanism for the separation of D,L-phenylalanine by an enantioselective ultrafiltration membrane is shown schematically in Figure 25.3. Depending on the transmembrane pressure, selectivities were found to be between 1.25 and 4.1, at permeabilities between $10^{-6}$ and $10^{-7}$ m s$^{-1}$ respectively.

**25.3 Technology of Optical Resolution Membranes**

**25.3.1 Liquid Membranes in Optical Resolution**

Flores-López et al. [25] reported the characterization of new synthesized chiral polymeric membranes, based on a cellulose acetate propionate polymer. The flux and permselective properties of the membrane were studied using 50% ethanol solution of (R,S)-trans-stilbene oxide as feed solution. Scanning electron microscopy revealed the asymmetric structure of these membranes. The roughness of the surface was measured by atomic force microscopy. The resolution of over 97% enantiomeric excess was achieved when the enantioselective membrane was prepared with 18 wt% cellulose acetate and 8 wt% cellulose acetate propionate in the casting solution of dimethyl formamide/N-methyl-2-pyrrolidone/acetone, at 20 °C and 55% humidity, and a water bath at 10 °C for the gelation of the membrane. The operating pressures used were 275.57, 345.19 and 413.84 kPa and the feed concentration of the trans-stilbene oxide was 2.6 mM.

Studies on the possible use of phosphate and phosphonate esters bearing chiral menthol or nopol moieties as carriers for the transport of amines, amino acids and amino acid esters through SLMs were presented by Dżygiel et al. [26]. Additionally, the enantioselectivity of the SLM transport of alkyl esters of aromatic amino acids and a non-protein amino acid was also evaluated. It was concluded that the extent of transport depended strongly on the hydrophobicity of the amino compound. Moreover, the carrier structure also influenced the transport of those compounds through the SLM: chiral phosphate

![Figure 25.3](image-url)
and phosphonate esters appeared to be poor or moderate carriers for enantioselective SLM transport of amino acids and their esters. The transport efficiency and selectivity were strongly dependent on the structure of both the transported compounds and the carrier. However, no meaningful relationship existed between these structural features and transportation or enantioselectivity.

A number of artificial carriers for the transport of zwitterionic aromatic amino acids across bulk model membranes (U-tube type) were prepared and evaluated by Breccia et al. [27]. 1,2-Dichloroethane and dichloromethane were employed in the organic phase. All compounds were based on a bicyclic chiral guanidinium scaffold that ideally complemented the carboxylate function. The guanidinium central moiety was attached to crown ethers or lasalocid A as specific subunits for ammonium recognition as well as to aromatic or hydrophobic residues to evaluate their potential interaction with the side chains of the guest amino acids. The subunits were linked to the guanidinium through ester or amide connectors. Amides were found to be better carriers than esters, though less enantioselective. On the other hand, crown ethers were superior to lasalocid derivatives. As expected, transport rates were dependent on the carrier concentration in the liquid membrane. Reciprocally, enantioselectivities were much higher at lower carrier concentrations. The results showed that their previously proposed three-point binding model [28], involving the participation of the aromatic or hydrophobic residue interacting with the side chains of the amino acid guest, is unnecessary to explain the high enantioselectivities observed. Molecular dynamics fully support a two-point model involving only the guanidinium and crown ether moieties. These molecules constituted the first examples of chiral selectors for underivatized amino acids acting as carriers under neutral conditions.

Goto and co-workers [29] developed a highly enantioselective separation system for the optically active compounds (S)-ibuprofen and l-phenylalanine from their racemic mixtures by employing an SLM encapsulating a surfactant–lipase complex (or a surfactant–α-chymotrypsin complex). In their system, enzymes encapsulated in the liquid-membrane phase effectively drove the enantioselective transport of optically active compounds through the SLM. This novel SLM allowed high enantioselectivity (over 91% ee) in the optical resolution of racemic ibuprofen and phenylalanine.

Goto and co-workers [30] also encapsulated a surfactant–protease complex (the main protease used being α-chymotrypsin) in an organic phase of an SLM for the optical resolution of various amino acids. The l-isomers of amino acids were enantioselectively permeated through the SLM. The mechanism of the amino acid permeation through the SLM was considered to be as follows: an l-amino acid was enantioselectively esterified with ethanol by a surfactant–protease complex encapsulated in the SLM, and the resulting l-amino acid ethyl ester dissolved into the organic phase of the SLM and diffused across the SLM. Another surfactant–α-chymotrypsin complex in the receiving phase catalysed ester hydrolysis to produce the initial l-amino acid and ethanol, which are water soluble. Thus, the l-amino acid was selectively transported to the receiving phase through the SLM on the basis of the molecular recognition of the surfactant–protease complex in the SLM. It was found that the catalytic activity and enantioselectivity of the surfactant–protease complex governed the permeate flux of amino acids and the enantiomeric excess in the membrane separation.

Enantioseparation of salbutamol solute was carried out by Jiao et al. in liquid-supported membrane by using a polyvinylidene fluoride hollow-fibre module [31]. The enantioselective transport of solute was facilitated by combinatorial chiral selectors, which were dissolved in toluene organic solvent. The effects of molar concentration ratios of salbutamol to combinatorial chiral selectors and of the pH value of buffer solution on enantioseparation were investigated. The results showed that when the molar concentration ratio is 2 : 1 : 1, the maximum separation factor and enantiomer excess are 1.49 and 19.74% respectively, and the R-enantiomer flux is more than the S-enantiomer; the pH value of buffer solution influenced the performances of enantioseparation obviously, and the appropriate range of pH value was 7.0–7.2.
Chiral separation of racemic mixtures is essential in the production of many pharmaceutical compounds. Rousseau and co-workers [32] described a novel chiral separation technique that combined cooling crystallization and a membrane separation that is used in DL-glutamic acid resolution. The process utilized two crystallization chambers separated by a membrane that prevented transport of crystals from one chamber to another. Importantly, conditions had to be controlled so that only a pure species crystallized in each of the chambers. This was done by appropriate addition of seed crystals to each chamber and by restricting the formation of new crystals to secondary nucleation mechanisms. The seed crystals may grow or participate in secondary nucleation, but the conditions must be controlled so as to prevent primary nucleation, which would result in the formation of both crystal species in each chamber. Experiments were conducted with different amounts of seed crystals to determine operating conditions that produced the high product yield and purity. The results showed that this novel chiral separation process is promising: the product purity was over 94% (with a separation factor of 16) and the product yield was increased by as much as 56% more than could be obtained with simple cooling crystallization.

The chirality of drugs plays a significant role in most chemical and biochemical processes. In the paper by Zhang et al., chiral liquid membrane used L-tartaric ester solved in n-octane as liquid membrane phase and polyvinylidene fluoride hollow fibres as membrane support was investigated to separate racemic ibuprofen [33]. For L-dipentyl tartrate ester, the separation factor was 1.18. The favourable L-dipentyl tartaric ester concentration was 0.20 mol L$^{-1}$. With an increased flow rate on two sides, a flux change of mass transfer in the stripping phase was not observed. The same trend was obtained in the feed phase. The concentration of both R-ibuprofen and S-ibuprofen in the stripping phase increased with increase in pH. The best pH in the stripping phase was 2.5, and the separation factor was about 1.2. The best separation factor was up to 1.38 after a six-level experiment.

25.3.2 Solid Membranes in Optical Resolution

Because DNA has optical resolution properties and strongly combines with the L-form in racemic phenylalanine, an immobilized-DNA cellulose membrane surface was prepared [34,35].

Figure 25.4 shows the relationship between the concentration of feed solution and separation factor, $\alpha_{D/L}$ and $\alpha_{D/L(C)}$, through a DNA–Cell8000 membrane, whose pores do not permeate a solute of molecular weight >8000. $\alpha_{D/L}$ and $\alpha_{D/L(C)}$ were obtained from the following equations:

$$\alpha_{D/L} = \frac{P_D}{P_L} \frac{F_D}{F_L}$$

(25.2)

$$\alpha_{D/L(C)} = \frac{C_L}{C_D}$$

(25.3)

where $P_D$ and $P_L$ are the concentrations of D- and L-phenylalanine respectively in the permeate, and $F_D$ and $F_L$ are the concentrations of D- and L-phenylalanine respectively in the feed solution. $C_D$ and $C_L$ are the concentrations of D- and L-phenylalanine respectively in the concentrated liquid.

As can be seen from Figure 25.4, when using an unmodified Cell8000 membrane, the separation coefficient of the concentrate of the supply liquid side after transmission for 8 h $\alpha_{D/L}$ is approximately unity and there are no optical resolution characteristics. However, $\alpha_{D/L}$ for the immobilized-DNA–Cell8000 membrane is less than unity. These results suggest that L-phenylalanine is predominantly permeated. This predominant permeation of L-phenylalanine through the immobilized-DNA–Cell8000 membrane is due to the fact that L-phenylalanine preferentially couples to the
immobilized-DNA–Cell8000 membrane, deposits in the DNA–Cell8000 membrane pores and is preferentially permeated.

In Figure 25.4, \( \alpha_{D/L(C)} \), the separation coefficient of the concentrate liquid in the feed solution side after permeation for 8 h, is more than unity. This result suggests that the concentration of \( \text{D-phenylalanine} \) in the feed side becomes higher. From these results, the immobilized-DNA–Cell8000 membrane is regarded as a functional film similar to a biomembrane, not a simple adsorbent-like affinity membrane.

The \( \alpha_{D/L} \) of racemic phenylalanine was bigger than unity for an immobilized-DNA–Cell1000 membrane, which has a reduced amount of immobilized-DNA and a smaller pore size than the immobilized-DNA–Cell8000 membrane, and \( \alpha_{D/L(C)} \) became smaller than unity and was reversed with an immobilized-DNA–Cell8000 membrane. The difference in optical resolution characteristics of racemic phenylalanine between an immobilized-DNA–Cell8000 membrane and an immobilized-DNA–Cell1000 membrane is explained by the model shown in Figure 25.5[34,35].

The difference in optical resolution characteristics for racemic phenylalanine through DNA–Cell8000 and DNA–Cell1000 immobilized membranes in ultrafiltration can be explained as follows. When DNA is immobilized to a Cell1000 membrane with small pores, DNA is immobilized only on the membrane surface because DNA cannot enter inside the pores. On the other hand, DNA also can be immobilized inside the pores in the Cell8000 membrane, which has a bigger pore size.

Chemical separations represent a large portion of the cost of bringing any new pharmaceutical product to the market. Membrane-based separation technologies in which the target molecule is selectively extracted and transported across a membrane are potentially more economical and easier to implement than competing separations methods; but membranes with higher transport selectivities are required. Lakshmi and Martin described an approach for preparing highly selective membranes which involves immobilizing apoenzymes within a microporous composite. The apoenzyme selectively recognizes its substrate molecule and transports it across the composite membrane, without affecting the unwanted chemical conversion of the substrate molecule to product. They demonstrated this approach using three different apoenzymes. Most importantly, it can be used to make enantioselective membranes for chiral separations, one of the most challenging and important problems in
bioseparation technology. They were able to achieve a fivefold difference between the transport rates of D- and L-amino acids [36].

A membrane containing hexokinase and phosphatase was made asymmetric by a pH gradient by Selegny et al. D-Glucose phosphorylated in the presence of adenosine triphosphate on entering and regenerated on leaving the membrane is consequently pumped (i.e. is actively transported through the membrane), whereas L-glucose diffuses passively. Enantiomer separations were made possible by using the membrane for selective pumping of the D-isomer or as a selective barrier against its retro-diffusion [37].

Optical resolution of various racemates, such as (±)-tryptophan and (±)-1,3-butanediol, was achieved by permeation through a self-supporting membrane of (+)-poly[1-[dimethyl(10-pinanyl)silyl]-1-propyne] ((+)-poly(DPSP)) prepared by homopolymerization of (-)-1-[dimethyl(10-pinanyl)silyl]-1-propyne ((-) -DPSP) by Aoki et al. Almost complete optical resolution (permeate enantiomeric excess 81–100%) was achieved at an initial period of concentration-driven permeation, and stable permeation with moderate permselectivity (permeate enantiomeric excess 12 – 54%) continued for more than 600 h. In addition, by permeation of vapour permeant such as by evapomeation and pervaporation, higher permeation rates were attained while maintaining high enantioselectivity. The sign of the enantiomer that predominantly permeated through a (+)-poly(DPSP) membrane was opposite to that through a (-)-poly(DPSP) membrane. In the permeation through a (+)-poly(DPSP) membrane of a solute or a solvent having a high affinity for (+)-poly(DPSP) and in the permeation through a membrane from the copolymer of (-)-DPSP with a small amount of 1-(trimethylsilyl)-1-propyne, their enantioselectivities were much lower. These findings suggest that the permeating route surrounding chiral pinanyl groups in a (+)-poly(DPSP) membrane that can enantioselectively separate various racemates was easily deformed by using a solute or solvent having a high affinity for (+)-poly(DPSP) or by removing a small amount of pinanyl groups [23].

**Figure 25.5** Pore size dependency of mechanism for optical resolution by immobilized-DNA–cellulose membranes. 

- **D**: D-phenylalanine; **L**: L-phenylalanine; **DNA**: DNA.
A lipase-immobilized membrane reactor was applied for the optical resolution of racemic naproxen by Drioli and co-workers, and the effect of various operation conditions on reaction rate and enantioselectivity was examined [38]. The membrane reactor consisted of an organic phase dissolving naproxen ester, a lipase-immobilized polyamide membrane, and an aqueous phase to recover the reaction products. The lipase immobilized in the membrane reactor showed a stable activity for more than 200 h of continuous operation, while the native lipase in an emulsioned stirred tank reactor quickly lost its activity showing a half-life time of about 2 h. When crude lipase was used, the biphasic enzyme membrane reactor gave smaller enantioselectivity compared with the native lipase in the emulsioned tank reactor, whilst the use of pure lipase gave similar results to the native lipase. There is then a discussion concerning that other hydrolases present in the crude enzyme powder caused the decrease of enantioselectivity. Enantioselectivity depended on the substrate concentration, amount of enzyme loaded in the membrane and immobilization site. In fact, these parameters affect the organic–aqueous interface that plays an important role in the enhancement of enantioselectivity.

In contrast to analytical methods, the range of technologies currently applied for large-scale enantiomer separations is not very extensive. Therefore, a new system was developed by van der Ent et al. for large-scale enantiomer separations that can be regarded as the scale-up of a capillary electrophoresis system. In this stacked membrane system, chiral selectors that are retained by size-selective membranes were used. Upon application of an electrical potential, selective transport of the free enantiomer occurred, thus providing separation. In principle, this system can handle the same extensive range of enantiomers that can be separated in capillary electrophoresis systems on an analytical scale. In a system containing four separation compartments, α-cyclodextrin was used as a chiral selector to separate D,L-tryptophan. Based on a transport model, a factorial design was used to investigate the effects of various process parameters. The results showed that the addition of methanol was of minor influence, whereas the pH had a major effect, both on the operational selectivity and on the transport number. Experiments with AgNO₃ as the background electrolyte showed that the operational selectivity had a plateau value of 1.08 at a pH ranging from 3 to 6. Because of the ease of scale-up of electrodialysis processes, this operational selectivity will allow for the separation of enantiomers on a large scale [39].

A pressure-driven separation process, using self-supporting cross-linked sodium alginate membranes with different swelling indices, enabled the optical resolution of α-amino acids, including the optical isomers of tryptophan and tyrosine [40]. The sodium alginate membranes were prepared by the casting and drying of sodium alginate solutions on an acryl plate, followed by cross-linking with glutaraldehyde. They were characterized with analytical methods such as Fourier transform infrared and swelling index measurements. During optical resolution with the sodium alginate membranes, the effects of experimental factors were studied, such as the concentration of the feed solutions, the operating pressure and the degree of cross-linking of the membranes. When a sodium alginate membrane with a swelling index of 80% was used, a good optical resolution of tryptophan isomers was obtained: an enantiomeric excess of 54% and a flux of 24.8 mg m⁻² h⁻¹.

Chiral activated membranes were tested for the enantioseparation of the racemic drug propranolol [41]. Polysulfone-based membranes were prepared for this purpose, using N-hexadecyl-L-hydroxyproline and L-di-n-dodecyltartrate as chiral carriers. Kinetic experiments were carried out using a membrane module with two rectangular channels separated by the membrane, which allowed for a well-defined hydrodynamics of the feed and stripping phases. The transport properties of the phase transfer reaction components through a multiphase enzyme-loaded membrane system were identified by Giomo et al. The multiphase system was of interest for the preparation of a two-separate-phase enzyme membrane reactor used for the enantioselective conversion of the racemic ester of naproxen into the corresponding S-naproxen acid. The transport
properties of the system were measured in the absence of biochemical reaction. Therefore, the overall mass transfer coefficients of the reactant (naproxen ester) and product (S-naproxen acid) through the two-separate-phase membrane system were measured using a deactivated enzyme-loaded membrane. The multiphase system of interest was composed of an organic and an aqueous phase separated by a polymeric membrane containing the immobilized enzyme. The enzyme was immobilized alone or in the presence of an oil–water emulsion, in order to either improve enzyme distribution at the o–w interface or to enhance the transport of reaction components through the membrane. This mass transfer rate through the membrane as a function of the axial velocity was evaluated. The transport performance through the membrane itself, the membrane loaded with enzyme and the membrane loaded with the enzyme in the presence of emulsion were studied [42].

The asymmetric hydrolysis of racemic ibuprofen ester catalysed by lipase is one of the most important methods for the chiral separation of ibuprofen. A special microstructure in the composite hydrophilic cellulose acetate–hydrophobic polytetrafluoroethylene membrane was designed for lipase immobilization by ultrafiltration by Wang et al. A biphasic enzymatic membrane reactor and an emulsion reaction system with free lipase were both used, and the activity, enantioselectivity and half-life of the immobilized versus free enzymes were compared. The morphology of the composite membrane and the position of the entrapment in the microstructure of the composite membrane where lipase was immobilized were observed by scanning electron microscopy (SEM). The effects of the substrate concentration, enzyme loading, reaction temperature and pH on this separation were investigated. The experimental results showed that the lipase was entrapped at the interface of the composite membrane, which is consistent with the interface of the aqueous phase and organic phases. Since the enzyme was immobilized by a new method that did not destroy the enzyme structure, it retained higher activity; the enzyme activity was more than 60% compared with the free lipase when the enzyme loading was under 1 g protein per square metre. Furthermore, the immobilized enzyme provided better chiral selectivity and a longer half-life. High enzyme activity and chiral selectivity were obtained with a substrate concentration of 0.35 M, enzyme loading of 0.7–1.0 g protein per square metre in an aqueous phase of pH 8.0 and a temperature of 40 °C [43].

Semi-interpenetrating-networks-structured chitosan–β-cyclodextrin composite membranes were prepared by Wang et al. to investigate the influence of β-cyclodextrin on permselectivity and permeate flux of chitosan composite membranes in the enantiomer separation of tryptophan racemate [44]. Diffusion selectivity, sorption selectivity, and overall permselectivity of the composite membranes toward tryptophan racemate were investigated in detail. Diffusion selectivity, compared with sorption selectivity, was found to be preponderant in the enantiomer separation process. With the increase of β-cyclodextrin polymer (β-CDP) content within the chitosan–β-cyclodextrin composite membrane, the permselectivity decreased considerably due to relatively lower complexation selectivity of β-CDP that reduced both the diffusion selectivity and the overall permselectivity. Therefore, the greater the β-CDP content within the membrane, the lower the permselectivity of the membrane; on the other hand, permeate flux was found to increase significantly as a result of the facilitated tryptophan mass transport through β-CDP within the membrane.

A membrane-based chiral separation system for the separation of racemic tryptophan solutions is developed by the covalently binding β-cyclodextrin onto the surface of commercial cellulose membranes [48]. The immobilization process was monitored by X-ray photoelectron spectroscopy. Atomic force microscopy demonstrated the evolutionary transition of membrane surface morphology before and after the cyclodextrin immobilization. Owing to their different complexations with immobilized cyclodextrin, dialysis transport experiments show d-tryptophan preferential permeability through the immobilized cyclodextrin membranes, and the enantioselectivity was 1.10. A model based on the existence of a thin chiral solution layer of amino acid at the interface between the feed solution
and the membrane was proposed. This chiral separation model was verified using the chiral separation results of racemic amino acids and binding constants of amino acids with cyclodextrin. The effect of membrane pore size on enantioselectivity was also investigated. The immobilized cyclodextrin membrane, having a molecular weight cut-off of 1000, exhibited the highest enantioselectivity to the racemic tryptophan solution.

Copolymer of 1,2-bis(2-methyl-1-triethylsiloxy-1-propenyloxy)ethane and dialdehyde was synthesized by Mukaiyama aldol polymerization using lipase as the catalyst (Scheme 25.1). The chirality of the polymer was tested by optical rotation and circular dichroism study. The membrane-forming ability of this chiral polymer was examined by casting the membrane in three different solvents – N-methyl-2-pyrilidone (NMP), dimethyl formamide and dimethyl acetamide – using the phase inversion method, and it was found that chiral polymer–NMP membranes formed more uniform and regular surface morphology, as was evident from SEM analysis. The enantioselective membranes prepared in the solvents were tested for resolution of racemic alcohol and it was found that NMP was the best solvent for obtaining the highest enantioselectivity value. It was also found that the enantioselectivity for adsorption favoured the (S)-isomer, whereas permeation favoured the (R)-isomer, which is confirmed from interpretation of the adsorption isotherm by the Langmuir model. Accordingly, the enantioselective permeation was caused by suppression of the (S)-isomer permeation. Optical resolution of (+)-trans-sobrerol was achieved by pressure-driven permeation through the membrane. The highest enantioselectivity, enantiomeric excess and permeation coefficient was obtained as 98.59%, 20.42 and 13.627 m² h⁻¹ respectively. With an increase in polymer content in the membrane, the permeation rate increased [46].

A chiral polymer from 1,2-bis(2-methyl-1-triethylsiloxy-1-propenyloxy)ethane and dialdehyde from adipoyl chloride and 4-hydroxy benzaldehyde was prepared at gram-scale level and characterized by infrared, nuclear magnetic resonance, thermogravimetric analysis, differential scanning calorimetry, optical rotation and circular dichroism study [47]. The same was used for preparation of enantioselective membrane by the phase inversion technique, and the membrane was characterized for pore size and surface morphology through SEM analysis. The enantioselective property of the membrane in the resolution of racemic compounds was studied using aqueous solution of atenolol, captopril, and the membrane was proposed. This chiral separation model was verified using the chiral separation results of racemic amino acids and binding constants of amino acids with cyclodextrin. The effect of membrane pore size on enantioselectivity was also investigated. The immobilized cyclodextrin membrane, having a molecular weight cut-off of 1000, exhibited the highest enantioselectivity to the racemic tryptophan solution.

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propranolol hydrochloride and salbutamol as feed solution. Pressure-driven membrane processes were studied under pressures of $4.84 \times 10^{-2}$, $24.22 \times 10^{-2}$ and $48.44 \times 10^{-2}$ N m$^{-2}$. The effect of feed concentration and operating pressure on membrane performance were studied differently. A solution-diffusion model was used to explain the permeation behaviour of the membrane. From this type of membrane 95% ee and 6.4 mg m$^{-2}$ h$^{-1}$ of flux were obtained.

A new process was developed by Wang et al. to separate ketoconazole (KTZ) enantiomers by membrane extraction, with the oppositely preferential recognition of hydrophobic and hydrophilic chiral selectors in organic and aqueous phases respectively. This system was established by adding hydrophobic l-isopentyl tartrate in the organic strip phase (shell side) and hydrophilic sulfobutylether-β-cyclodextrin in the aqueous feed phase (lumen side), which preferentially recognizes (+)-2R,4S-KTZ and (−)-2S,4R-KTZ respectively. The studies performed involve two enantioselective extractions in a biphasic system, where KTZ enantiomers form four complexes with sulfobutylether-β-cyclodextrin in the aqueous phase and l-isopentyl tartrate in the organic phase. The membrane was permeable to the KTZ enantiomers but non-permeable to the chiral selector molecules. Fractional chiral extraction theory, mass transfer performance of hollow-fibre membrane, enantioselectivity and some experimental conditions were investigated to optimize the separation system. A mathematical model of $I/II = 0.893e^{0.039}$ NTU for racemic KTZ separation by hollow-fibre extraction was established. The optical purity for KTZ enantiomers was up to 90% when nine hollow-fibre membrane modules of 30 cm in length in series were used [48].

Sueyoshi et al. prepared nanofibre membranes for chiral separation from chitin, which is the most abundant natural amino polysaccharide [49]. The membrane showed chiral separation ability by adopting concentration gradient as a driving force for membrane transport. In other words, the chitin nanofibre membrane selectively transported the D-isomer of glutamic acid, phenylalanine and lysine from the corresponding racemic amino acid mixtures.

Porous and nonporous supported liquid crystalline membranes were produced by impregnating porous cellulose nitrate supports with cholesteric liquid crystal materials consisting of 4-cyano-4'-pentylbiphenyl (5CB) mixed with a cholesterol-based dopant (cholesteryl oleyl carbonate (COC), cholesteryl nonanoate (CN) or cholesteryl chloride (CC)) [50]. The membranes exhibited selectivity for R-phenylglycine and R-1-phenylethanol because of increased interactions between the S enantiomers and the left-handed cholesteric phase. The selectivity of both phenylglycine and 1-phenylethanol in 5CB–CN membranes decreased with effective pore diameter, while the permeabilities increased, as expected. Phenylglycine, which is insoluble in the liquid crystal phase, exhibits no transport in the nonporous (completely filled) membranes; however, 1-phenylethanol, which is soluble in the liquid crystal phase, exhibits transport but negligible enantioselectivity. The enantioselectivity for 1-phenylethanol was higher (1.20 in 5CB–COC and 5CB–CN membranes) and the permeability was lower in the cholesteric phase than in the isotropic phase. Enantioselectivity was also higher in the 5CB–COC cholesteric phase than in the nematic phase of undoped 5CB (1.03). Enantioselectivity in the cholesteric phase of 5CB doped with CC (1.1), a dopant lacking hydrogen bonding groups, was lower than in the 5CB–COC phases. Finally, enantioselectivity increases with the dopant concentration up to a plateau value at approximately 17 mol%.

An enantioselective composite membrane was prepared by polycondensation between p-cyclodextrin on a polysulfone support and a heptane solution of 1,6-diisocyanatohexane (1,6-DCH) [51]. The flux and permselective properties of the composite membrane were studied using an aqueous solution of D,L-mandelic acid as the feed solution. The influences of a number of parameters, such as the air-drying time of the p-cyclodextrin solution on polysulfone, the time of polymerization, the operating pressure and the feed concentration of the racemate, were studied. Chemical characterization was carried out using Fourier transform infrared spectroscopy, and the
top surface/cross-section was analysed by SEM. The results showed that when using the enantioselective composite membrane for the optical resolution of the D,L-mandelic acid racemic mixture, an enantiomeric excess of over 85% could be obtained. Tian et al. thus detail for the first time how a poly (3-cyclodextrin cross-linked with 1,6-DCH)–polysulfone composite membrane can be used as an optical resolution membrane material to isolate the optical isomers of D,L-mandelic acid.

Enantioselective thin-film composite polymer membranes were prepared by interfacial co-polymerization of L-arginine with trimesoyl chloride in situ on polysulfone ultrafiltration membrane by Ingole et al. [55]. The chemical compositions of composite membranes were determined by attenuated total reflection Fourier transform infrared spectroscopy. Membranes were characterized by using SEM and atomic force microscopy. The optical resolution of α-amino acids was performed in pressure-driven separation mode. The performances of membranes were compared in terms of flux, permselectivity, enantioselectivity and separation factor. The composite membranes exhibited 64–78% separation of amino acids. The membrane permeated D-enantiomers preferentially such that enantiomeric excesses of ~92% for D-enantiomer of lysine in permeates were achieved. The corresponding separation factors were in the range 4–21. As an immediate application, this study would help in the design of more efficient, nature-inspired selective chiral membranes that are able to separate enantiomers of chiral species.

Optical resolution of racemic mixtures of arginine and alanine was performed by chiral selective nanofiltration membrane. The chiral selective layer of the membrane was prepared by interfacial polymerization of metathenylene diamine, trimesoyl chloride, and S-(−)-2-acetoxypropionyl chloride (S-2-actoxpcl) in situ on polysulfone ultrafiltration membrane. S-2-Actoxpcl consists of a chiral carbon atom that has an induced chiral environment in the membrane. The membranes were characterized by Fourier transform infrared, SEM and atomic force microscopy to establish a structure–performance relationship. The optical resolution was performed on the membrane testing module and the effect of process parameters was determined. The results indicated that the incorporation of S-2-actoxpcl made membrane chiral selective; hence, membranes performed optical resolution. The resolution capacity increased by increasing S-2-actoxpcl in polymerizing solution up to 0.03%, but any increase beyond 0.03% reduced the resolution capacity. More than 92% enantiomeric excess of the D-enantiomer was observed in the permeate of the membrane which was prepared from 0.07% trimesoyl chloride and 0.03% S-2-actoxpcl. The membrane prepared without the chain terminator exhibited less volumetric flux but more solute rejection compared with those prepared with the chain terminator. The flux of the membrane increased as the amount of the chain terminator in the reaction increased [53].

References


Material Separations by Other Membrane Processes

26.1 Carbon Nanotube Membranes

A carbon nanotube (CNT) is a material that has a six-membered ring network (graphene sheet, see Figure 26.1) formed by carbon into a single-layered or multilayered coaxial pipe form. As an allotropic form of carbon, it may be classified as a kind of fullerene. A single-layered instance is called a single-wall CNT (SWCNT), in which the diameter is around 1–10 nm and length is about 10 μm; a multilayered instance is termed a multiwall CNT (MWCNT), as shown in Figure 26.2. A two-layered instance in particular is called a double-wall CNT (DWCNT).

CNT membranes are developed by aligning CNTs; and, furthermore, aligned CNTs and polymer composites are fabricated. These unique materials are applied to various industries, such as separation technology, fuel cells, electronics and so on. In particular, many unique properties are expected in CNT membrane separation systems, such as kidney failure and ion removal (dialysis), desalination (reverse osmosis (RO) and nanofiltration (NF)), organic removal (NF), pathogen and turbidity and removal (ultrafiltration and microfiltration), volatile organic carbons removal and dehydration (per-vaporation), and CO₂ removal (gas separation).

Characteristics of CNT membranes are as follows: (1) they are chemically stable, (2) they are thermally stable, (3) they have high surface area, (4) they can facilitate immobilization in membranes, and (5) they can possibly be fabricated by self-assembly.

The geometric structure of the CNT is distributed between three kinds, as shown in Figure 26.3.

26.1.1 Fabrication of Carbon Nanotubes

CNTs are fabricated the following methods: (1) arc discharge [1–4]; (2) laser ablation [5,6]; (3) plasma torch [7,8]; (4) chemical vapour deposition (CVD) [9–11]; (5) super-growth CVD [12–28].

26.1.2 Chemical Modification of Carbon Nanotubes

CNTs can be functionalized to attain desired properties that can be used in a wide variety of applications. The two main methods of CNT functionalization are covalent and non-covalent modifications, as shown in Figure 26.4 [29].
Covalent modifications include (1) oxidation reactions [30], (2) esterification/amidation reactions [31], (3) halogenation reactions [32,33], (4) cycloaddition reactions [34-37], (5) radical addition reactions [38-41] and (6) electrophilic addition reactions [42,43]. Non-covalent modifications consist of (1) polynuclear aromatic compounds [44,45], (2) biomolecules [46-48] and (3) \(\pi-\pi\) stacking and electrostatic interactions [46].

### 26.2 Graphene Membranes

Graphene (graphite) membrane is consisted of the lamination of graphene sheets, in which it is very important that graphene sheet is planar (Figure 26.5) [49].

Figure 26.6 shows the preparation process of a graphene membrane.

1) The graphite powder of natural single crystal (particle diameter of 1–100 \(\mu\)m) is oxidized in concentrated \(\text{H}_2\text{SO}_4\) and \(\text{KMnO}_4\).
2) By irradiating with a supersonic wave the aqueous oxidized graphite solution or repeating centrifugal separation and re-dispersion of the precipitation, water molecules are infiltrated between layers and consequently a single-layered detachment is exfoliated.
3) An oxidized graphene solution in a mixture of water and aqueous organic solvent is coated on the support and a graphene membrane is prepared.
4) The prepared thin membrane is chemically reduced in hydrazine hydrate and furthermore by the vacuum heating reduction.
Figure 26.3 The geometric structure of the CNT. Source: https://ja.wikipedia.org/wiki/%E3%82%AB%E3%83%BC%E3%83%9C%E3%83%8A%E3%83%81%E3%83%A5%E3%83%BC%E3%83%96.

Figure 26.4 CNT modification chart.
26.3 Technologies of Carbon Nanotube and Graphene Membranes

26.3.1 Technology of Carbon Nanotube Membranes

26.3.1.1 Fabrication and Pore Size

Fabrication  Choi et al. prepared MWCNTs–polysulfone (PSF) blend membranes by a phase inversion process, using N-methyl-2-pyrrolidinone as a solvent and water as a coagulant [50]. Before making the blend membranes, MWCNTs were first treated with strong acid to make them well dispersed in organic solvents such as N-methyl-2-pyrrolidinone for the preparation of homogeneous MWCNTs–PSF blend solutions. The prepared MWCNTs–PSF blend membranes were then characterized using several analytical method, such as Fourier transform infrared (FTIR) spectroscopy, contact-angle goniometer, scanning electron microscopy (SEM) and permeation tests. Because of the hydrophilic MWCNTs, the surface of the MWCNTs–PSF blend membranes appeared to be more hydrophilic than just a PSF membrane. The carboxylic acid functional groups developed by the treatment with acid on the surface of the MWCNTs seemed to act to increase hydrophilicity of the blend membranes. The morphology and permeation properties of the blend membranes were also found to be dependent on the amounts of MWCNTs used. The pore size of the blend membranes increased along with the contents of MWCNTs up to 1.5%, then decreased, and at 4.0% of MWCNTs it became even smaller than PSF membrane. The PSF membrane with 4.0% of MWCNTs showed higher flux and rejection than the PSF membrane without MWCNTs.

Ornthida and Mitra [51] demonstrated that the incorporation of CNTs in the pores of a membrane can offer several advantages. A dispersion of CNTs in polyvinylidene fluoride (PVDF) was injected through a porous membrane, which immobilized the nanotubes in the pore structure. The CNTs
served as a sorbent facilitating solute exchange between the two phases, leading to enhancement of the enrichment factor by as much as 93%. The presence of CNTs also developed a diffusion barrier by sorbing solvent on its surface, which led to higher retention of the extractant within the membrane.

Membranes based on CNTs have been highlighted as an emerging technology for water purification system applications [52]. With their ultrahigh water flux and low biofouling potential, CNT membranes are believed to lack various problems encountered when using a conventional membrane separation process that requires a large amount of energy and meticulous maintenance. Although diverse types of CNT membranes have been reported, no commercialized products are available. The article by Ahn et al. reviews the proper manufacturing methods for CNT membranes and speculates on their performances. Future applications of integrated CNT membrane systems are also outlined.

A novel functionalized MWCNT (FMWCNT) immobilized polyethyleneimine–poly(amide–imide) hollow fibre membrane was designed and fabricated using an easily scalable method. Poly(amide–imide) hollow fibre was spun via phase inversion, followed by FMWCNTs immobilization via vacuum filtration before a chemical post-treatment using polyethyleneimine was applied to obtain a positively charged selective layer. The resulting membranes were evaluated in the forward osmosis (FO) process. The membrane prepared using 0.62 mg L\(^{-1}\) of MWCNTs solution showed a pure water permeability of 4.48 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) with an MgCl\(_2\) rejection of 87.8% at 1 bar. This was a 44% enhancement in water permeability without significant compromise on the salt permeability when compared with membranes without MWCNTs. In addition, FO water fluxes of membranes prepared using 0.31 and 1.25 mg L\(^{-1}\) of MWCNTs solutions were also enhanced up to 29% without compromising the solute flux in the active layer facing feed water orientation using 0.5 M MgCl\(_2\) solution as the draw solution and deionized water as the feed water. These encouraging results suggest that hollow-fibre membranes immobilized with commercial MWCNTs exhibit good potential to be further developed for applications in the FO process [53].

Zhang et al. [54] reported a simple and effective method for the preparation of high-density and aligned CNT membranes. The CNT arrays were prepared by water-assisted CVD and were subsequently pushed over and stacked into dense membranes by mechanical rolling. It was demonstrated
that various gases and liquids – including H₂, He, N₂, O₂, Ar, water, ethanol, hexane and kerosene – could effectively pass through the aligned CNT membranes. The membranes exhibited different selections on different gases, indicating that there was a separation potential for the gas mixtures. The selectivities (H₂ relative to other gases) of H₂/He, H₂/N₂, H₂/O₂ and H₂/Ar were found to be lower than that of the ideal Knudsen model. For pure water, the permeability was measured to be 3.23 ± 0.05 mL min⁻¹ cm⁻² at 1 atm, indicating that the CNT membranes were promising for applications in liquid filtration and separation.

**Pore Size** Membranes are crucial in modern industry, and both new technologies and materials need to be designed to achieve higher selectivity and performance. Exotic materials such as nanoparticles offer promising perspectives, and combining both their very high specific surface area and the possibility to incorporate them into macrostructures has already been shown to substantially increase the membrane performance. Dumee et al. report on the fabrication and engineering of metal-reinforced CNT buckypaper (BP) composites with tuneable porosity and surface pore size. A BP is an entangled mesh non-woven-like structure of nanotubes. Pure CNT BPs present both very high porosity (>90%) and specific surface area (>400 m² g⁻¹). Furthermore, their pore size is generally between 20–50 nm, making them promising candidates for various membrane and separation applications. Both electroplating and electroless plating techniques were used to plate different series of BPs and offered various degrees of success. Dumee et al. reported mainly on electroless plated gold–CNT composites. The benefit of this method resides in the versatility of the plating and the opportunity to tune both average pore size and porosity of the structure with a high degree of reproducibility. The CNT BPs were first oxidized by short UV–O₃ treatment, followed by successive immersion in different plating solutions [55].

A new approach was proposed by Yang et al. for accurate measurement of the pore sizes in a track-etched polyethylene terephthalate membrane from a nanometre scale to a submicrometre scale, which only entailed UV–visible spectrometry [56].

### 26.3.1.2 Dialysis

The obtaining of nanofunctionalized membranes is one of the newer trends for enhancing the performances of the membrane processes. In the paper by Nechifor et al., results concerning the synthesis of new polymeric–CNT composite membranes based on PSF with different types of nanotubes (SWCNTs and DWCNTs) were shown with applications in the medical field of advanced separations of heavy metal (Pb and Hg) from blood or other physiological liquids. At a maximum concentration of CNTs (5% against polymer), the maximum adsorption capacity of Pb on a membrane with SWCNTs was 49.2 mg dm⁻² and for a membrane with DWCNTs (covalent interaction) it was 56.2 mg dm⁻². A study about the dependence of adsorption capacity on the concentration of CNTs in polymers was performed. The materials were characterized by FTIR spectroscopy and SEM, and the results of haemodialysis adsorption of the heavy metals on the nanotubes surface were investigated by the atomic adsorption method [57].

Nano-modification of membrane is another recent technique used to improve membrane performance. Chan et al. investigated the influence and interaction of FMWCNTs with polyethylene glycol (PEG) as an additive on PVDF membrane. The nano-modified membranes were then characterized in terms of pure water permeation, molecular weight cut-off, contact angle and calculated pore size distributions. FTIR spectroscopy and SEM were then used to characterize the structure and morphology of the membranes. The separation properties of the membranes with respect to bovine serum albumin (BSA) retention, urea and creatinine clearances were investigated. The results revealed that the
interaction of FMWCNTs with PEG as an additive improved the performance of PVDF as a potential dialysis membrane in terms of pure water permeation, hydrophilicity retention, and urea and creatinine clearances [58].

26.3.1.3 Reverse Osmosis
Polyamide RO membranes incorporating carboxy-functionalized MWCNTs were prepared by interfacial polymerization of metathylene diamine and trimesoyl chloride. The pristine MWCNTs were pretreated with mixed acids before being modified with diisobutyl peroxide to enhance their dispersity and chemical activity. The prepared nanocomposite membranes had a 100–300 nm skin layer and the modified MWCNTs were embedded within the skin layer, which was confirmed by SEM and transmission electron microscopy (TEM). The surface of the nanocomposite membrane was shown to be more negatively charged than bare polyamide membrane. It was shown that the membrane morphology changed distinctly with an increase in the CNT loading in the membrane, leading to a significantly improved flux without sacrificing the solute rejection. Meanwhile, the nanocomposite membranes showed better antifouling and antioxidative properties than MWCNT-free polyamide membranes, suggesting that the incorporation of modified MWCNTs in membranes is effective for improving the membrane performance [59].

The electrochemical prevention and removal of CaSO₄ and CaCO₃ mineral scales on electrically conducting CNT–polyamide RO membrane was investigated [60]. Different electrical potentials were applied to the membrane surface while filtering model scaling solutions with high saturation indices. Scaling progression was monitored through flux measurements. CaCO₃ scale was efficiently removed from the membrane surface through the intermittent application of a 2.5 V potential to the membrane surface, when the membrane acted as an anode. Water oxidation at the anode, which led to proton formation, resulted in the dissolution of deposited CaCO₃ crystals. CaSO₄ scale formation was significantly retarded through the continuous application of 1.5 V DC to the membrane surface, when the membrane was operated as an anode. The continuous application of a sufficient electrical potential to the membrane surface leads to the formation of a thick layer of counter-ions along the membrane surface that pushed CaSO₄ crystal formation away from the membrane surface, allowing the crystals formed to be carried away by the crossflow. Duan et al. developed a simple model, based on a modified Poisson–Boltzmann equation which qualitatively explained their observed experimental results.

Polyamide RO membranes with CNTs were prepared by Kim et al. by interfacial polymerization using trimesoyl chloride solutions in n-hexane and aqueous solutions of m-phenylenediamine containing functionalized CNTs [61]. The functionalized CNTs were prepared by the reactions of pristine CNTs with an acid mixture (sulfuric acid and nitric acid of 3 : 1 volume ratio) by varying amounts of acid, reaction temperature and reaction time. CNTs prepared by an optimized reaction condition were found to be well dispersed in the polyamide layer, which was confirmed from atomic force microscopy (AFM), SEM and Raman spectroscopy studies. The polyamide RO membranes containing well-dispersed CNTs exhibited larger water flux values than polyamide membrane prepared without any CNTs, although the salt rejection values of these membranes were close. Furthermore, the durability and chemical resistance against NaCl solutions of the membranes containing CNTs were found to be improved compared with those of the membrane without CNTs. The high membrane performance (high water flux and salt rejection) and the improved stability of the polyamide membranes containing CNTs were ascribed to the hydrophobic nanochannels of CNTs and well-dispersed states in the polyamide layers formed through the interactions between CNTs and polyamide in the active layers.
The use of solvents in desalination processes limits the use of certain materials in the construction of the RO membranes. Therefore, research effort has now focused on improving new materials. In particular, nanostructured materials will probably form the basis for new RO membrane materials. Rodriguez-Calvo et al. reviewed the new materials used for the construction of RO membranes, highlighting the advantages and disadvantages that each of them gives to the desalination process. Firstly, inorganic membranes, made mainly from zeolites, offer higher tolerance to a variety of feed waters and harsh cleaning methods. Secondly, two carbon-derived materials as CNTs exhibited high permeability and high rejection rate, and graphene had high breaking strength and impermeability to molecules of small standard gases. Finally, the novel concept of mixed matrix membranes (MMMs), which combine organic and inorganic materials and the benefits of each one, was discussed [62].

Aromatic polyamide membranes, which are prepared by interfacial polymerization of \( m \)-phenylene diamine in water solution and trimesoyl chloride in organic solution, have been widely used as RO membranes for desalination of seawater [63]. However, it has been pointed out that polyamide RO membranes have weak resistance to chlorine, causing deteriorated separation performance. In the study by Park et al., nanocomposite RO membranes containing MWCNTs were developed to enhance the chlorine resistance of polyamide membranes. The resulting membranes were analysed and tested to see the desalination performance. Nonionic surfactant (Triton-X-100) was used in the interfacial polymerization of organic–inorganic nanocomposite RO membranes to improve the dispersion of MWCNTs in the polymer matrix. SEM images and X-ray diffraction (XRD) spectra confirmed that MWCNTs were uniformly distributed in the polymer matrix. When 0.1–1 wt% of MWCNTs were added to polyamide RO membranes, chlorine resistance was measurably improved compared with the conventional polyamide membranes.

As water molecules permeate ultrafast through CNTs, many studies have prepared CNT-based membranes for water purification as well as desalination, particularly focusing on high flux membranes [64]. Among them, vertically aligned CNT membranes with ultrahigh water flux have been successfully demonstrated for fundamental studies, but they lack scalability for bulk production and sufficiently high salt rejection. CNTs embedded in polymeric desalination membranes – that is, polyamide thin-film composite (TFC) membranes – can improve water flux without any loss of salt rejection. This improved flux is achieved by enhancing the dispersion properties of CNTs in diamine aqueous solution and also by using cap-opened CNTs. Hydrophilic CNTs were prepared by wrapping CNT walls via bio-inspired surface modification using dopamine solution. Cap-opening of pristine CNTs was performed by using a thermo-oxidative process. As a result, hydrophilic, cap-opened CNTs-embedded polyamide TFC membranes were successfully prepared, showing much higher water flux than pristine polyamide TFC membrane. On the other hand, less-disperse, less cap-opened CNT-embedded TFC membranes do not show any flux improvement and rather lead to lower salt rejection properties.

26.3.1.4 Nanofiltration

Vatanpour et al. [65] reported the preparation, characterization and evaluation of performance and antifouling properties of mixed matrix NF membranes. The membranes were prepared by acid-oxidized MWCNTs embedded in polyethersulfone (PES) as matrix polymer. The hydrophilicity of the membrane was enhanced by blending MWCNTs due to migration of FMWCNTs to membrane surface during the phase inversion process. The morphology studies of the prepared NF membranes by SEM showed that very large macro-voids appeared in the sublayer by addition of a low amount of FMWCNTs, leading to an increase of pure water flux. By using the proper amount of modified MWCNTs, it was possible to increase both the flux and the salt rejection of the membranes. In this work, the effect of CNT–polymer membrane for fouling minimization was presented. The antifouling
performance of membranes fouled by BSA was characterized by means of measuring the pure water flux recovery. The results indicated that the surface roughness of membranes plays an important role in antifouling resistance of MWCNT membranes. The membrane with lower roughness (0.04 wt% MWCNT–PES) presented superior antifouling properties. The salt retention by the negatively charged MWCNT embedded membrane indicated a Donnan exclusion mechanism. The salt retention sequence for 0.04 wt% MWCNT was Na₂SO₄ (75%) > MgSO₄ (42%) > NaCl (17%) after 60 min filtration.

PES–CNT-based MMMs were prepared by the phase inversion method for NF application by Wang et al. Carboxylated CNTs with different diameter and concentration were incorporated into the polymer matrix to enhance the performances of the NF membranes [66]. The PES–CNTs membranes prepared were characterized and evaluated in terms of membrane morphology, structure, surface properties and separation performances. Two types of CNTs with different diameters (20 nm and 40 nm, identified as CNT1 and CNT2 respectively) were chosen to investigate the effect of CNT diameter on membrane performances. The effect of CNT concentrations (from 0.01 to 1 wt%) was also tested by introduction of CNT2 in the MMMs. As a result, the MMMs embedded with CNT1 achieved better NF performances. When CNT2 concentration reached 0.1 wt%, the PES–CNT2 membranes obtained the highest water flux (38.91 L m⁻² h⁻¹) and Na₂SO₄ rejection (87.25%) at 4 bar. The solute rejection was in the sequence of \( R(\text{Na}_2\text{SO}_4) > R(\text{MgSO}_4) > R(\text{NaCl}) \).

MWCNTs coated by anatase titanium dioxide (TiO₂) nanoparticles were synthesized via the precipitation of TiCl₄ precursor on the acid-oxidized MWCNTs and used in preparation of nanocomposite PES membranes. The effect of embedding TiO₂-coated MWCNTs in PES matrix on membrane morphology, properties and antifouling was presented by Vatanpour et al. and the results obtained were compared with the prepared oxidized MWCNTs and TiO₂ blended PES membranes [67]. XRD and TEM analyses showed that the TiO₂ formed on the surface of MWCNTs had an anatase nanostructure with size in the range of 10–20 nm. The SEM images displayed a finger-like and porous structure for all NF membranes and showed that agglomeration of TiO₂-coated MWCNTs was very low. Contact-angle measurements indicated that coating of TiO₂ nanoparticles on the surface of oxidized MWCNTs improved the hydrophilicity of the membranes obtained. The pure water flux of the blend membranes increased with the content of TiO₂-coated MWCNTs. Fouling resistances of membranes evaluated by whey solution filtration revealed that 0.1 wt% TiO₂-coated MWCNT membrane had the best antifouling properties due to its lowest surface roughness and synergistic photocatalytic activity induced by incorporated nanoparticles.

Madaeni et al. [68] fabricated a novel superhydrophobic NF membrane by deposition of MWCNTs on the surface of a PVDF microfiltration membrane followed by polydimethylsiloxane (PDMS) coating. The superhydrophobic property of the membrane surface diminishes interaction between the feed water solution and membrane surface. This causes a reduction in the fouling tendency and self-cleaning characteristic. The influences of two surfactants, Triton X-100 and sodium dodecyl sulfate (SDS), as dispersing agents of MWCNTs and the concentration of PDMS coating solution on the membrane permeation flux, morphology and antifouling performance were investigated. The membrane structure and characteristic were analysed using AFM, SEM, contact angle and salt rejection measurements. The pure water flux of the membrane prepared with Triton X-100 was high compared with the SDS-dispersed MWCNTs due to low dispersing capability of SDS surfactant and pore blocking of the membrane with agglomerated MWCNTs. The pure water flux was reduced by increasing the concentration of PDMS. SEM images showed that, at low concentration of PDMS, MWCNTs are almost vertically oriented on the surface of NF membranes and reasonably coated with a PDMS layer. The salt retention sequence was \( R(\text{Na}_2\text{SO}_4) > R(\text{MgSO}_4) > R(\text{NaCl}) \). Static adsorption and
fouling resistances were elucidated using whey as a foulant. The results revealed that the flux recovery ratio for a membrane coated with 5 wt% PDMS was 82%. This showed that the fabricated superhydrophobic NF membrane possessed a superior antibiofouling property.

26.3.1.5 Ultrafiltration
MWCNTs were carboxylated by a chemical method. Poly(phenylene sulfone) (PPSU), MWCNT and functionalized (carboxylated) MWCNT–PPSU blend membranes were synthesized via the phase inversion method. The resultant membranes were then characterized by attenuated total reflectance FTIR spectroscopy, SEM, AFM and contact angle. The FMWCNT blend membranes appeared to be more hydrophilic, with higher pure water flux than did the pure PPSU and MWCNT–PPSU blend membranes. It was also found that the presence of MWCNTs in the blend membranes was an important factor affecting the morphology and permeation properties of the membranes. Model protein rejection experiments were carried out using trypsin (20 kDa), pepsin (35 kDa), egg albumin (45 kDa) and BSA (69 kDa) under identical operational conditions employing both PPSU and blend membranes. The membranes were also subjected to the determination of molecular weight cut-off using different molecular weights of proteins. During trypsin ultrafiltration, PPSU–MWCNT and PPSU–FMWCNT membranes showed a slower flux decline rate than did the PPSU membrane [69].

Novel ultrafiltration membranes were prepared by incorporating MWCNTs into a matrix of brominated polyphenylene oxide (BPPO) and using triethanolamine (TEOA) as the cross-linking agent [70]. The membranes exhibited not only high permeability and hydrophilicity but also excellent separation performance and chemical stability. Furthermore, the water permeability increased as the weight fraction of MWCNTs increased, reaching a maximum of 487 L m⁻² h⁻¹ at 5 wt% of MWCNTs, while maintaining a 94% membrane rejection rate to egg albumin. The addition of TEOA into the BPPO–MWCNTs casting solution might result in an increase in water permeation rate of membrane if the amount of TEOA exceeded a threshold value; however, the membrane rejection rate was essentially constant despite increasing the molar fraction of TEOA in the casting solution. Using an adequate amount of MWCNTs and a proper TEOA/BPPO ratio, it is feasible to make MWCNTs–polymer ultrafiltration membranes with both high permeation flux and excellent selectivity.

MWCNTs functionalized by isocyanate and isophthaloyl chloride groups were synthesized via the reaction between carboxylated CNTs and 5-isocyanato-isophthaloyl chloride. Furthermore, blends of PSF and FMWCNTs with different composition dissolved in dimethylformamide were used to prepare ultrafiltration membranes by a classical phase inversion method. It was found that the content of FMWCNTs was an important factor influencing the morphology and permeation properties of the blend membranes. The pure water flux of the blend membranes increased with the content of FMWCNTs, up to 0.19%, and then gradually decreased. The static water contact angle of the blend membrane surface showed that the hydrophilicity of the surface increased with the content of FMWCNTs in the blend. In addition, SEM images of the blend membrane surface and cross-section showed that the average pore size and pore structure of the blend membranes changed with the content of FMWCNTs up to 0.19%, and after that the average pore size decreased. Finally, the protein adsorption performance of membrane indicated that MWCNT content suppressed the adsorption of protein on the membrane, and thus alleviated membrane fouling [71].

26.3.1.6 Microfiltration
Pharmaceuticals and personal care products (PPCPs) have been widely used in modern society and persistently released into aquatic environments. Energy-efficient technologies are in immediate need to control PPCPs pollution. Nanocomposite membranes containing SWCNTs and MWCNTs were fabricated in this study and used in the filtration of triclosan (TCS), acetaminophen (AAP), and
ibuprofen (IBU) to determine the capabilities and mechanisms of PPCPs removal. The removals ranged from approximately 10–95%, and increased with increasing number of aromatic rings (AAP ≈ IBU < TCS), decreasing surface oxygen content (oxidized MWCNT < MWCNT), increasing specific surface area (MWCNT < SWCNT), and elimination of natural organic matter. Also, variations of solution pH from 4 to 10 influenced PPCPs removal by up to 70%; greater removals were observed with neutral PPCP molecules than with ions due to reduced electrostatic repulsion (TCS and IBU) or formation of hydrogen bonds (AAP). These results suggest that the capabilities of CNT membranes in removing PPCPs became high when strong adsorption existed due to favourable PPCPs–CNT interactions. Future study is warranted to identify and strength CNT–PPCPs interactions in order to enhance the efficiency of CNT composite membranes used for PPCPs removal [72].

Disposal and penetration of CNTs into the environment have raised increasing concerns over the years. In this study, a laboratory-scale electro-microfiltration (EMF) was used to treat water containing SWCNTs and MWCNTs. The goal was to examine and compare the performance during EMF of SWCNTs and MWCNTs. The results showed that the initial flux was increased as the applied electrical voltage increased. At an applied pressure of 49 kPa, the final flux was comparable to pure water flux when the applied electrical field strength was greater than the critical electrical field strength. In addition, dissolved organic carbon (DOC) removal efficiency increased as the electrical voltage increased. Owing to high convective transport of organic matter toward the membrane at 98 kPa, a decrease in DOC removal efficiency with increasing electrical field strength was observed. Overall, the fluxes and DOC removal efficiencies for EMF of SWCNTs and MWCNTs were not significantly different with a 95% confidence [73].

26.3.1.7 Gas Permeation
Theoretical work by Sholl and co-workers [74] predicted that CNTs, if used as membranes, have flux/selecitivity properties that far exceed those of any other known inorganic or organic material. To verify that prediction, Marand et al. [75] fabricated nanocomposite membranes consisting of SWCNTs embedded in a poly(ime siloxane) copolymer and evaluated their transport properties. While the siloxane segment enhanced the interfacial contact, the polyimide component imparted mechanical integrity. A poly(ime siloxane) was synthesized using an aromatic dianhydride, an aromatic diamine and amine-terminated PDMS for the siloxane block. The weight per cent of PDMS was determined to be 41 using 1H nuclear magnetic resonance. Permeability measurements of He showed drops in permeability with the addition on close-ended CNTs. This large drop in permeability of He suggests that the copolymer adhered well to the CNTs and that the CNT MMMs prepared were defect free. However, the permeability of O2, N2 and CH4 increased in proportion to the amount of open-ended CNTs in the polymer matrix. This suggested that CNTs offer an attractive additive for universally enhancing the gas permeability of polymers.

Novel nanocomposite membranes containing SWCNTs inside a PSF matrix were prepared and characterized by Kim et al. The CNTs were functionalized with long chain alkyl amines to facilitate dispersion in the polymer. Both permeabilities and diffusivities of the membranes increased with increasing weight fraction of CNTs at 4 atm. Experimental sorption isotherms of H2, O2, CH4 and CO2 were consistent with isotherms predicted by atomistic simulations. Comparison of CO2 adsorption of closed and open nanotubes with simulations of closed and partially open CNT bundles suggested that high-pressure carbon monoxide nanotubes are approximately 47% open [76].

Porous CNTs, which are SWCNTs having tailored pores in their sidewalls, are proposed as potential membrane materials for separating gas mixtures with high selectivity and high permeance. Johnson and co-workers [77] presented both quantum mechanical calculations and classical statistical mechanical calculations with empirical potentials showing that porous CNTs having the correct pore
size can very effectively separate mixtures of H₂/CH₄ and also of CO₂/CH₄. In each of these mixtures, CH₄ is effectively prevented from entering the pore due to size exclusion. These porous CNTs could be used in mixed matrix polymer membranes to increase both the permeance and the selectivity for targeted gas mixtures.

The synergistic combinations of organic polymers for separation applications with inorganic substances such as MWCNTs have resulted in a new class of membrane material called MMM for the separation of CO₂/CH₄ gases. MMM-incorporated FMWCNTs were fabricated by the solution casting method, in which the FMWCNTs were embedded into the polyimide membrane and the resulting membranes were characterized. The effect of nominal MWCNTs content between 0.5 and 1.0 wt% on the gas separation properties was investigated. The MMMs showed 100% enhancement for the selectivity of CO₂/CH₄ compared with the corresponding neat polymer membrane. This new class of MMM has the ability to separate gases at the molecular level and has the potential to ultimately reduce the energy consumed in present-day separation operations. Sanip et al. showed that addition of CNTs to polymeric membranes improved separation properties of the membranes to a certain extent [78].

Khan et al. [79] reported on the gas transport behaviour of MMMs which were prepared from MWCNTs and dispersed within polymers of intrinsic microporosity (PIM-1) matrix. The MWCNTs were chemically functionalized with PEG for a better dispersion in the polymer matrix. MMM-incorporating FMWCNTs were fabricated by dip-coating method using microporous polyacrylonitrile membrane as a support and were characterized for gas separation performance. Gas permeation measurements show that MMM incorporated with pristine MWCNTs or FMWCNTs exhibited improved gas separation performance compared with pure PIM-1. The MMM FMWCNTs showed better performance in terms of permeance and selectivity in comparison with pristine MWCNTs. The gas permeances of the derived MMM were increased to approximately 50% without sacrificing the selectivity at 2 wt% of FMWCNTs’ loading. The PEG groups on the MWCNTs had strong interaction with CO₂ which increased the solubility of polar gas and limited the solubility of nonpolar gas, which is advantageous for CO₂/N₂ selectivity. The addition of FMWCNTs inside the polymer matrix also improved the long-term gas transport stability of MMM in comparison with PIM-1. The high permeance, selectivity and long-term stability of the fabricated MMM suggested that the reported approach can be utilized in practical gas separation technology.

26.3.1.8 Pervaporation
Ornthida and Mitra [80] reported the development of novel CNT immobilized composite membranes for pervaporative removal of organics from an aqueous matrix. The nanotubes were immobilized into the pores of a composite, where they served as sorption sites that provided additional pathways for enhanced solute transport, affecting both the partitioning and diffusion through the membrane. Depending upon the process conditions, the enhancement in organic removal and mass transfer rates were higher by 108% and 95% respectively. The CNT immobilized composite membranes demonstrated several advantages, including enhanced recovery at low concentrations, lower temperatures and higher flow rates. Overall, these led to more energy-efficient processes.

Novel poly(vinyl alcohol) (PVA)–CNT hybrid membranes were prepared and CNTs were dispersed by using β-cyclodextrin (β-CD) [81]. These hybrid membranes were characterized by TEM, SEM and dynamic mechanical analysis. Both pure PVA and β-CD–CNT–PVA hybrid membranes are uniform, and these hybrid membranes exhibited significant improvement in Young’s modulus and thermal stability compared with pure PVA and β-CD–PVA membranes. These membranes were applied to
pervaporation separation of benzene–cyclohexane mixtures and showed excellent pervaporation properties. The permeation flux of benzene could be 61.0 g m\(^{-2}\) h\(^{-1}\) and separation factor could be 41.2, which are above the upper bound trade-off curve summarized by Lue and Peng. The effects of \(\beta\)-CD–CNT content, operating temperature and feed flow rate on pervaporation properties were also investigated.

Poly(sodium 4-styrenesulfonate) (PSS)-wrapped MWCNTs were incorporated into PVA solution for the preparation of PVA–MWCNTs–PSS nanocomposite membranes. According to field-emission SEM observations, wrapping MWCNTs with PSS leads to better dispersion of the MWCNTs in the polymer matrix. The membrane performances were tested in the pervaporation process for the dehydration of isopropanol. Upon addition of 0–3 wt% MWCNTs–PSS to the PVA matrix, the permeance decreased, whereas the selectivity increased. For example, the water permeance decreased from 4200.8 to 3243.9 GPU, and the selectivity increased from 39.8 to 249.4 when the MWCNTs–PSS content was increased from 0 to 3 wt%. The estimated permeation and diffusion parameters show that the prepared membranes provide high separation performance for water–isopropanol mixtures [82].

New polymer nanocomposites consist of poly(phenylene isophthalamide) (PA) modified by CNTs were obtained by the solid-state interaction method to prepare dense membranes [83]. The investigation of the PA–CNT nanocomposites was made by Raman spectroscopy. The morphology of the dense membrane was analysed by SEM. The transport properties of the dense polyamide membranes modified by 2 and 5 wt% CNTs were studied in pervaporation of methanol–methyl tert-butyl ether mixture. It was shown that the selectivity with respect to methanol and permeability were the highest for membranes containing 2 wt% CNTs as compared to membranes of pure PA and containing 5 wt% CNTs. To analyse transport properties, sorption tests and contact-angle measurements were employed.

Nanocomposites are endowed with the ability to exhibit properties that substantially differ from those of the neat polymer. They tend to be useful for molecular separations, including chemical separation and bioseparation. Novel nanocomposite membranes were prepared by Sudhakar et al. through the induction of MWCNTs into chitosan biopolymer. To further explore the intrinsic correlation between pervaporation performance and free volume characteristics, a molecular dynamics simulation was first performed, in order to qualitatively analyse the contribution of MWCNT incorporation on improving free-volume characteristics of the nanocomposite membranes. Second, the pervaporation performance of chitosan–MWCNT nanocomposite membranes was evaluated with respect to permeation flux and selectivity under varying operating conditions. The membranes cross-linked with glutaraldehyde were tested for the separation of an isopropanol–water azeotropic mixture (87.5% isopropanol) at 30 °C and found to exhibit permeation flux and selectivity of 0.09 kg m\(^{-2}\) h\(^{-1}\) and 55.8 respectively for neat chitosan polymer. The corresponding values for chitosan with 0.4% MWCNTs incorporated were observed to be 0.50 kg m\(^{-2}\) h\(^{-1}\) and 296.2 respectively. To further explain the simultaneous increase of permeation flux and selectivity, the membranes were characterized by FTIR spectroscopy, XRD, SEM and thermogravimetric analysis [84].

26.3.1.9  Forward Osmosis

The FO process has attracted increasing interest because of its potential applications for low-energy desalination. However, the internal concentration polarization has been considered as one of the key issues that can significantly reduce the water flux across the FO membrane. Wang et al. reported the preparation of PES–MWCNT substrate for the formation of a high-performance FO membrane.
Nanocomposite MWCNT–PES substrates were obtained by dispersing carboxylated MWCNTs within PES via solution blending and a subsequent phase inversion process. The FO membranes were then prepared by depositing a polyamide active layer in situ on the MWCNT–PES substrate with a finger-like macrovoid structure. The influence of addition of MWCNTs on morphology and properties of substrates and final FO membranes was systematically investigated. The results showed that the performance of the FO membranes with MWCNT–PES nanocomposite substrates was better than that of the commercial membranes. Furthermore, the tensile strength of the substrate with MWCNTs was also greater than that of the neat PES. This work indicates that the FO membranes prepared from MWCNT–PES substrates are promising for practical FO applications [85].

As noted earlier, a novel FMWCNT immobilized polyethylenimine–poly(amide–imide) hollow fibre membrane was designed and fabricated using an easily scalable method [53]. PAI hollow fibre was spun via phase inversion, followed by functionalized MWCNTs immobilization via vacuum filtration before a chemical post-treatment using polyethylenimine was applied to obtain a positively charged selective layer. The resulting membranes were evaluated in the FO process. The membrane prepared using a 0.62 mg L$^{-1}$ of MWCNTs solution shows a pure water permeability of 4.48 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ with an MgCl$_2$ rejection of 87.8% at 1 bar. This is a 44% enhancement in water permeability without significant compromise on the salt permeability when compared with membranes without MWCNTs. In addition, FO water flux of membranes prepared using 0.31 and 1.25 mg L$^{-1}$ of MWCNTs solutions have also been enhanced up to 29% without compromising the solute flux in the active layer facing feed water orientation using 0.5 M MgCl$_2$ solution as the draw solution and deionized water as the feed water. These encouraging results suggest that hollow-fibre membranes immobilized with commercial MWCNTs exhibit good potential to be further developed for applications in the FO process.

Novel thin-film nanocomposite (TFN) membranes were synthesized by interfacial polymerization for the FO application. Amine FMWCNTs were used as additive in aqueous solution of 1,3-phenylendiamine to enhance the FO membranes’ performance. Different concentrations of FMWCNTs (0.01, 0.05 and 0.1 wt%) were added to the aqueous solution. The fabricated TFN membranes were characterized in terms of membrane structure and surface properties, separation properties and FO performance and subsequently compared with traditional TFC membrane. The surface hydrophilicity of TFN membranes was improved with increasing FMWCNTs concentration in the aqueous solution. The morphological studies showed that the incorporation of FMWCNTs significantly changed the surface properties of modified membranes. The FO performance was evaluated using 10 mM NaCl solution as feed solution along with 2 M NaCl solution as draw solution in both orientations. The TFN membranes exhibited high water permeability and acceptable salt rejection in the range of 0.01–0.1 wt% FMWCNTs loading in comparison with TFC membrane. The most permeable TFN had a water flux (95.7 L m$^{-2}$ h$^{-1}$) nearly 160% higher than TFC membrane, which represents an excellent improvement in FO membranes [86].

26.3.1.10 Membrane Distillation

New technologies are required to improve desalination efficiency and increase water treatment capacities. One promising low energy technique to produce potable water from either sea or sewage water is membrane distillation (MD). However, to be competitive with other desalination processes, membranes need to be designed specifically for the MD process requirements. Dumée et al. reported on the design of CNT-based composite material membranes for direct contact MD (DCMD). The membranes were characterized and tested in a DCMD set-up under different feed temperatures and test conditions. The composite CNT structures showed significantly improved performance compared with their pure self-supporting CNT counterparts. The best composite CNT membranes gave
permeabilities as high as $3.3 \times 10^{-12} \text{ kg m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ with an average salt rejection of 95% and lifespan of up to 39 h of continuous testing, making them highly promising candidates for DCMD [87].

CNT-enhanced MD is presented by Gethard et al. as a novel waste concentration method that also generates pure water. In a CNT-immobilized membrane, the CNTs serve as sorbent sites and provide an additional pathway for enhanced water vapour transport. The enrichment effect and mass transfer coefficients using CNT-immobilized membrane were as much as 421% and 543% respectively greater than in membranes without the nanotubes. Compared with the original water, the purified water contained less than 10% of residual organics [88].

Self-supporting BP membranes were processed from CVD-grown CNTs and coated with a thin layer of poly(tetrafluoroethylene) to enhance their hydrophobicity and improve their mechanical stability over time, without drastically changing their average pore size and porosity. Contact angles and bubble-point pressure were respectively increased by 23% and 28%. After coating, the membranes were tested in a DCMD set-up at various feed temperatures with 35 g L$^{-1}$ NaCl feed solution, and coated samples exhibited improved lifespan and water vapour permeability at salt rejection higher than 99%. The BP membranes were also compared with commercial poly(tetrafluoroethylene) membranes of similar properties [89].

CNT-enhanced MD is presented for water desalination by Gethard et al., who demonstrated that the immobilization of the CNTs in the pores of a hydrophobic membrane favourably alter the water–membrane interactions to promote vapour permeability while preventing liquid penetration into the membrane pores. For a salt concentration of 34 000 mg L$^{-1}$ and at 80 °C, the nanotube incorporation led to 1.85 and 15 times increase in flux and salt reduction respectively [90].

26.3.1.11 Membrane Reactor and Membrane Contactor

**Membrane Reactor** Composite porous PSF–CNT membranes were prepared by Voicu et al. by dispersing CNTs into a PSF solution followed by the membrane formation by a phase inversion–immersion precipitation technique. The CNTs with amino groups on the surface were functionalized with different enzymes (carbonic anhydrase, invertase, diastase) using cyanuric chloride as linker between enzyme and CNT. The composite membrane was used as a membrane reactor for a better dispersion of CNTs and access to reaction centres. The membrane also facilitated the transport of enzymes to active CNTs centres for functionalization (amino groups). The functionalized CNTs were isolated by dissolving the membranes after the end of reaction. CNTs with covalent immobilized enzymes were used for biosensors fabrications. The membranes obtained were characterized by SEM, thermal analysis, FTIR spectroscopy and nuclear magnetic resonance, and functionalized CNTs were characterized by FTIR spectroscopy [91].

**Membrane Contactor** The large interest in nanostructures results from their numerous potential applications in various areas such as biomedical sciences, composite materials, electronics, optics, magnetism, energy storage and electrochemistry. The review by Charcosset et al. deals with the preparation of nanomaterials, including nanotubes, nanowires and nanoparticles, on the basis of two processes using membranes as shaping tools: the membrane template method and the membrane contactor. They focus on a description of the types of membranes and of the synthesis techniques used to produce a large variety of nanomaterials in terms of morphology and chemical composition. In the membrane template method, a nanoporous membrane with oriented nanochannels is used as a mould (hard template) and filled with the desired material or precursors. Subsequently, the membrane is removed to generate a panel of desired nanostructures (nanotubes or nanowires) with a size-replication effect. The spatial distribution of the ensuing nano-objects is governed by the pore distribution in the starting membrane. In the second process, the membrane contactor, a first solution flows
tangentially to the membrane surface and then mixes/reacts with a second solution coming from the membrane pores. Using this technique, polymeric nanoparticles, solid lipid nanoparticles and nanocrystals have been prepared. Selected examples were presented [92].

26.3.2 Technologies of Graphene Membranes

26.3.2.1 Dialysis

Haemodialysis is one of the most commonly used treatments for patients suffering from irrecoverable kidney damage. Mohan and co-workers [93] investigated poly(ether imide) MMMs as a potential candidate for haemodialysis applications due to their efficient clearance and high biocompatibility. Graphene oxide (GO) was synthesized by the modified Hummers’ method and was then confirmed by XRD spectroscopy, FTIR spectroscopy, Raman spectroscopy and high-resolution TEM. The GO–polyvinylpyrrolidone nanocomposite-incorporated poly(ether imide) MMMs were fabricated by a semiautomatic casting unit using the nonsolvent-induced phase separation technique. The effect of the nanocomposite loading ratio was evaluated by water content, ultrafiltration rate and porosity, which were all found to increase as the nanocomposite content increased. Cross-sectional and top surface morphology was visualized using SEM and AFM. The hydrophilicity of these membranes was in consonance with contact angle values. These MMMs demonstrated an increase in biocompatibility: reduced protein adsorption, suppressed platelet adhesion and lower complement activation. Furthermore, the prolonged blood clotting time was an indication of the heparin mimic anticoagulant properties of these membranes. The cytocompatibility results by 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-tetrazolium bromide assay and live cell/dead cell staining indicated that there was an increase in cell viability. The membranes with 0.1 wt% GO showed an excellent clearance of the model uremic toxins, namely urea, vitamin B-12 and cytochrome-c in vitro. The diffusive permeability of these membranes could be comparable to the existing commercial haemodialysis membranes. Thus, it was concluded that these membranes containing a composite of both functional nanosheets and bioactive polymers have a tremendous potential to be utilized commercially in haemodialysis modules if shown successful in further in vivo studies with an animal model.

26.3.2.2 Reverse Osmosis

Cohen-Tanugi and Grossman [94] showed that nanometre-scale pores in single-layer freestanding graphene can effectively filter NaCl salt from water. Using classical molecular dynamics, they reported the desalination performance of such membranes as a function of pore size, chemical functionalization and applied pressure. Their results indicated that the membrane’s ability to prevent the salt passage depended critically on pore diameter, with adequately sized pores allowing for water flow while blocking ions. Further, an investigation into the role of chemical functional groups bonded to the edges of graphene pores suggested that commonly occurring hydroxyl groups can roughly double the water flux thanks to their hydrophilic character. The increase in water flux comes at the expense of less consistent salt rejection performance, which they attributed to the ability of hydroxyl functional groups to substitute for water molecules in the hydration shell of the ions. Overall, their results indicated that the water permeability of this material was several orders of magnitude higher than conventional RO membranes, and that nanoporous graphene may have a valuable role to play for water purification.

By creating nanoscale pores in a layer of graphene, it could be used as an effective separation membrane due to its chemical and mechanical stability, its flexibility and, most importantly, its one-atom thickness. Theoretical studies have indicated that the performance of such membranes should be superior to state-of-the-art polymer-based filtration membranes, and experimental studies have recently begun to explore their potential. Surwade et al. show that single-layer porous graphene
can be used as a desalination membrane. Nanometre-sized pores were created in a graphene mono-
layer using an oxygen plasma etching process, which allowed the size of the pores to be tuned. The
resulting membranes exhibited a salt rejection rate of nearly 100% and rapid water transport. In par-
ticular, water fluxes of up to $10^6 \text{ g m}^{-2} \text{s}^{-1}$ at 40 °C were measured using pressure difference as a driv-
ing force, while water fluxes measured using osmotic pressure as a driving force did not exceed 70 g
m$^{-2} \text{s}^{-1} \text{atm}^{-1}$ [95].

Globally, the problem of fresh water scarcity has continued to escalate. One of the most powerful
techniques to fully secure the availability of fresh water is desalination. Searching for more efficient
and low-energy-consumption desalination processes is the highest priority on the research agenda.
Recent progress has been achieved using GO-assisted membranes in desalination applications.
GO’s abundant functional groups, including epoxide, carboxyl and hydroxyl, provide functional reactive
sites and hydrophilic properties. Its freestanding membrane, with a thickness of a few nanometres,
has been applied recently in pressurized filtration, which is an ideal candidate for the application of
desalination membranes. The multilayer GO laminates have a unique architecture and superior perfor-
ance that enable the development of novel desalination membrane technology. With good mechanical
properties, they are easily fabricated and have the ability to be industrially scaled up in the future. The review by Hegab and Zou considered the different fabrication and modification stra-
tegies for various innovative GO-assisted desalination membranes, including freestanding GO mem-
branes, GO-surface modified membranes and casted GO-incorporated membranes. Their
desalination performance and mechanism are discussed, and their future opportunities and challenges
highlighted [96].

Cohen-Tanugi and Grossman [97] examined the potential and the challenges of designing an ultra-
thin RO membrane from graphene, focusing on the role of computational methods in designing,
understanding and optimizing the relationship between atomic structure and RO performance. In
recent years, graphene has emerged as a promising material for improving the performance of RO.
Beginning at the atomic scale and extending to the RO plant scale, they review applications of com-
putational research that have explored the structure, properties and potential performance of nano-
porous graphene in the context of RO desalination.

26.3.2.3 Nanofiltration
Han et al. fabricated a sort of novel high-flux NF membrane by synergistic assembling of graphene and
MWCNTs, in which graphene played the role of molecular sieving and MWCNTs expanded the inter-
layer space between neighbouring graphene sheets [98]. The MWCNT-intercalated graphene NF
membrane (G-CNTm) showed a water flux up to $11.3 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$, more than two times that
of the neat graphene NF membrane (GNm), while keeping high dye rejection (>99% for direct yellow
and >96% methyl orange). The G-CNTm also showed good rejection ratio for salt ions (i.e. 83.5% for
Na$_2$SO$_4$, 51.4% for NaCl). Han et al. also explored the antifouling performance of G-CNTm and GNm
with BSA, sodium alginate and humic acid. Both G-CNTm and GNm possessed excellent antifouling
performance for sodium alginate and humic acid but inferior performance for BSA because of the
strong interaction between protein and graphene sheets.

Solvent-resistant NF (SRNF) is considered an emerging process capable of replacing conventional
energy-consuming methods of separating organic mixtures in diverse industrial fields. The study by
Shao et al. optimized the performance of polypyrrole (PPy) composite SRNF membranes by varying
the polymerization conditions, including the types and concentrations of oxidants and pyrrole concen-
trations, forming integral selective layers on hydrolysed polyacrylonitrile (PAN-H) support mem-
branes with better separation properties. The PAN-H support was partially hydrolysed as indicated by
the FTIR spectrum and was compatible with the PPy selective layer, as demonstrated by the apparent
lack of an interfacial phase observed in the cross-sections of the composite membranes. The PPy–PAN-H composite SRNF membrane fabricated by reacting 0.5 mol L\(^{-1}\) (NH\(_4\))\(_2\)S\(_2\)O\(_8\) and 5.0 wt% pyrrole exhibited a rose Bengal rejection of 99.2% in isopropanol, with a relatively high solvent permeance. For the first time, GO was incorporated into the PPy–PAN-H composite SRNF membrane by dispersing it into the pyrrole ethanol solution before polymerization. GO led to a significant enhancement in solvent permeance without compromising rose Bengal rejection. Compared with pure PPy–PAN-H composite SRNF membranes, the methanol, ethanol and isopropanol permeances of the GO–PPy–PAN-H membrane were approximately 945%, 635% and 302% higher respectively. In a long-term experiment, the GO–PPy–PAN-H composite SRNF membrane exhibited a constant isopropanol permeance of 1.21 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) and a rose Bengal rejection of approximately 99.0%. Therefore, the newly developed GO–PPy–PAN-H composite SRNF membranes in this study have significant potential for practical applications [99].

26.3.2.4 Ultrafiltration

Fouling of ultrafiltration membranes in oil–water separation is a long-standing issue and a major economic barrier to their use in a broad range of applications. Currently reported membranes typically show severe fouling, resulting from the strong oil adhesion on the membrane surface and/or oil penetration inside the membranes. This greatly degrades their performance and shortens service lifetime. Huang et al. used GO as a novel coating material to fabricate fully recoverable ultrafiltration membranes for antifouling oil–water separation, with the desired hierarchical surface roughness being accomplished by a facile vacuum filtration method. The combination of ultrathin, ‘water-locking’ GO coatings with the optimized hierarchical surface roughness, provided by the inherent roughness of the porous supports and the corrugation of the GO coatings, minimized underwater oil adhesion on the membrane surface. Cyclic membrane performance evaluation tests revealed approximately 100% membrane recovery by facile surface water flushing, establishing their excellent easy-to-recover capability. The novel GO functional coatings with optimized hierarchical structures may have broad applications in oil-polluted environments [100].

Flat-sheet ultrafiltration membranes with photocatalytic properties were prepared by Pastrana-Martínez et al. with lab-made TiO\(_2\) and GO–TiO\(_2\) (GOT), and also with a reference TiO\(_2\) photocatalyst from Evonik (P25) [101]. These membranes were tested in continuous operation mode for the degradation and mineralization of the pharmaceutical compound diphenhydramine and the organic dye methyl orange under both near-UV–visible and visible light irradiation. The effect of NaCl was investigated considering simulated brackish water (NaCl 0.5 g L\(^{-1}\)) and simulated seawater (NaCl 35 g L\(^{-1}\)). The results indicated that the membranes prepared with the GOT composite (M-GOT) exhibited the highest photocatalytic activity, outperforming those prepared with bare TiO\(_2\) (M-TiO\(_2\)) and P25 (M-P25), both inactive under visible light illumination. The best performance of M-GOT may be due to the lower band-gap energy (2.9 eV) of GOT. In general, the permeate flux was also higher for M-GOT probably due to a combined effect of its highest photocatalytic activity, highest hydrophilicity (contact angles of 11°, 17° and 18° for M-GOT, M-TiO\(_2\) and M-P25 respectively) and higher porosity (71%). The presence of NaCl had a detrimental effect on the efficiency of the membranes, since chloride anions can act as hole and hydroxyl radical scavengers, but it did not affect the catalytic stability of these membranes. A hierarchically ordered membrane was also prepared by intercalating a freestanding GO membrane in the structure of the M-GOT membrane. The results showed considerably higher pollutant removal in darkness and good photocatalytic activity under near-UV–visible and visible light irradiation in continuous-mode experiments.

Functionalized GO (f-GO) was synthesized by Xu et al. by a simple covalent functionalization with 3-aminopropyltriethoxysilane [102]. The hybrid PVDF ultrafiltration membranes were then prepared
by adding different ratios of GO and f-GO via phase inversion induced by the immersion precipitation technique. Zeta potential demonstrated that covalent functionalization of GO with 3-aminopropyltriethoxysilane was favourable for its homogeneous dispersion in organic solvents. SEM images showed that very large channels appeared in top-layer by the addition of additives. Furthermore, the PVDF–f-GO membranes exhibited superior hydrophilicity, water flux, BSA flux and rejection rate compared with nascent PVDF membranes and PVDF–GO membranes. Filtration results indicated that the fouling resistance parameters declined significantly due to higher hydrophilicity of hybrid membranes. An AFM analysis with a BSA-immobilized tip revealed that the adhesion forces between membrane and foulants increased in the following order: PVDF–f-GO < PVDF–GO < PVDF. After a ternary cycle BSA solution inner fouling process, PVDF–f-GO membranes exhibited higher water flux recovery ratio values than PVDF–GO. Meanwhile, tensile strength and elongation-at-break of PVDF–f-GO membranes were increased by 69.01% and 48.38% respectively compared with those of PVDF–GO membranes, which is believed to be attributed to the strong interfacial interaction between f-GO and matrix by covalent functionalization of GO. As a result, GO functionalization will provide a promising method to fabricate graphene-based hybrid membranes with effective reinforced permeation, antifouling and mechanical performance.

26.3.2.5 Microfiltration

To achieve both high permeate flux and high oil rejection in oil–water emulsion microfiltration, a novel membrane material was synthesized by Hu et al. through GO modification on the commercial 19-channels Al2O3 ceramic microfiltration membrane [103]. TEM and X-ray photoelectron spectroscopy (XPS) measurements showed that GO had been coated on the pore surface of membrane homogeneously, and a covalent bond had been formed between GO and the Al2O3 surface. During the treatment of oil–water emulsion, the water permeation fluxes of unmodified and modified membranes were about 522 L h⁻¹ m⁻² bar⁻¹ and 667 L h⁻¹ m⁻² bar⁻¹ respectively after 150 min. The flux of the modified membrane was higher than that of the unmodified membrane by about 27.8%. The experimental results of oil–water emulsion microfiltration also demonstrated that the modified membrane exhibited higher oil rejection than the unmodified membrane. All this indicated that GO modification plays a crucial role and endows the membrane with excellent oil–water separation performance.

PVDF–GO microfiltration membranes were prepared by Zhao et al. via a phase inversion process. Taguchi experiments were designed to optimize the preparation conditions of composite membranes. PVDF content, solution type, GO content, and poly-(N-vinyl-2-pyrrolidone) content were chosen as important effecting parameters. Membrane filtration resistance was optimized by calculating the signal-to-noise ratio of the parameters. The group consisting of 12 wt% PVDF, N,N-dimethylacetamide solution type, 3 wt% GO and 5 wt% poly-(N-vinyl-2-pyrrolidone) was the optimal combination, and solution type was the most effective factor. SEM images showed that all membranes had thicker finger-like substructures. To further investigate the influence of GO on antifouling and mechanical properties, the pure PVDF and PVDF–GO composite membranes (3.0 wt%) were prepared according to the optimum conditions. The PVDF–GO composite membranes presented better antifouling performances due to the improvement of membrane hydrophilicity. The tensile strength and Young’s modulus reached values of 10.33 MPa and 148.47 MPa, which corresponded to a 55.11% and 67.14% increase respectively [104].

Membrane materials based on PVDF have received great attention recently due to their outstanding mechanical properties and chemical resistance. However, this material can easily cause a membrane fouling problem due to its hydrophobic nature. Jang et al. describe how to overcome this problematic issue by incorporating hydrophilic GO into PVDF-based membranes. PVDF nanofibre membranes
loaded with GO were prepared via an electrospinning method and the hybrid membranes were characterized for water treatment applications. GO sheets were initially prepared by Hummer’s method. The pore properties of the PVDF–GO hybrid nanofiber membrane for microfiltration applications were controlled by systematically increasing the number of nanofibre layers and thermal treatment. These resulting materials were characterized by SEM, FTIR, UV–visible, Raman spectroscopy and tensometer. The overall results showed the reliable formation of the hybrid membranes which possessed controlled pore-diameters (~0.2 μm) and narrow distribution. Based on contact-angle tests, these PVDF–GO nanofibre hybrid membranes exhibited very hydrophilic characteristics. In addition, the hybrid membrane showed up to three times higher pure water flux results and outstanding flux decline with 0.1 g L⁻¹ kaolin solutions compared with a neat PVDF nanofibre membrane. Based on all these results, it was speculated that the incorporation of GO into PVDF could also improve the anti-fouling ability of the membrane system and allow for its use as a water-treatment membrane [105].

26.3.2.6 Gas Permeation

Jiang et al. [106] investigated the permeability and selectivity of graphene sheets with designed sub-nanometre pores using first principles density functional theory calculations. They found high selectivity on the order of 10⁸ for H₂/CH₄ with a high H₂ permeance for a nitrogen-functionalized pore. They found extremely high selectivity on the order of 10²³ for H₂/CH₄ for an all-hydrogen passivated pore whose small width (at 2.5 Å) presents a formidable barrier (1.6 eV) for CH₄ but which is easily surmountable for H₂ (0.22 eV). The results suggested that these pores are far superior to traditional polymer and silica membranes, where bulk solubility and diffusivity dominate the transport of gas molecules through the material. Recent experimental investigations, using either electron beams or bottom-up synthesis to create pores in graphene, suggest that it may be possible to employ such techniques to engineer variable-sized graphene nanopores to tune selectivity and molecular diffusivity. Hence, Jiang et al. proposed using porous graphene sheets as one-atom-thin, highly efficient and highly selective membranes for gas separation. Such a pore could have a widespread impact on numerous energy and technological applications, including carbon sequestration, fuel cells and gas sensors.

Graphene is a one-atom-thick sheet of graphite comprising sp²-hybridized carbon atoms arranged in hexagonal honeycomb lattices. By removing the honeycomb lattices and forming nanopores with specific geometry and size, nanoporous graphene has been demonstrated as a very high efficiency separation membrane, due to the ultrafast molecular permeation rate for its one-atom thickness. The review by Sun et al. focuses on the recent advances in nanoporous graphene membrane for the applications of gas separation and water purification, with a major emphasis on the molecular permeation mechanisms and the advanced fabrication methods of this state-of-the-art membrane. They highlight the advanced theoretical and experimental works and discuss the gas–water molecular transport mechanisms through the graphene nanopores accompanied with theoretical models. In addition, they summarize some representative membrane fabrication methods, covering the graphene transfer to porous substrates and the pore generation. They anticipate that this review can provide a platform for understanding the current challenges to make the conceptual membrane a reality and attract increasing attention from scientists and engineers [107].

Graphene-based materials have generated tremendous interest in a wide range of research activities. A wide variety of graphene-related materials have been synthesized for potential applications in electronics, energy storage, catalysis, and gas sorption, storage, separation and sensing. Recently, gas sorption, storage and separation in porous nanocarbons and metal–organic frameworks have received increasing attention. In particular, the tuneable porosity, surface area and functionality of the lightweight and stable graphene-based materials open up great scope for those applications. Such structural features can be achieved by the design and control of the synthesis routes. Gadipelli and Guo
highlight recent progress and challenges in the syntheses of graphene-based materials with hierarchical pore structures, tuneable high surface area, chemical doping and surface functionalization for gas (H₂, CH₄, CO₂, N₂, NH₃, NO₂, H₂S, SO₂, etc.) sorption, storage and separation.

Ultrathin GO (<5 nm) membranes were prepared by Kim et al. via spin-casting onto microporous polymeric support membranes. GO membranes exhibited a highly CO₂ permeable character, which is suitable for CO₂ separation. In the presence of water vapour, high CO₂ selectivity (e.g. CO₂/H₂, CO₂/N₂ and CO₂/CH₄) was achieved by enhanced CO₂ sorption [109].

26.3.2.7 Pervaporation
Pervaporation is an important alternative membrane separation process compared with the distillation technique, and a relatively high separation factor is required to lower the energy demand. Solution-processable nanocomposite membranes prepared by incorporating functionalized graphene sheets loaded in various concentrations into the chitosan matrix were employed by Dharupaneedi et al. for the pervaporative dehydration of ethanol and isopropanol. Incorporation of functionalized graphene sheets leads to an increase of surface hydrophilicity of the chitosan membranes along with an increase in membrane tortuosity that is favourable to the selective permeation of water molecules. The nanocomposite membrane containing 2.5 wt% functionalized graphene sheets gave the highest selectivities of 7781 and 1093 for isopropanol–water and ethanol–water mixtures respectively, when tested for 10 wt% water-containing feed mixture. Membranes were characterized by wide-angle XRD, SEM, contact angle and optical profilometry techniques. The Flory–Huggins theory was employed to estimate the polymer–solvent interaction parameter. Diffusion values and Arrhenius activation energy parameters provided quantitative evidence for the observed increase in water selectivity at higher loading of functionalized graphene sheets [110].

The stability of the membrane for pervaporation separation of aromatic–aliphatic mixtures is critical for industrial applications. To improve the stability of the membrane, Wang et al. prepared a ‘pore-filling’ membrane by dynamic pressure-driven assembly of a PVA–GO nanohybrid layer onto an asymmetric polyacrylonitrile ultrafiltration membrane. The results of the swelling experiment suggested that the pore-filling structure could effectively reduce swelling of the nanohybrid membrane. Assembly of the nanohybrid membrane by molecular-level dispersion of GO in PVA led to enhanced affinity of the membrane to aromatic compounds and thus improved performance in the pervaporation of toluene–n-heptane mixtures. Moreover, the dynamic assembly process could easily be used to adjust the separation performance by controlling the pressure, filtration time, polymer and GO concentration [111].

As a new kind of two-dimensional nanomaterial, GO with two to four layers was fabricated via a modified Hummers method and used for the preparation of pervaporation membranes by Chen et al. [112]. Such GO membranes were prepared via a facile vacuum-assisted method on anodic aluminium oxide disks and applied for the dehydration of butanol. To obtain GO membranes with high performance, effects of pretreatments, including high-speed centrifugal treatment of GO dispersion and thermal treatment of GO membranes, were investigated. In addition, effects of operation conditions on the performance of GO membranes in the pervaporation process and the stability of GO membranes were also studied. It is of benefit to improve the selectivity of GO membrane by pretreatment that centrifuges the GO dispersion with 10 000 rev min⁻¹ for 40 min, which could purify the GO dispersion by removing the large-size GO sheets. As-prepared GO membrane showed high separation performance for the butanol–water system. The separation factor was 230, and the permeability was as high as 3.1 kg m⁻² h⁻¹ when the pervaporation temperature was 50 °C and the water content in feed was 10% (by mass). Meanwhile, the membrane still showed good stability for the dehydration of
butanol after running for 1800 min in the pervaporation process. GO membranes are suitable candidates for butanol dehydration via pervaporation process.

26.3.2.8  Forward Osmosis

FO, as an emerging technology for seawater desalination and wastewater reuse, has been attracting significant interest because of its energy efficiency. However, membrane fouling represents one of the major limitations for this technology, notably for TFC polyamide membranes, which are prone to chlorine attack. In the study by Soroush et al., silver nanoparticle (AgNP)-decorated GO nanosheets (as an effective biocidal material) were covalently bonded to the polyamide surface to impart improved hydrophilicity and antibacterial properties to the membrane. AgNPs were synthesized in situ by the wet chemical reduction of silver nitrate onto the surface of GO nanosheets. The formation of the composite was verified by UV-visible spectroscopy, XRD and TEM techniques. The synthesized GO–Ag nanocomposites were then covalently bonded onto the TFC polyamide membrane surface using cysteamine through an amide-forming condensation reaction. Attenuated total reflectance FTIR and XPS results confirmed the covalent bonding of the nanocomposite onto the TFC polyamide surface. Overall, the GO–Ag nanocomposite functionalized membranes exhibited super-hydrophilic properties (contact angles below 25°) and significant bacterial (Escherichia coli) inactivation (over 95% in static bacterial inactivation tests) without adversely affecting the membrane transport properties [113].

GO nanosheets were attached by Hegab et al. to the polyamide selective layer of TFC FO membranes through a poly-γ-lysine (PLL) intermediary using either layer-by-layer or hybrid (H) grafting strategies [114]. FTIR spectroscopy, zeta potential and thermogravimetric analysis confirmed the successful attachment of GO–PLL, the surface modification enhancing both the hydrophilicity and smoothness of the membrane’s surface as demonstrated by water contact angle, AFM and TEM. The biofouling resistance of the FO membranes determined using an adenosine triphosphate bioluminescence test showed a 99% reduction in surviving bacteria for GO–PLL-H modified membranes compared with pristine membrane. This antibiofouling property of the GO–PLL-H modified membrane was reflected in reduced flux decline compared with all other samples when filtering brackish water under biofouling conditions. Further, the high density and tightly bound GO nanosheets using the hybrid modification reduced the reverse solute flux compared with the pristine membrane, which reflects improved membrane selectivity. These results illustrate that the GO–PLL-H modification is a valuable addition to improve the performance of FO TFC membranes.

Reduced GO (rGO) modified graphitic carbon nitride (g-C₃N₄), CN/rGO, was synthesized as a modifier for porous PES substrate for the preparation of TFC polyamide FO membrane [115]. The effect of CN/rGO addition on the PES substrate formation was investigated using viscosity and light transmittance measurements, and the PES–CN/rGO substrates and the FO membranes were characterized by SEM, TEM, AFM, XPS and contact-angle measurements. The results indicated that the addition of CN/rGO had a significant effect on the membrane properties. The FO membrane with an appropriate amount of CN/rGO in the PES substrate exhibited excellent FO performance. The osmotic water flux with 0.5 wt% CN/rGO in the substrate of TFC membrane reached 41.4 L m⁻² h⁻¹ using 2 M NaCl as draw solution and deionized water as feed, which was around 20% greater than with the control membrane without CN/rGO. The FO performance improvement should be attributed to the modified structure of the PES substrate, and thus lower structure parameter and the reduction of internal concentration polarization. This study by Wang et al. suggests that CN/rGO is an effective additive for modifying the porous substrate for the development of FO membranes.

The preparation and performances of newly synthesized TFC FO membranes with GO-modified support layer were presented by Park et al. [116]. GO nanosheets were incorporated in the PSF to
obtain PSF–GO composite membrane support layer. Polyamide active layer was subsequently formed on the PSF–GO by interfacial polymerization to obtain the TFC-FO membranes. The results revealed that, at an optimal amount of GO addition (0.25 wt%), a PSF–GO composite support layer with favourable structural properties measured in terms of thickness, porosity and pore size can be achieved. The optimum incorporation of GO in the PSF support layer not only significantly improved water permeability but also allowed effective polyamide layer formation, in comparison to that of pure PSF support layer which had much lower water permeability. Thus, a TFC-FO membrane with high water flux (19.77 L m\(^{-2}\) h\(^{-1}\) against 6.08 L m\(^{-2}\) h\(^{-1}\) for pure PSF) and reverse flux selectivity (5.75 L g\(^{-1}\) against 3.36 L g\(^{-1}\) for pure PSF) was obtained under the active layer facing the feed solution membrane orientation. Besides the improved structural properties (reduced structural parameter S) of the support layer, enhanced support hydrophilicity also contributed to the improved water permeability of the membrane. Beyond a certain point of GO addition (≥0.5 wt%), the poor dispersion of GO in dope solution and significant structure change resulted in lower water permeation and weaker mechanical properties in support as well as FO flux/selectivity of the consequent TFC membrane. Overall, this Park et al. study suggests that GO modification of membrane supports could be a promising technique to improve the performances of TFC-FO membranes.

26.3.2.9 Membrane Distillation
The availability of fresh water is dwindling in many parts of the world, a problem that is expected to grow with populations. Desalination has been increasingly adopted over the last decades as an option, and sometimes as a necessity to overcome water shortages in many areas around the world. Today, several thermal and physical separation technologies are well established in large-scale production for domestic and industrial purposes. One promising source of potable water is the world’s virtually limitless supply of seawater, but desalination technology has been too expensive so far for widespread use. Membrane distillation is a novel thermally driven process that can be adapted effectively for water desalination or water treatment in industrial applications, owing to its potential lower energy consumption and simplicity. The general objective of the paper by Priya et al. is to contribute to the technical understanding of MD as a new technology in water treatment for both industrial and drinking water purposes, as a starting point for further improvement. Their study includes experimental and numerical investigations that highlight some aspects of the technology application and fundamental aspects. Their new approach used a different kind of filtration material: sheets of graphene, a one-atom-thick form of the element carbon, which can be far more efficient and possibly less expensive than existing desalination systems [117].

26.3.3 Comparison of Carbon Nanotubes and Graphene Membranes
Two carbon materials of graphene and SWCNTs were mixed in various compositions by Kim et al.: 0% SWCNT’s solution (graphene only), hybrid with 8, 50 and 92 wt% graphene, and 100% SWCNTs suspension. All samples were sonicated for 5 h at room temperature. Graphene–SWCNTs hybrid films were produced on cellulose mixed ester filter membranes with 0.2 μm pore size (ADVENTEC) using a vacuum filtration apparatus. After the hybrid film which was attached to the cellulose mixed ester membrane was wetted with water, it was placed on the substrate of interest and aligned as desired. The membrane was subsequently a flat plate, to keep the film flat as it dried in an oven at 90 °C for 60 min. The high surface tension of the water brings the film and the substrate into close contact as the assembly dries. The film and substrate assembly was then transferred into fresh solvent baths to remove the cellulose mixed ester membrane, leaving the thin hybrid film on the substrate [118].
MWCNTs, nano-graphene platelets and superfine powdered activated carbon (S-PAC) were comparatively evaluated by Ellerie et al. for their applicability as adsorptive coatings on microfiltration membranes [119]. The objective was to determine which materials were capable of contaminant removal while causing minimal flux reduction. Methylene blue and atrazine were the model contaminants. When applied as membrane coatings, MWCNTs had minimal retention capabilities for the model contaminants, and S-PAC had the fastest removal. The membrane coating approach was also compared with a stirred vessel configuration, in which the adsorbent was added to a stirred flask preceding the membrane cell. Direct application of the adsorbent to the membrane constituted a greater initial reduction in permeate concentrations of the model contaminants than with the stirred flask set-up. All adsorbents except S-PAC showed flux reductions less than 5% after application as thin-layer membrane coatings, and flux recovery after membrane backwashing was greater than 90% for all materials and masses tested.

Seetharaman et al. successfully prepared a series of nanocomposites containing reduced GO versus MWCNTs as filler contents anchored with sulfonated PSF (SPSF) polymer matrix by sol–gel technique with up to 0.5 wt% [120]. The influence of reduced GO compared with MWCNTs to enhance the conductivity of nanocomposite SPSF membranes for higher efficient water electrolysis applications was studied. The nanocomposite membranes were characterized using SEM, AFM, Raman spectroscopy, TEM, optical microscopy, electrical conductivity and tensile testing. The membrane porous structure, porosity and pores uniformity plus the uniformity of dispersion of mixture were investigated. The conductivity of the composite membranes for water electrolysis applications were characterized using localized probes across the surface. The results showed SPSF–GO nanocomposite membranes offer higher conductivity and improved performance than those of SPSF–MWCNT. A uniform constant and high current density of 1.39 A cm$^{-2}$ was achieved in SPSF–GO membranes at 60 °C.

Nanomaterial oxides are common formations of nanomaterials in the natural environment. Hu et al. compared the nanotoxicology of typical GO and carboxyl-SWCNTs (C-SWCNTs). The results showed that cell division of *Chlorella vulgaris* was promoted at 24 h and then inhibited at 96 h after nanomaterial exposure. At 96 h, GO and C-SWCNTs inhibited the rates of cell division by 0.08–15% and 0.8–28.3% respectively. Both GO and C-SWCNTs covered the cell surface, but the uptake percentage of C-SWCNTs was twofold higher than that of GO. C-SWCNTs induced stronger plasmolysis and mitochondrial membrane potential loss and decreased the cell viability to a greater extent than GO did. Moreover, C-SWCNT-exposed cells exhibited more starch grains and lysosome formation and higher reactive oxygen species (ROS) levels than GO-exposed cells did. Metabolomics analysis revealed significant differences in the metabolic profiles among the control, C-SWCNTs and GO groups. The metabolisms of alkanes, lysine, octadecadienoic acid and valine were associated with ROS and could be considered as new biomarkers of ROS. The nanotoxicological mechanisms involved the inhibition of fatty acid, amino acid and small molecule acid metabolisms. These findings provide new insights into the effects of GO and C-SWCNTs on cellular responses [121].

Graphene, exhibiting superior mechanical, thermal, optical and electronic properties, has attracted great interest. Considering it is one-atom-thick and there is reduced mechanical strength at grain boundaries, the fabrication of large-area suspended CVD graphene remains a challenge. Lin et al. reported the fabrication of an ultrathin free-standing CNT–graphene hybrid film, inspired by the vein-membrane structure found in nature. Such a square-centimetre-sized hybrid film can realize the overlaying of large-area single-layer CVD graphene on to a porous vein-like CNT network. The vein-membrane-like hybrid film, with graphene suspended on the CNT meshes, possesses excellent mechanical performance, optical transparency and good electrical conductivity. The ultrathin
hybrid film features an electron transparency close to 90%, which makes it an ideal gate electrode in vacuum electronics and a high-performance sample support in TEM [122].

26.3.4 Hybrids of Carbon Nanotubes and Graphene Membranes

Graphenated CNTs are a relatively new hybrid that combines graphitic foliates grown along the sidewalls of multiwalled or bamboo-style CNTs. Yu et al. [123] reported on ‘chemically bonded graphene leaves’ growing along the sidewalls of CNTs. Stoner et al. [124] described these structures as ‘graphenated CNTs’ and reported in their use for enhanced supercapacitor performance. Hsu et al. [125] further reported on similar structures formed on carbon-fibre paper, also for use in supercapacitor applications. The foliate density can vary as a function of deposition conditions (e.g. temperature and time), with the structure ranging from a few layers of graphene (<10) to being thicker, more graphite-like [126].

The fundamental advantage of an integrated graphene–CNT structure is the high surface area three-dimensional framework of the CNTs coupled with the high edge density of graphene. Graphene edges provide significantly higher charge density and reactivity than the basal plane, but they are difficult to arrange in a three-dimensional, high-volume-density geometry. CNTs are readily aligned in a high-density geometry (i.e. a vertically aligned forest) [127] but lack high charge-density surfaces – the sidewalls of the CNTs are similar to the basal plane of graphene and exhibit low charge density except where edge defects exist. Depositing a high density of graphene foliates along the length of aligned CNTs can significantly increase the total charge capacity per unit of nominal area compared with other carbon nanostructures [128] – and see https://en.wikipedia.org/wiki/Carbon_nanotube.

Graphene and CNTs are very much known as effective field emitter materials. However, field emission applications with hybrid carbon nanostructures have mostly remained elusive so far. Roy et al. [129] reported on the top assembly of a very thin layer of reduced GO by the Langmuir–Blodgett method over an MWCNTs thin film–indium tin oxide substrate to investigate the dual field-emission property of the hybrid structure. The non-functionalized type of attachment in between the hybrid carbon nanostructures mainly due to van der Waals force of attraction ensured an easy fabrication procedure. Evidence of uniform distribution of web-like networks of very thin transparent reduced GO sheets top assembled over densely packed MWCNTs thin film was found from the field-emission SEM analysis. The base layer conductivity was enhanced due to the incorporation of an MWCNTs bottom layer over indium tin oxide, and the former also additionally facilitated as emitter site pockets in between reduced GO planes. Finally, the reduced GO top assembly resulted in achieving significant improvement in current density and turn-on field in tandem with the MWCNTs bottom layer bed, making this hybrid system a much more feasible candidate for future field-emission-based device applications.

MWCNT–graphene nanoplatelet hybrid membranes with lower liquid permeability and better barrier effect compared with MWCNT membranes were successfully synthesized by vacuum filtering by Zhuo et al. [130]. Their morphologies, water permeability and pore structures were characterized by SEM and nitrogen adsorption isotherms. Furthermore, MWCNT–graphene nanoplatelet membranes were used to improve the flame retardancy of carbon-fibre-reinforced polymer (CFRP) composites, and the influence of weight percentage of graphene nanoplatelets on the permeability and flame retardancy of MWCNT–graphene nanoplatelet membranes was systematically investigated. The results showed that incorporation of MWCNT–graphene nanoplatelet membranes on CFRP composite plates can remarkably improve the flame retardancy of CFRP composites. Specifically, the incorporation of hierarchical MWCNT–graphene nanoplatelet membrane with 7.5 wt% of GNP displays a 35% reduction in the peak heat release rate (PHRR) for a CFRP composite plate with the epoxy as
matrix and a 11% reduction in PHRR compared with the incorporation of an MWCNT membrane only. A synergistic flame retarding mechanism is suggested to be attributed to these results, which includes controlling the pore size and penetrative network structure.

Sahoo et al. chemically altered GO using PEG to produce functionalized GO (f-GO). An ensemble of reduced f-GO sheets and MWCNTs, referred to as few-layer graphene–MWCNT sandwiches (GCSs), were synthesized by a catalysis-assisted CVD method and explored as the electrocatalyst support material for oxygen reduction reaction (ORR) in a proton exchange membrane fuel cell (PEMFC). Platinum nanoparticles were decorated on the carbon supports by a modified glycol reduction technique. As-prepared electrocatalysts were characterized by Raman spectroscopy, XRD and TEM. Electrocatalytic performance was evaluated by cyclic voltammetry and PEMFC measurements and compared with a commercially available Pt–C electrocatalyst. The Pt–GCS electrocatalyst gave a maximum PEMFC performance of 495 mW cm$^{-2}$ at 60 °C temperature. The improvement in the ORR activity was ascribed to the uniform dispersion of Pt nanoparticles with an optimal particle size (~3.5 nm) over a well-organized conducting catalyst support [131].

Porous Pt–graphene–MWCNT composite cathodes were fabricated for PEMFCs and their electrochemical performances were examined by Yun et al. [132]. Rod-like MWCNTs with a high aspect ratio induced a porous network structure and Pt–graphene was bound homogeneously to the porous network structure of MWCNTs in the form of a very rough surface, which facilitated simultaneous access between the Pt electrocatalyst and reactant. In addition, the porous MWCNT network enabled the Pt–graphene electrode to overcome the deficiency induced by high electrical resistance by providing an electrical pathway for the ORR. Therefore, the ORR charge transfer resistance of the Pt–graphene–MWCNT composite cathode was much smaller than that of the Pt–graphene cathode, and the maximum power density of the Pt–graphene–MWCNT composite cathode was four times higher than that of the Pt–graphene cathode.

Polyamide RO membranes containing CNTs with acidic groups (CNTa), GO, and both CNTa and GO (CNTa–GO) were prepared by Kim et al. via the interfacial polymerization of trimesoyl chloride solutions in hexane and m-phenylenediamine aqueous solutions containing carbon nanomaterials [133]. All of the polyamide membranes containing the carbon nanomaterials showed considerably improved membrane performances, such as water flux, chlorine resistance, long-term durability and mechanical properties, compared with the polyamide membrane without any of the carbon nanomaterials, due to the advantageous properties of the CNT and GO as the filler materials. The largest improvement of membrane performances was observed in the polyamide membrane with CNTa–GO (the mixture of CNTa and GO). CNTa–GO can be more well dispersed in an aqueous solution than the one-component carbon nanomaterials, such as CNTa and GO, due to the surfactant effects of GO, and then the polyamide membrane with CNTa–GO can contain the largest amount of the carbon materials among the membranes and show the best membrane performances.

References

9 Radushkevich, J.V. (1952) О Структуре Углерода, Образующегося При Термическом Разложении Оксис Углерода На Железном Контакте. Журнал Физической Химии, 26, 88–95.


Conclusions and Prospects for the Future

The ultimate aim of the separation membrane is both high permeability and high separation selectivity. To get closer to this accomplishment, the functionalization of the chemical and physical structures of the membrane materials is very important; the functionalization of the membrane structure built from membrane materials and the improvement of the conditions at the time of the membrane permeation examination are strongly required. Here, the possibilities of the functionalization of the membrane separation method and the separation membrane which were described in each chapter are prospected.

Thinning of the dense skin layer of reverse osmosis, nanofiltration and ultrafiltration membranes that have an asymmetric structure is one possibility for improving the permeability without changing the rejection characteristics. However, when this asymmetric membrane is applied to a system under a high pressure, the permeation rate is remarkably decreased by the compaction of the porous layer which is a supporting layer of membrane. On the other hand, there is a limit technically in the thinning of a surface dense layer by the solution casting wet method. When a surface dense layer and a porous layer are comprised of the same polymer materials in this membrane, the membrane formation method of the composite membrane was suggested as a method to solve the problem mentioned above.

When a dense layer and a substrate comprising a compound membrane of heterologous polymer materials is used, super-thinning of the dense layer and improvement in consolidation of the substrate can be enabled. Since this composite membrane is composed of different polymer materials, improvements of super-thinning of the dense layer and the compaction of support layer can be enabled. In addition, with this method we can obtain membranes for a specific purpose, such as chemical resistance, organic solvent resistance, oxidation resistance, bacteria resistance, contamination resistance and heat resistance. If a Langmuir–Blodgett membrane is prepared from polymerization of a monomer by the Langmuir–Blodgett method, a membrane superior in the regular cohesion structure and orientation at the molecular level is provided, and the control of high permeability and high selectivity are enabled.

When we want to separate a material by close filtering by a polymer membrane, the conformation of the polymer constituting the membrane, the microstructure of membrane, the pore size and the pore size distribution porosity must be regulated precisely. To enable this, polymer membrane materials have to be selected carefully with regard to chemical structure, molecular weight, molecular weight distribution and stereoregularity.

In a microfiltration membrane, a physical opening method using an electron beam or a laser is possible. To this end, the membranes must be prepared from heat-resistant polymer materials.
As mentioned earlier, the functionalization of such membranes gives a high permselectivity in reverse osmosis, nanofiltration, ultrafiltration, microfiltration and dialysis, and an improvement of membrane performance in the application field is expected.

In the case of pervaporation membranes, if a membrane can be designed that is not swollen by the liquid targeted for that separation, it can become a high-selectivity membrane. In addition, hydrophilic–hydrophobic asymmetric membranes and membranes that have a hydrophilic group gradient or a hydrophobic group gradient along the membrane thickness are very likely to lead to improvement in permselectivity. These membranes lead to the possibility of increasing the permeation and separation performance of organic liquid mixtures, including water–alcohol mixtures.

When an electrochemical potential gradient exists between two solutions separated by a transport membrane with a fixed carrier, an active transport rate, active transport fraction and extension to the active transport time are possible. Furthermore, improvements to both the active transport efficiency and selective transport can be obtained when an asymmetric membrane with a carrier gradient in the membrane is used and an electrochemical potential gradient exists in the system. Also, when the physicochemical conditions in both the right and left solutions are well selected in the membrane transport through a fixed carrier active transport membrane, each component is actively cross-transported from the same mixture in both the right and left solutions to the right and left chambers, and it is expected that a perfect concentration and recovery of materials can be expected.

On the other hand, the crown ether in a composite membrane from polymer–liquid crystalline–azobenzocrown ether acts as a super-selective carrier. The introduction to a polymer of a carrier having such a molecular recognition ability will enable the resolution of optical isomers, and when such membranes are applied to active transport functional membranes, there are a lot of applications, such as in the concentration of radioactive materials, recovery of expensive materials, concentration of valuable resources, dialysis for artificial kidney, and so on.

A composite membrane which fixed urease, ion-exchange resin and active carbon in a cellulose nitrate membrane decomposes urea in the membrane and the ion-exchange resin adsorbs the NH$_4^+$ ion formed and at the same time adsorbs metabolism products in the blood, such as creatinine and vitamin B$_{12}$, with high efficiency. Furthermore, this membrane has superior water permeability. Thus, an implantable artificial kidney using such an enzyme might be possible if a biocompatible compound fixed membrane can be found. The membrane is swollen by turning hydrogen peroxide to glucose by enzymatic reaction when the membrane-immobilized glucose oxidase is composited in the polymer membrane with nicotine amido groups. The swelling degree of the membrane depends on the quantity of glucose. The swelling of this membrane enables diffusion transportation of insulin, which lets glucose exist on the other side. Membranes which are compounded by such an enzyme function and the function of the polymer membrane will appear much in future.

When an enzyme is uniformly fixed in a polymer complex matrix by the ultrafiltration technique, which is one technology used in the membrane separation methods, an enzyme-immobilized membrane can be easily formed at the same time. Because this method of immobilization is a water system without organic solvents, the enzyme activity is almost spoiled. Furthermore, application development for syntheses of organic compounds is enabled by reaction not only through using an enzyme immobilization membrane as a simple reactor, but also by using a laminated enzyme membrane for some stages where several kinds of enzymes can be immobilized on different laminations, as can be seen in Figure 27.1 [1].

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$E_1$</th>
<th>$E_2$</th>
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**Figure 27.1** Model of some enzyme-immobilizing polyion complex membranes, where $E_1$–$E_4$ are different enzymes.
It is well known that polymer–metal complex and ion-exchange resins catalyse various kinds of reactions. Therefore, the appearance of functional membranes which can perform a reaction and separation at same time is strongly expected. These membranes can be easily prepared from polymer–metal complexes and ion-exchange resins. In a gas separation membrane, the development of membranes introducing a super-selective carrier for a specific gas molecule is strongly expected.

It is hoped that membrane use technologies will play an active part in many fields in this century, and it is predicted by many people that it will develop greatly. Variety and pluralistic function with the progress of civilization are required from the membrane separation technologies. We perform analysis of the basic data from conventional membrane separation technology so that we can answer these expectations more exactly, as it is important to produce the original function of that membrane. On the other hand, the appearance of materials with an epoch-making new function is also awaited eagerly. One case where this is desired is in the creation of materials that simulate a highly advanced function of a living body. Even though the development of such high-performance separation membranes is dependent on past scientific technological changes, this is not considered to be impossible.

On the other hand, when we look from the viewpoint of membrane separation technology, the following developments are strongly expected to enable a high separation efficiency in a system that conventionally had low separation performance, a separation that, in addition, was impossible conventionally:

1) New suggestions and development of the membrane separation method (such as temperature-difference-controlled evapomeation (TDEV)).
2) Construction of new separation systems by the hybridization of conventional plural membrane separation methods.
3) Construction of new separation systems by the combination of the membrane separation method and other separation technology.

In TDEV, when effective ethanol concentration from an aqueous ethanol solution is desired, we first control the aggregation state of the permeants. Then, when we use a porous membrane to get the separation and concentration performance with high efficiency, the separation and concentration are enabled based on the principle of general filtration, and both the difficult theory and explanation are not necessary. In this case, how ethanol–water aggregates change from their existing state is an important point.

It is very important that we find the key to the real important solution to the problem from such a simple, clear thought.

We expect the appearance of new membrane separation technologies with an epoch-making function to be offered for practical use in the near future.

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Figure 2.38 Electron microscope picture of a porous membrane, showing supporting layers and a selective hybrid silica top layer (thickness: 0.1 μm; pore size: few ångströms). Source: https://www.utwente.nl/tnw/im/introduction/IMintroduction/.
Figure 5.10 Tapping-mode AFM images of (a) NF-PES-10 and (b) Desal 5DL. Note that the $X$ and $Y$ dimensions are both 3 $\mu$m, while the $Z$-scale is 200 nm.
**Figure 17.6** Tentative mechanism of the separation for aqueous ethanol solutions through a dense PDMS membrane in TDEV.

**Figure 17.21** Tentative mechanism of the separation for aqueous ethanol solutions through porous PDMS membrane in TDEV.
Figure 22.5 Structure of TODGA. Three molecules of oxygen (O, red) participate in complex formation and have characteristics as three seat ligands. Control of hydrophilicity or hydrophobicity of the DGA compound is when the length of the alkyl group binding to nitrogen (N, blue) is charged.
Figure 24.2 Combined system using the ionic water-permselective membrane in an EV cell and microwave heating.
Figure 26.3 The geometric structure of the CNT. Source: https://ja.wikipedia.org/wiki/%E3%82%AB%E3%83%BC%E3%83%9C%E3%83%B3%E3%83%8A%E3%83%8E%E3%83%A5%E3%83%BC%E3%83%96.