Water Purification by Membranes: The Role of Polymer Science

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ABSTRACT: Two of the greatest challenges facing the 21st century involve providing sustainable supplies of clean water and energy, two highly interrelated resources, at affordable costs. Membrane technology is expected to continue to dominate the water purification technologies owing to its energy efficiency. However, there is a need for improved membranes that have higher flux, are more selective, are less prone to various types of fouling, and are more resistant to the chemical environment, especially chlorine, of these processes. This article summarizes the nature of the global water problem and reviews the state of the art of membrane technology. Existing deficiencies of current membranes and the opportunities to resolve them with innovative polymer chemistry and physics are identified. Extensive background is provided to help the reader understand the fundamental issues involved. © 2010 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 48: 1685–1718, 2010

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James E. McGrath received his B.S in chemistry from Siena College and an M.S and Ph.D. in Polymer Science from the University of Akron. He spent 19 years in industrial research on cellulosic fibers, synthetic rubbers, engineering thermoplastics, and polyethylene at Rayonier, Inc., Goodyear and Union Carbide. He joined the Department of Chemistry at Virginia Tech in 1975 and started an active polymer program. He has advised 110 Ph.D. students and over 80 post doctoral fellows. McGrath was Director of one of the first 11 NSF Science and Technology Center for High Performance Polymeric Adhesives and Composites, and is now a codirector of the Macromolecules and Interfaces Institute and a University Distinguished Professor of Chemistry. His fundamental chemistry has included many contributions to organolithium polymerizations, block copolymers, step polymerization, and in ring opening polymerization with a specialty in epoxides and organosiloxanes. His current focus is on polymeric materials for membranes, including fuel cells, reverse osmosis water purification, the electrolysis of water and gas separations. He has 50 patents and over 400 publications, has received numerous awards including election to the National Academy of Engineering, The ACS Applied Polymer Science and Polymer Chemistry awards and the International Award of Plastics Engineers (SPE). He remains active as one of the US and International leaders in polymer science and engineering.

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INTRODUCTION It has been widely recognized that the depletion of conventional energy resources combined with their environmental impact pose major issues for our society and that new technologies must be developed to achieve a sustainable global energy supply. It is not so well appreciated that there is an analogous situation in meeting the

world's need for water; this problem is already acute in some regions and shortages are rapidly spreading to other areas of the world. As in the case of energy, new technology is the key to current and future needs, and many companies are investing heavily to meet these challenges. The ultimate source of sustainable energy is from the sun, and there is an abundant supply of solar energy reaching the earth; the problem is capturing it in an efficient and economical way. There is also a lot of water on the planet, but increasingly this water is not where it is needed or it is of inadequate quality (purity) for human consumption or for other beneficial (e.g., industrial/agricultural) purposes. Thus, advanced technologies for water purification are an essential part of meeting the current and future needs for water.

Membrane processes are currently used in several ways to purify water with desalination by reverse osmosis being the most obvious, but not the only, example. Because of their energy efficiency, membranes will grow in importance compared to other technologies. This combined with the growing need to purify more and more water represents a growth opportunity for membrane technology. Better membranes are needed to meet these challenges. As the membranes of major interest are polymeric, this represents an opportunity for polymer science.

The purposes of this article are to review the current state of polymeric membranes for water purification and to identify areas where improvements, via polymer science, are needed. Further background on membrane technology as it relates to water purification can be found in a number of books and reviews.[1–14]

BACKGROUND

World Water Resources

Less than one percent of all freshwater on earth is usable by humans. Most freshwater is inaccessibly locked into polar icecaps or permanent mountain snow cover. Freshwater as a whole only constitutes 2.5% of Earth's water—the vast majority is saltwater (97%) in the ocean, and the small remainder is brackish water (0.5%) found in surface estuaries and salty underground aquifers.[15] Of the freshwater that humans consume, 70% is used for irrigation, 20% is allocated for industry, and only 10% finds domestic use.[16] Clearly, the latter figure is not enough since 1.2 billion people worldwide are without safe drinking water and 2.6 billion lack adequate sanitation.[17] Diarrheal diseases alone result in 1.8 million deaths each year, 88% of which are attributable to unsafe drinking water and inadequate sanitation.[18] The World Health Organization publishes comprehensive reports on acceptable levels of microorganisms, chemicals, and other impurities found in drinking water.[19]

With water use growing twice as rapidly as population over the last century,[20] an improvement in these circumstances is unlikely. The lack of safe water resources has impacts beyond human health, however. By the year 2050, the world's population is expected to increase by 3 billion people and roughly 2.7 billion of these people will be in developing countries where the economic impact of poor water

and sanitation availability is devastating.[20] The overall annual loss in Africa due to a lack of clean water and basic sanitation is estimated at $28 billion (5% of GDP).[20] In the southeastern Asia countries of Indonesia, Cambodia, the Philippines, and Vietnam, $9 billion (2% of GDP) is lost each year.[20] Because there is such a significant negative economic impact of substandard water access and sanitation there are tremendous benefits from appropriate investments.

Freshwater availability is also inextricably linked to energy production. Webber[21] recently described the vicious cycle linking water purification and energy production. Delivery of one million gallons of clean water from a lake or river requires 1.4 megawatt-hours of energy; desalination raises that figure to 9.8–16.5 megawatt-hours for the same amount of clean water derived from seawater. One megawatt-hour of electricity produced using coal or oil, however, requires 21,000–50,000 gallons of water; nuclear plants require 25,000–60,000 gallons of water to make the same amount of electricity. Gasoline vehicles consume 7–14 gallons of water for every 100 miles they travel; more "environmental-friendly" vehicle technologies consume even more water: 24 gallons per 100 miles for plug-in hybrids, 42 gallons per 100 miles for hydrogen-fuel cell vehicles, and up to 6200 gallons per 100 miles for vehicles running on ethanol.[21] Development of energetically efficient methods of water purification will be key to finding solutions within this cycle.

Agriculture consumes 70% of all human freshwater withdrawals. Water shortages, therefore, will limit food production and place pressure on food imports. The growing population, as noted above, will also drive up the demand for food. Increased energy costs contribute to elevated fertilizer costs which, in turn, raise food prices.[18] The link between water and food supplies can be illustrated by examining how much water is consumed during the production of various food products. A single hamburger, for example, requires 635 gallons of water. A glass of milk requires 53 gallons, a single egg requires nearly 36 gallons, and a slice of bread requires 10.5 gallons.[22]

With the current and future pressures on water supply, low-cost, high-efficiency means of water purification from a variety of sources will be of utmost importance. Many of the most arid and water-stressed regions of the world lie near water sources that have not been traditionally accessed to provide large volumes of clean water. The world's oceans could easily satisfy human water needs with appropriate purification and desalination. The high osmotic pressure of seawater makes desalination an energy-intensive process with current technology. Brackish water does not require as much desalination and may represent a more energetically favorable source. Many other nontraditional sources require different types of separation. Singapore is breaking new ground in reclaiming public wastewater and purifying it for human re-consumption with its NEWater program.[23] Petroleum refining produces large volumes of wastewater that contains residual oil and refining byproducts. Each barrel of refined oil generates 7–10 barrels of wastewater.[24] Each of these sources may become important contributors to water for
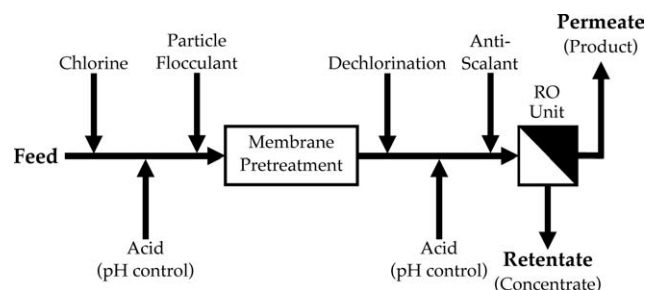
FIGURE 1 Simplified process flow diagram of a water purification process involving two applications of membrane technology; one for pretreatment and the other for salt removal via reverse osmosis.[12]

human consumption, but each has unique separation requirements. Membranes represent an energetically efficient solution for carrying out many of these separations.

Membrane Basics

Before discussing details of water purification via membrane technology, it is important to recognize how the membrane fits into a typical water purification process such as desalination.

Membrane Separation as a Unit Operation

A simplified flow diagram for a membrane-based water purification process is shown as Figure 1.[12] In this example, there are two membrane separation steps: a membrane pretreatment unit for removal of particulates and other macromolecules followed by a reverse osmosis (RO) unit for salt removal. The flow diagram indicates several other process steps related to microbial control (chlorine addition), pH control, particle flocculation, dechlorination (to protect the reverse osmosis membrane), and scaling control. The relevance of the process steps to membrane development will be discussed in some detail later.

The membrane technologies of primary interest are pressure-driven processes where a pressurized feed is supplied to the membrane unit to produce purified permeate (product). Some of these membrane processes use cross-flow geometry whereby a retentate (or concentrate) containing high levels of total dissolved solids (TDS) is also produced.

Osmotic Pressure

Dissolved solutes in an aqueous feed create an osmotic pressure, π, thermodynamically defined in terms of the activity of the solvent (water) in the solution

$$\pi \equiv -\frac{RT}{\overline{V}_w} \ln a_w \qquad (1)$$

where $\overline{V}_w$ is the partial molar volume of the solvent, R is the gas constant, T is the absolute temperature, and a_w is the activity of the solvent.[25] For sufficiently dilute solutions, eq 1 simplifies to the well-known van't Hoff equation

$$\pi \cong C_s RT \qquad (2)$$

where C_s is the molar concentration of the solute.[25] To accomplish purification using a semipermeable membrane, the applied trans-membrane pressure difference must be greater

than the osmotic pressure difference between the feed and permeate solutions. The flux of water through the membrane can, therefore, be positive (in the direction of the solution of lower solution concentration) or negative (in the direction of the solution of higher concentration) depending on the applied pressure difference as illustrated in Figure 2.

The data in Table 1 represent the reasonable range of osmotic pressures to be expected for water purification applications. It is important to note that the osmotic pressure is highly dependent on the salinity and composition of the solution. Note that osmotic pressure is sensitive to the total concentration of species (ions and molecules) in solution;[26,27] therefore, in Table 1, the brackish water sample with a TDS of 2000 mg L^{-1} has a lower osmotic pressure than a 2000 mg L^{-1} solution of sodium chloride. This is due to the presence of heavier ions (in terms of molar mass) in the brackish water sample. Particulate matter or polymeric solutes do not make a significant contribution to osmotic pressure.

Two Membrane Transport Mechanisms

Membranes of interest here can function by two fundamentally different mechanisms: pore flow or solution-diffusion as depicted schematically in Figure 3.[8,12,29]

Simple filtration involves pore flow where separation is predominantly accomplished via a size-sieving mechanism. However, when the pore size is small enough, such as in nanofiltration (NF) membranes, polymer surface charge may cause pore flow membranes to exhibit low to moderate rejection of higher valent ions whereas they exhibit low rejection of monovalent ions.[9,12,13,30–33] These membranes typically have a molecular weight cutoff for organic solutes in the range of 200–1000 daltons as nanofiltration membranes have a "loose" structure whereby some transport occurs via pore flow.[9,12,31–33] The mass flux, n, of a solution of density, ρ, and viscosity, μ, through pore flow membranes with a porosity, ε, can be modeled as flow through a circular tube of radius, R, and length, L, using the well-known Hagen-Poiseuille equation[34]

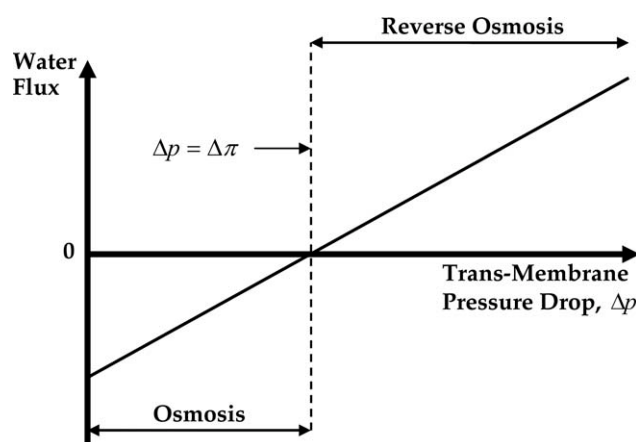**FIGURE 2** Membrane flux versus an applied trans-membrane pressure difference, Δp, with a given osmotic pressure difference, $\Delta \pi$.

TABLE 1 Osmotic Pressure for Typical Feed Solutions (25 °C)[28]

Solute or Solution	Total Dissolved Solids (mg/L)	Molar Concentration (mmol/L)	Osmotic Pressure (psi)	Osmotic Pressure (bar)
Brackish Water	2,000–5,000	–	15–40	1.0–2.7
Seawater	32,000	–	340	23.4
NaCl	2,000	34.2	22.8	1.7
NaCl	35,000	598.9	398	27.4
NaHCO$_3$	1,000	11.9	12.8	0.883
NaSO$_4$	1,000	7.1	6.0	0.41
MgSO$_4$	1,000	8.3	3.6	0.25
MgCl$_2$	1,000	10.5	9.7	0.67
CaCl$_2$	1,000	9.0	8.3	0.57
Sucrose	1,000	2.9	1.05	0.0724
Dextrose	1,000	5.5	2.0	0.14

$$n = \frac{\varepsilon \rho R^2}{8 \mu L} [p_0 - p_L] \qquad (3)$$

where the pressure difference between the entrance of the pore and the exit of the pore $[p_0 - p_L]$ drives the flow.

On the other hand, in the solution-diffusion case, penetrants molecularly dissolve in the polymer matrix of the membrane, diffuse through the thickness of the membrane, and desorb from the polymer matrix at the downstream side of the membrane.[35–37] In desalination, the water flux results from a concentration gradient of water in the membrane established by the applied pressure difference across the membrane.[38–40]

In the practice of reverse osmosis, the flux of water and salt are often described by the following phenomenological equations.[35–37]

$$\text{Water Flux} = A[\Delta p - \Delta \pi] \qquad (4)$$

$$\text{Salt Flux} = B \Delta C_s \qquad (5)$$

The salt flux is driven by a difference in salt concentration between the feed side and the permeate side of the membrane and is essentially independent of the driving pressure. The parameters A and B are useful for describing the performance of a membrane but they are not material properties of the membrane and offer no insight about the structure of the membrane or the mechanism by which it operates; these issues will be dealt with in depth later.

For transport of a penetrant through a polymer film, permeability can be defined as

$$P_i = \frac{(\text{Penetrant Flux})(\text{Film Thickness})}{(\text{Driving Force for Transport})} \qquad (6)$$

where P_i is the permeability of component i. The explicit flux equations for water and salt permeability will be presented later.
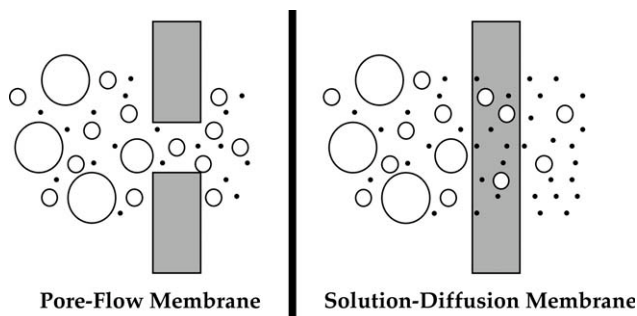
FIGURE 3 Pore-flow membrane transport contrasted with solution-diffusion membrane transport.

Solute or salt rejection, **R**, is a commonly used as a measure of how effectively the membrane performs the separation; rejection is defined as follows.[12]

$$\mathbf{R} \equiv \left[1 - \frac{C_{s\ell}^s}{C_{s0}^s} \right] \times 100\% \qquad (7)$$

Using eqs 4 and 5, salt rejection can also be expressed as a function of the A and B parameters and the pressure driving force.

$$\mathbf{R} = \left[1 - \frac{\rho_w B}{A(\Delta p - \Delta \pi)} \right] \times 100\% \qquad (8)$$

where ρ_w is the density of water.[12] The salt rejection is not a material property but depends on the pressure driving force.

Membrane Flux in Practical Applications
External factors often contribute to the performance of membrane separation systems. Concentration polarization results when the flux of water through a membrane is greater than the flux of solutes back into the bulk feed solution.[12,41,42] When this condition is met, the solute concentration at the upstream face of the membrane can be dramatically elevated in the boundary layer region as illustrated in Figure 4.

The effect of this polarization can be multi-fold. An increase in the concentration of solution at the membrane surface, as
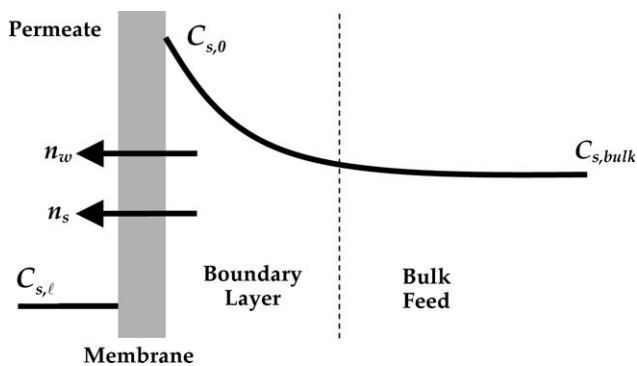
FIGURE 4 Concentration polarization occurs when the flux of water through the membrane is greater than the flux of ions back into the bulk feed solution. When this condition is met, the concentration of salt at the membrane face can increase dramatically in a boundary layer region.

shown in Figure 4, will lead to a greater osmotic pressure difference and a greater solution concentration difference across the membrane. This will decrease water flux and increase salt flux according to eqs 4 and 5. The severity of polarization can be reduced by making the boundary layer thinner via managing the upstream hydrodynamics, for example, high flow rates or creating turbulence.[12,34]

Other flux reducing phenomena may occur in membrane systems. Fouling and scaling are both significant challenges in membrane processes.[13,43–52] Similar to filter cake formation on a dead-end filter, fouling and scaling decrease flux through a membrane by adding an additional mass transfer resistance to transport through the membrane. Several factors contribute to fouling and scaling tendencies in membrane systems; these include, membrane chemistry (including surface charge), operating flux, permeate recovery, chlorination, feed water composition, and module design.[13,43–52] Fouling and scaling issues will be discussed in more detail later.

FILTRATION (POROUS) MEMBRANES AND PROCESSES

Molecules pass through RO membranes primarily by a solution-diffusion mechanism as discussed in a later section. Microfiltration (MF) and ultrafiltration (UF) membranes operate exclusively by pore-flow, whereas NF membranes show a combination of solution-diffusion and pore-flow character. This section will discuss MF, UF, and NF membranes. The four major types of polymer membranes and conventional filtration (CF) materials effectively remove particles of sizes that are shown in Figure 5.[53]

Filtration membranes may have a relatively uniform pore structure throughout the thickness; such symmetrical structures act as depth filters. Alternatively, the membrane may consist of a thin layer with fine pores (active layer or "skin") overlaying a thicker layer with larger pores to provide mechanical support but little resistance to water flow; such asymmetric membranes are sometimes called screen filters because the separation of particulates occurs at the surface of the membrane in a very thin, selective layer. Unlike screen filters, where rejection of large solutes takes place on the membrane surface, depth filters capture solute particles within the membrane. Depth filters may capture particles by several mechanisms, including simple size sieving, adsorption, Brownian diffusion, and electrostatic adsorption. Sieving
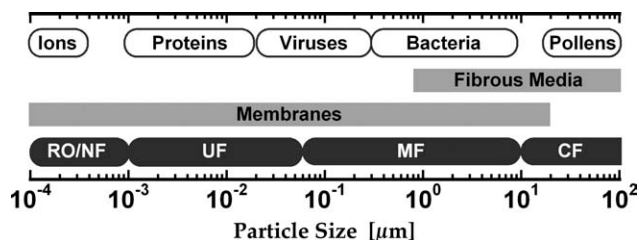
FIGURE 5 Size of particles removed by RO, NF, UF, and MF membranes along with conventional filtration.[53]

typically accounts for only a small fraction of the membrane's rejection.[54,55]

Formation of a Pore-Flow Membrane

The oldest and most common technique for forming porous polymeric membranes consists of forming a concentrated solution of the polymer in a solvent with subsequent immersion into a liquid bath, typically water or a mixture with the solvent, in which the solvent is miscible but the polymer is not. Water vapor adsorption from a humid atmosphere, solvent evaporation, or some combination of techniques may be used in place of immersion in the liquid bath.[12] Methods were summarized by Pinnau and Koros.[56] Under proper conditions, a film is formed comprised of a continuous phase of solid polymer and an interconnecting phase of voids, chambers, or pores through which liquids can flow. The distribution of phases during solvent exchange dictates the physical structure of the solid membrane.[57] Anisotropic membranes are created by contacting the top surface of the cast film with the nonsolvent first, creating a finely porous selective skin layer. The precipitated skin layer slows the penetration of nonsolvent into the film, causing polymer below the skin layer to precipitate more slowly. As a result, the substructure is more porous than the skin layer. In the membrane literature, this process has been called "phase inversion";[58–60] structures of this type were being studied more than a century ago. An analogous procedure is used to make fibers by wet spinning[61–64] where the solidification step is called "coagulation." The pore structure, that is, pore size, shape, and volume, is affected by many factors. There is a sizable body of literature devoted to analysis of the phase inversion or coagulation process;[65–76] however, the practice is still largely an empirical art.

Early membranes made in this way consisted of a similar pore structure through the entire membrane, and because of their thickness such membranes had low fluxes. Loeb and Sourirajan[77] introduced a solvent evaporation step prior to precipitating the polymer; the polymer concentration gradient in the nascent film leads to a gradation of pore size upon phase inversion. This effectively gives a "thin skin" with very fine pores, that is, the separating layer, overlaying a substrate consisting of much larger pores that provide mechanical support but relatively little resistance to water flow. With a wet annealing step, Loeb and Sourirajan were able to make the first practical reverse osmosis membrane as described later.

The polymer solution can be cast in batch mode to make laboratory membranes or in a continuous fashion and used to form commercial membranes. The solution can be cast on a fabric or other porous substrate for additional support. An analogous process with an evaporation step, known as dry-jet wet spinning, is used to make hollow fiber membranes.[3,8,60]

One of the most important membrane preparation methods is the Loeb-Sourirajan process described in 1963.[77] The Loeb-Sourirajan process uses water as the phase inversion nonsolvent and was originally used to produce cellulose

acetate reverse osmosis membranes. Today, reverse osmosis and nanofiltration membranes are usually of the polyamide thin-film composite type which will be discussed later. The Loeb-Sourirajan process is, however, still the predominant method of making ultrafiltration and microfiltration membranes. Common ultrafiltration membrane materials include cellulose acetate,[78] polyacrylonitrile, poly(ether imides),[79] aromatic polyamides, polysulfone, poly(ether sulfone),[12,79] poly (vinylidene fluoride), and poly(vinyl pyrrolidone).[80] Early microfiltration membranes were nitrocellulose and cellulose acetate;[12] materials used more recently are poly(vinylidene fluoride), polysulfone, polyamide, poly(tetrafluoroethylene),[12,79] and polyethylene.[79]

Several other methods of producing pore-flow membranes have been reported. Thermally induced phase separation (TIPS) bears some similarity to the phase inversion process but uses a temperature decrease rather than a nonsolvent to coagulate the polymer. A polymer solution is spread on a support and one face of the film is cooled, initiating phase separation. The rest of the film is gradually cooled and phase inversion gradually propagates to form an isotropic or anisotropic porous membrane.[81] To create the selective surface layer in the case of anisotropic membranes, solvent evaporation at the selective surface is sometimes used to enhance the phase inversion process rather than only a simple thermal gradient in the solvent. TIPS also makes a number of polymers accessible for membrane formation that cannot be used in the traditional phase inversion technique.[82] TIPS has been carried out on a number of different polymers including homopolymers such as polypropylene and diphenyl ether[83] and copolymers such as poly(ethylene-co-acrylic acid).[82] Connected pore structures form at low polymer concentrations; as polymer concentration and cooling rate increased, pore size is found to decrease.[67] When evaporation is used to create anisotropic membranes, the polymer molecular weight does not significantly affect the cell size of the selective layer and, therefore, does not greatly influence the membrane performance.[84]

Pore flow membranes have also been created without solvent by stretching melt-cast polymer films. This process was developed extensively by Celanese to produce the product Celgard® based on polypropylene and is described in several patents.[85,86] These patents are directed at medical dressings and battery separators and cover a wide range of polymers. Gore also applied the stretching technique to production of porous fabrics made of polytetrafluoroethylene.[87] The process begins with a precursor film which shows row-nucleated lamellar morphology. The precursor film is typically annealed to eliminate any inconsistencies in the crystal structure. Stretching is then carried out at low temperature to introduce voids and subsequently at high temperature to enlarge those voids.[88] The morphology of the precursor film is of utmost importance for the success of the stretching technique. The crystals form as a result of stress and elongation induced during the extrusion process and their formation is a strong function of processing conditions and, most importantly, polymer molecular weight.[89] A critical molecular

weight for crystal formation is known to exist which is dependent on shear rate and temperature up to a particular shear rate after which it is independent of process conditions.[90] High molecular weights were found to increase pore size and pore uniformity, leading to high water vapor transmission in polypropylene membranes.[88] In the case of poly (vinylidene fluoride) membranes, the necessary crystalline structure in the precursor film was found to form most readily when a blend of low- and high-molecular weight polymer was used.[91]

Another type of solvent-less membrane formation is track etching. By this technique, a polymer film is bombarded with α-particles to create "tracks" through the film. The film is then immersed in a chemical etchant to create straight-through circular pores. Polycarbonate membranes have been formed by this technique. Unlike membranes prepared by the other methods described here, track-etch membranes are typically of a very uniform thickness and have precisely defined pore diameters. As a result of the unity tortuosity and the uniform thickness (which allows the membrane to be exceedingly thin everywhere), the porosity of a track-etch membrane may be significantly lower than that of a solvent-cast membrane but both membranes may show similar permeability.[29]

Semiporous nanofiltration membranes bear a strong compositional similarity to reverse osmosis membranes. Both reverse osmosis and nanofiltration membranes, though formerly produced by the Loeb-Sourirajan process from cellulose acetate, are today thin-film composite membranes. Soon after, Loeb and Sourirajan published their phase inversion method, Francis[92] developed composite membranes. Petersen provided an extensive review of composite reverse osmosis and nanofiltration membranes.[9] Composite membranes consist of an ultra-thin selective layer atop a porous support backing. These two components are almost always of differing chemical compositions (unlike Loeb-Sourirajan integrally skinned membranes) and may, therefore, be optimized for their particular roles. Cellulose acetate was initially used as the support material; polysulfone and polyethersulfone (PES) are the backings of choice now. The composite structure may be formed in a number of ways, including laminating together separately formed backing and selective layers, but the vast majority of nanofiltration membranes are produced by interfacial polymerization of a set of monomers on the support surface. Linear aromatic polyamides are one of the few polymers with the necessary solute rejection and flux characteristics for the selective layer.[9]

Applications of Pore-Flow Membranes

Membranes are used for sterilization in a variety of applications. Microfiltration membranes are often assembled into disposable cartridges which are typically used for short periods of time before being replaced. The pharmaceutical and microelectronics industries have been extensive users of microfilters over the past several decades. Microfiltration cartridges are typically used to sterilize injectable drug solutions because 200 nm microfilters are able to remove

virtually all bacteria. Filters are sterilized by autoclaving or other means after manufacture and immediately before use. In the electronics industry, microfilters are used to polish ultrapure water before use. Filters with 100 nm pores are used to remove any contamination from piping between the water treatment facility and end-use point.[12]

The food and beverage industry extensively uses MF and UF membranes. In wine and beer purification applications, microfilters remove yeast and bacterial cells to clarify the final product.[93,94] Because of the low cost of wine and beer relative to products such as pharmaceuticals, prefilters are often used to extend the lives of the MF membranes.[12] Drinking water treatment is an ever-growing application for microfilters. MF/UF plants have been in use for ~2 decades in bringing surface water into compliance with USA EPA drinking water guidelines.[12,95] Similar guidelines exist in Europe. Hollow fiber membrane modules which are back-flushed frequently are typically found in these applications.[12]

Cheese production is another well-known application of membranes. Instead of traditional coagulation processes, which results in significant difficult-to-dispose whey production, MF or UF is used to concentrate proteins in milk for the direct production of yogurt and soft cheeses or for further processing in the production of hard cheeses.[96–98] When traditional coagulation is used, UF membranes are used to concentrate whey proteins and remove lactose concentrate and salts. The whey proteins are valuable and can be reused where they used to be discharged prior to ultrafiltration development.[12] Fruit juices, including apple, pear, orange, and grape, are all clarified using ultrafiltration. Crude filtration is performed immediately after crushing the fruit; ultrafiltration produces a perfectly clear, nearly sterile product.[12,99]

The first industrial UF application was the recovery of electrocoat automotive paint. Automotive paint is an emulsion of charged paint particles. Metal parts are coated by applying a charge opposite that of the paint particles. After electrocoating, the pieces are rinsed to remove excess paint. The rinse water becomes contaminated with otherwise reusable paint particles. In addition, the quality of the paint emulsion is degraded by ionic species which migrate from the metal cleaning process prior to painting. The electrostatic nature and high solids content of the paint emulsions make for difficult filtration as significant fouling layers readily develop on the membrane, resulting in low fluxes. Unlike MF, UF tends to be expensive, but the high value of the paint makes the ultrafiltration process worthwhile.[12,100]

Industrial UF systems are used to separate oil/water emulsions and to recover process water. Machining operations often use oil/water emulsions for lubrication and cooling. Ultrafiltration is used to separate water from the oil for safe disposal after use. Cleaning process water in-house and recycling it leads to reduced municipal water costs. Ultrafiltration has the added benefit of effectively operating at elevated temperatures. As many industrial process streams are hot, ultrafiltration provides a means of cleaning streams without the energetic expense of cooling and re-heating.[12]

NF membranes have been developed to fill market niches between RO and UF membranes. The polymeric matrix of NF membranes is more open than that of their RO counterparts, affording them some degree of porous flow while maintaining some salt selectivity. Reverse osmosis membranes provide very high salt rejections but low fluxes; nanofiltration membranes do not reject as much salt but do provide much higher fluxes. NF membranes typically reject of 20–80% of sodium chloride present, but reject much more of the large divalent salt ions. Molecular weight cutoffs for organic solutes are 200–1000 Da. The looser structure of the NF membranes allows them to operate at trans-membrane pressures that are much lower than those of RO systems. Most applications of NF membranes are in final polishing of already clean water. Low levels of contaminants may be readily removed from drinking water as a final step at a water treatment plant or at the end-use facility. Municipal water may be softened by removal of multivalent cations such as sulfate.[12]

Challenges Facing Pore-Flow Membranes

A significant hurdle to the widespread implementation of membranes for liquid purification is fouling. Fouling is the deposition of colloidal or particulate matter in a membrane's pores or on its surface that leads to changes in membrane transport characteristics [Fig. 6(a)].[43] As water containing particulates, colloids, macromolecules, or microbes is filtered through a membrane, the foreign material deposits inside the porous structure and onto the surface of the membrane, creating a cake layer which drastically reduces water flux and affects overall membrane rejection performance [Fig. 6(b)]. Because of fouling, the flux declines, which results in significant increases in the cost of membrane operation due to required membrane cleaning, periodic membrane replacement, and increased energy input to achieve high flux.

Pore-flow membranes may experience two kinds of fouling: surface and internal,[101] as shown in Figure 6(a). Surface fouling is caused by particulate adsorption to the membrane
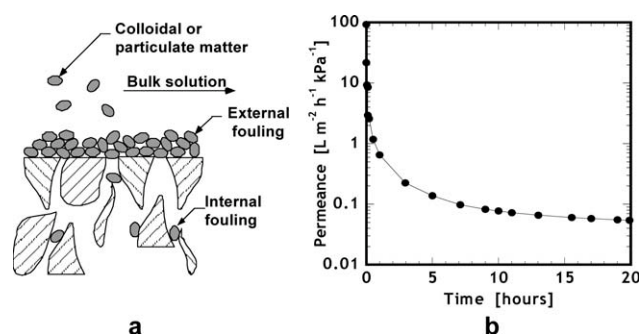

FIGURE 6 (a) Schematic of particulate fouling in porous water purification membranes (Reproduced from ref. 101, with permission from Advanced Materials for Membrane Separations, ACS Symposium Series 876. Copyright 2004 American Chemical Society). (b) Conventional MF membrane in crossflow protein filtration with 1 g L^{-1} bovine serum albumin in pH 7.4, phosphate-buffered solution, 25 cm s^{-1} crossflow, $\Delta p = 1000$ kPa (145 psi), 0.2 μm nominal pore size poly(vinylidene fluoride) membrane.

surface while internal fouling is the result of foulant entrainment in the membrane pores. Nonporous reverse osmosis membranes, in contrast, undergo surface fouling only. Internal fouling is largely irreversible because the particles entrained in the membrane cannot be easily removed, even with harsh chemical or mechanical cleaning. Surface fouling may be either reversible or irreversible. Reversible surface fouling consists of foulants that may be removed by cleaning. Some particulates, especially after extended exposure to the membrane surface, are so strongly adsorbed to the membrane surface that they cannot be removed, constituting irreversible surface fouling.

Surface modification has developed as a popular means of reducing the fouling propensity of many types of membranes.[102] Surface modification aims to change the surface properties of the membrane while maintaining its selective structure.[103] By reducing fouling, flux is maintained at a high level. Resistance to fouling also lessens the need to clean the membranes. Cleaning can be accomplished in many ways, such as through backpulsing, gas sparging, increasing shear at the membrane surface, or UV radiation. Chemical agents such as ozone, acids, bases, or chlorine may be used, but these compounds may pose deleterious environmental consequences or even degrade the membrane structure, such as in the case of chlorine compounds and polyamide membranes. To maximize output and minimize the need for membrane cleaning, membrane modifications aim to alter the surface properties of membranes to make fouling less likely.

Surface properties such as surface hydrophilicity, charge, and roughness are known to affect membrane fouling.[104–107] Hydrophilic and smooth surfaces typically show the best resistance to fouling. Negatively charged membrane surfaces may reduce some forms of fouling by electro-statically repelling negatively charged foulants.[108] However, negatively charged membrane surfaces may attract positively charged foulants; thus, un-charged membranes may exhibit a reduced tendency toward fouling. In measuring and quantifying surface properties, it is important to consider the effect of feed composition on surface properties as these properties are often measured under ideal and low TDS conditions.[108,109]

In water treatment, hydrophilic membranes show reduced fouling because of their affinity for water. Water is strongly bound to a highly hydrophilic membrane surface; foulants interact only with this water layer and not with the membrane surface. If the membrane surface is hydrophobic, water near the membrane can be easily displaced by foulants and hydrophobic-hydrophobic interactions bind the foulant to the membrane surface. To increase the surface hydrophilicity of a membrane, two types of surface modifications have appeared in the literature. Hydrophilic moieties may be coated or grafted to the membrane surface as shown in Figure 7.

In either case, additional mass transfer resistance is introduced to the membrane surface, so highly hydrophilic polymers (to permit high water uptake into the surface layer) are typically used. The hydrophilic coating layer is nonporous and, therefore, must be very thin to avoid introducing
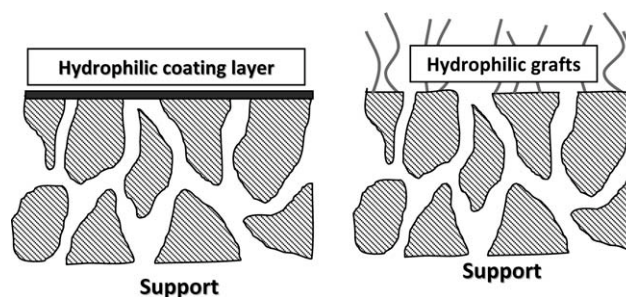

FIGURE 7 Membrane surface modification by hydrophilic coating or grafting.

catastrophic mass transfer limitations. Dense coatings, however, eliminate entrainment of foulants inside the membrane. Grafting of hydrophilic chains may be used as an alternative to the dense coating layer. The mass transfer limitations imposed by grafting modification are typically less than in the case of the coating layer, but foulants may still be able to find their way inside the membrane structure.

Hydrophilic polymers can be grafted directly to membranes surfaces by a variety of methods. Chemical grafting to the surface provide a more stable structure than simple adsorption of hydrophilic polymers to the membrane, which has shown some prevention of protein fouling in microfiltration and ultrafiltration.[110,111] Grafting can be achieved by inducing polymerization from the membrane surface or by tethering polymer chains to the surface. Plasma-induced polymerization techniques have been used to graft polyamides or poly(acrylic acid) to porous membrane surfaces.[112] This technique has also been reported on polyethylene surfaces,[113] polycarbonate[114] and poly(vinylidene fluoride)[112] microfilters, and poly(vinyl chloride),[115] poly(acrylonitrile), and polysulfone ultrafilters.[103] Photo-initiated graft polymerization has been used to attach a variety of monomers to polyethersulfone membranes by inducing radical formation in the PES backbone.[116,117] Photo-induced graft polymerization and subsequent crosslinking has been used to attach epoxy diacrylates to ultrafilters.[118] Photo-grafting acrylic acid, 2-hydroxyethyl methacrylate, and poly(ethylene glycol) methacrylate derivatives have also seen use in photo-induced polymerization onto poly(acrylonitrile) flat-sheet membranes.[119,120] Grafting by photo-polymerization has been carried out on membrane architectures other than flat sheets such as microporous hollow fibers.[121,122] Polymer chains may also be tethered to the surface to form a graft structure. Dextran derivatives were grafted to ultrafiltration membranes to reduce protein fouling.[111,123] Poly(ethylene glycol) (PEG) has proven to be extremely popular for use with this technique. Photo-induced grafting requires surface[124–126] or PEG functionalization[126–128] to achieve a covalent link between the surface and the polymer chain.

Dense hydrophilic coating layers have also been used to induce fouling resistance. Because of their notorious propensity for fouling, ultrafiltration membranes have been a popular substrate for such coating layers.[129] Composite

ultrafiltration membranes have been formed by crosslinking thin layers of poly(vinyl alcohol) on the membrane surfaces.[130,131] Poly(ethylene glycol) has also been used in the same manner.[132] Crosslink density in the coating layer may be manipulated by varying the polymer/solvent ratio in the thin-film casting solution.[133,134]

Membrane surface modifications explored to date, however, are not without limitations. Many modification techniques are membrane-specific. For example, photo-grafting induces radical formation on the backbone of PES[116,117] to which hydrophilic moieties may be grafted, as noted previously. Unfortunately, photo-grafting is not effective on other common membrane materials such as poly(vinylidene fluoride) (PVDF), poly(tetrafluoroethylene) (PTFE), and polyamides since, unlike PES, these polymers do not readily form surface radicals under UV irradiation. Other modification strategies such as plasma treatment[103,135–137] and multi-step organic reactions[138] may be difficult or expensive to apply in a manufacturing environment.

Measurement of the zeta potential is becoming a popular means of characterizing the surface of modified membranes. The zeta potential describes the potential induced between the membrane surface and the shear plane of fluid moving past the surface. As noted previously, uncharged surfaces typically show good fouling resistance. The zeta potential, therefore, can be used to predict the fouling resistance of a membrane. Surfaces become charged by ionization of chemical functionalities on the surface or by adsorption of charged particles. The pK, isoelectric point, and charge density all affect the zeta potential of a surface. The zeta potential has also been found, however, to depend on membrane pore diameter and surface roughness. Interaction of membrane surface with foulants, therefore, can only be compared among well-defined membranes.[139]

REVERSE OSMOSIS MEMBRANES

There are at least four requirements for a commercially viable reverse osmosis membrane system for desalination. First, the membrane must be made from a polymer whose intrinsic characteristics are capable of giving adequately high water permeation and low salt permeation rates. The high salt rejections required can be achieved by a solution-diffusion mechanism but not by pore flow. Second, to achieve the high fluxes needed, the membrane layer that does the separation must be made very thin, viz., about 100 nm in thickness. However, the membrane needs to have sufficient me-
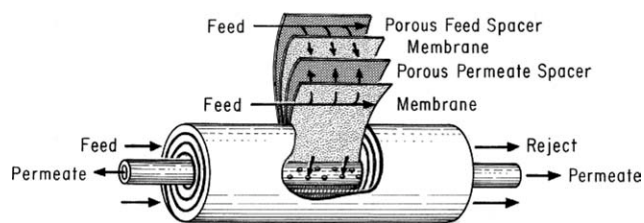
FIGURE 9 Illustration of a spiral wound module.

chanical integrity to be assembled into a module and to withstand the driving pressures imposed, that is, several times the osmotic pressure of the salt solution to be purified. A thin dense layer (or skin) overlaying a porous support structure has proven to be the ideal way to meet these opposing requirements (see Fig. 8). Third, these membranes must be assembled in a way that provides a high membrane area per unit volume of the pressure vessel. There are four types of membrane modules that have found some commercial utility: tubular, plate and frame, hollow fibers and spiral wound (see illustration in Fig. 9) systems; these are described in detail elsewhere.[3,8,12] Finally, the membrane needs to be chemically and physically robust enough to perform at specification for years in the environment of the reverse osmosis process. One of the more difficult of these is to resist the chlorination used to disinfect the feed water.

The following subsections review the development of membranes that meet most of the above requirements, the current state of the art, and some of the possibilities for next generation membranes. The last half-century has seen a remarkable evolution of membrane technology for this purpose. The rapidly growing need for water purification throughout much of the world will likely drive an even more accelerated evolution of better membranes in the coming years. The next section describes in more detailed mathematical terms the basis of transport by the solution-diffusion mechanism and point to areas where better understanding of these processes in polymers is needed.

Desalination of seawater and brackish water requires membranes with high levels of NaCl rejection, $> 98\%$.[13,140,141] For example, seawater typically contains about 35,000 mg L^{-1} TDS.[13,28,29,140–142] In a reverse osmosis plant run at 50% recovery,[13,140,141] the average upstream concentration would be 52,000 mg L^{-1} TDS. The World Health Organization does not publish a health related specification for sodium, chloride, or TDS in drinking water.[19] However, a typical TDS target for an RO desalination permeate is <500 mg L^{-1}.[29,140–142] To meet this specification, the membrane must have a salt rejection of 99.1%. This analysis neglects the effects of concentration polarization. If concentration polarization is considered, the required salt rejection will increase. Depending on the severity of concentration polarization, salt rejection greater than 99.7% may be required to make potable water from seawater.[143]

There are applications where such high rejections are not needed but higher fluxes are. "Nanofiltration" membranes have been developed for this market niche.[9,12] They have
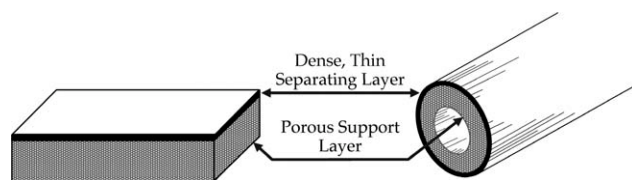

FIGURE 8 Schematics for flat-sheet (left) and hollow-fiber (right) membranes where each has a dense, thin selective separating layer supported by a porous layer.

poor rejection of single valence ions, which results in much higher permeate ion concentrations relative to RO membranes and, therefore, higher permeate osmotic pressure difference across the membrane, so the water flux is inherently higher at the same Δp (cf. eq 4). Such membranes can achieve high flux at low Δp values.

Asymmetric Membrane Structures

The first commercially useful reverse osmosis membranes were made from cellulose acetate. Interest in these materials for desalination stemmed from the pioneering work of Reid and coworkers[144,145] published in 1959, showing that cellulose acetate films were capable of much higher salt rejection than other polymers considered. However, because these films were relatively thick, 4–22 μm, fluxes were unacceptably low. The breakthrough that made reverse osmosis a viable process, and ultimately membrane separation of gases, was the discovery by Loeb and Sourirajan.[77] They developed a procedure for casting a complex solution of cellulose acetate followed by an evaporation period, immersion in cold water, and then wet annealing. Their membranes had fluxes orders of magnitude greater than those reported by Reid and Breton while maintaining equivalent salt rejection. The wet annealing step is essential for achieving high salt rejection; without this step, the membrane skin is porous.

Riley et al.[146] examined the structure of the Loeb-Sourirajan membranes by transmission electron microscopy and found they had an "asymmetric" morphology comprised of a very thin dense skin, ~100–200 nm in thickness, supported on an open cell porous substructure like that shown schematically in Figure 8. The wet annealing step closes the pores in the skin to make it dense. Merten and coworkers[1,35,37,147] developed a simple solution-diffusion model to describe the reverse osmosis process and did extensive experiments to characterize the equilibrium and transport behavior of the CA/water/salt system and verified the solution-diffusion mechanism. Their equations for flux and rejection will be presented later in the context of a broader analysis of the solution-diffusion mechanism for reverse osmosis.[39] An essential teaching of this simple model is the need for a sufficient level of swelling of the membrane by water to have adequate water permeation while not sorbing water to such an extent that high salt permeation rates destroy salt rejection. For example, the equilibrium water sorption by cellulose acetate materials is generally in the range of 15–30 wt %.[1,35,148]

Figure 10 shows the flux and rejection characteristics of experimental asymmetric cellulose acetate membranes.[1,35] The flux was measured for two different NaCl feed concentrations to show the effect of osmotic pressure. The flux plots are somewhat nonlinear; this plus some degree of hysteresis on decreasing the pressure has been attributed to compaction of the porous substructures but this feature can be significantly reduced by an optimized casting process. In the plot of rejection versus pressure, the points represent measurements for a feed containing 1000 mg L^{-1} NaCl using an experimental asymmetric membrane while the solid lines were calculated from separately determined water and salt permeabilities
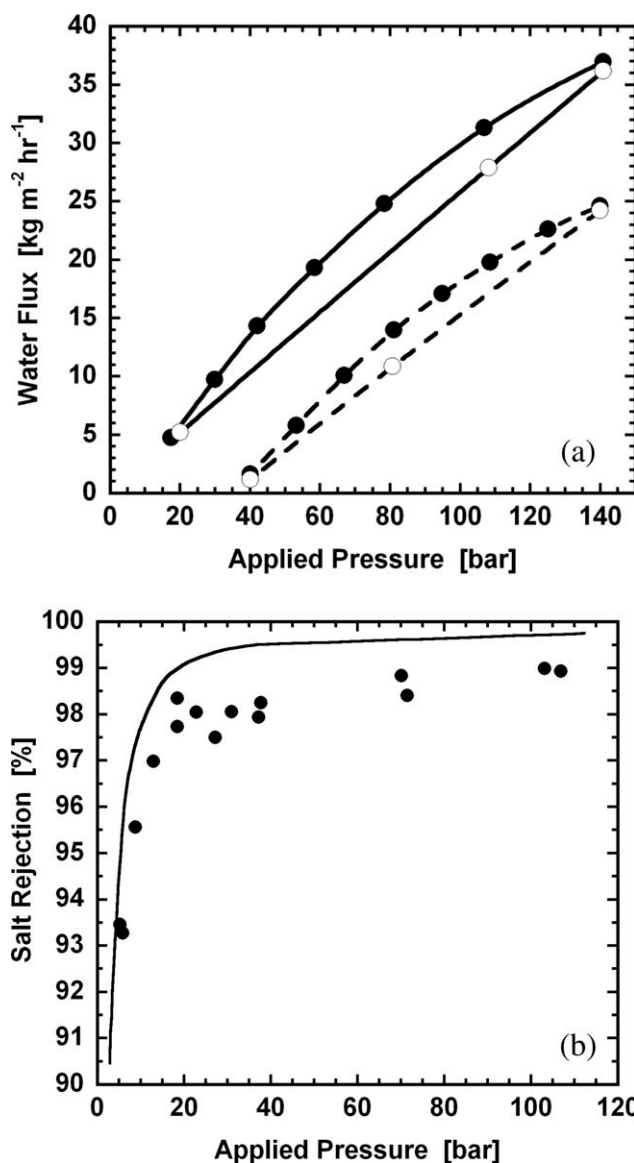

FIGURE 10 (a) Water flux versus applied pressure for a cellulose acetate membrane (solid lines indicate 0.13 wt % NaCl feed and dashed lines indicate 4.5 wt % NaCl feed) showing hysteresis between increasing (●) and decreasing (○) pressure. (b) Predicted salt rejection based on water and salt permeability measurements (lines) and experimental data (●) (Journal of Applied Polymer Science, Vol. 9, No. 4, 1965, 1341–1362. Copyright 1965 John Wiley & Sons, Inc.; Reprinted with permission of John Wiley & Sons, Inc.).

from the same cellulose acetate in film form. The points fall somewhat below the theoretical prediction presumably because of slight defects in the asymmetric membrane.[1,35]

As the degree of acetylation of the cellulose acetate increases, membranes made from them exhibit higher salt rejection but the flux decreases.[12,37] Some of the best membranes reported consist of blends of a 39.8 wt % acetylated polymer with small amounts of cellulose triacetate (44.2% acetate) or cellulose acetate butyrate;[12,149] seawater

salt rejections of 99.0–99.5%, which is close to the theoretical limit, were achieved but fluxes were modest.[12] Most commercial cellulose acetate membranes have been optimized to give higher fluxes and lower salt rejection.

Cellulose acetate membranes are resistant to the chlorine added to disinfect the feed water, which is advantageous for applications with significant bacterial content. However, cellulose acetate membranes do hydrolyze over time; the rate is at a minimum in the pH range of 4–6.[37,149] During the 1960–1970s, cellulose acetate and other polymers were made into hollow fiber membranes having an asymmetric structure as illustrated in Figure 8.[150–153] DuPont commercialized a polyamide hollow fiber membrane for RO;[150] however, by the year 2000, hollow fiber polyamide membranes were no longer being sold for reverse osmosis. Nevertheless, a successful cellulose triacetate hollow fiber membrane is still being sold for reverse osmosis. Hollow fiber technology has been successfully translated, with different polymers and some modifications, into a significant commercial business for gas separations.

The DuPont hollow fibers were not resistant to chlorine, which is the case for all polyamides including the very successful thin film composites that now dominate the reverse osmosis market. A few other polymers like poly(vinyl alcohol), postpolymerization sulfonated polysulfone, etc., have found niche applications.

Polyamide Thin Film Composites

Thin film composite (TFC) membranes made from aromatic polyamides currently dominate the market for desalination applications.[9,154] Commercially available TFC membranes typically consist of three distinct layers (Fig. 11). The top layer is an ultrathin dense layer of the order of 100 nm thick (Figs. 11 and 12). The material for the ultrathin layer can vary for a specific application but aromatic polyamides with a crosslinked architecture is the most frequently used. This barrier layer is highly selective to water and ionic solute passage due to its dense, nonporous structure, and being ultrathin enables high water flux. The middle layer is a microporous support made of asymmetric polysulfone (Figs. 11 and 12). An anisotropic microporous structure of the layer can be produced by a single step phase-inversion method.[155] The microporous polysulfone material by itself can also be used for nanofiltration applications. The bottom layer is a woven
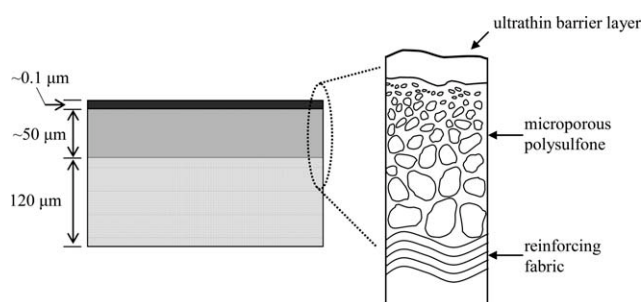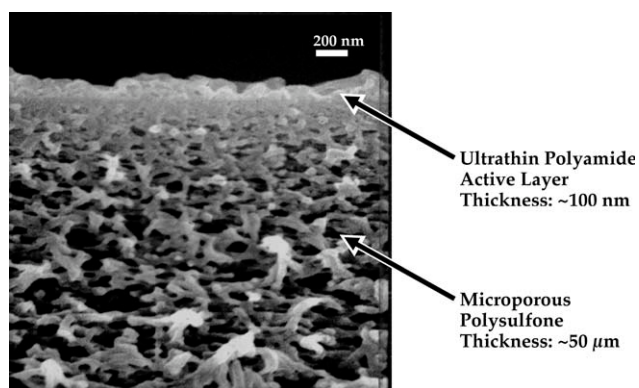

FIGURE 12 Scanning electron micrograph of a state-of-the-art thin-film composite polyamide-based reverse osmosis membrane showing the ultrathin polyamide active layer and the microporous polysulfone portion of the support layer (micrograph courtesy of Dr. Bill Mickols, DOW Water and Process Solutions).[156]

or nonwoven fabric (usually polyester) that provides additional mechanical strength. One of the major advantages of a TFC system is the ease of achieving optimal separation performance by tailoring each individual layer.

The fabrication of a commercial TFC membrane starts with the formation of the microporous asymmetric polysulfone support layer on top of the reinforcing fabric via phase-inversion.[157] Polysulfone dissolved in a water-soluble, polar aprotic solvent such as N,N-dimethylformamide (DMF) is cast on polyester fabric and the coated fabric is immersed in a bath that is a nonsolvent for the polymer (usually water). When the swollen polysulfone membrane makes contact with a nonsolvent, the polymer coagulates and forms micropores in the membrane. The resulting membrane features small pores on the surface that faced the nonsolvent and the porosity of the system gradually increases in the direction toward the support web. On top of the preformed microporous polysulfone layer, a selective ultrathin barrier layer can be subsequently fabricated via interfacial polymerization.[158] The generation of the polyamide barrier layer consists of two steps. First, the microporous polysulfone layer on the support web is coated with an aqueous solution containing a water soluble monomer. Then, a water immiscible organic solution containing a second monomer is applied on top of the aqueous layer. Because of the immiscibility of the aqueous and organic solutions, monomers in the different layers react essentially only at the interface, via diffusion, and form a thin and dense polymer layer.

As interfacial polymerization as a route to formation of the thin selective layer was introduced in the early 1970s, numerous monomers have been used as the reactants. So far, the most successful system is a fully aromatic polyamide synthesized from m-phenylene diamine and trimesoyl chloride (Fig. 13).[159,160] This system, typically known as the FT-30, was developed by Cadotte at FilmTec (currently Dow Water and Process Solutions) in 1981 and it, along with subtle variations, has dominated the membrane desalination
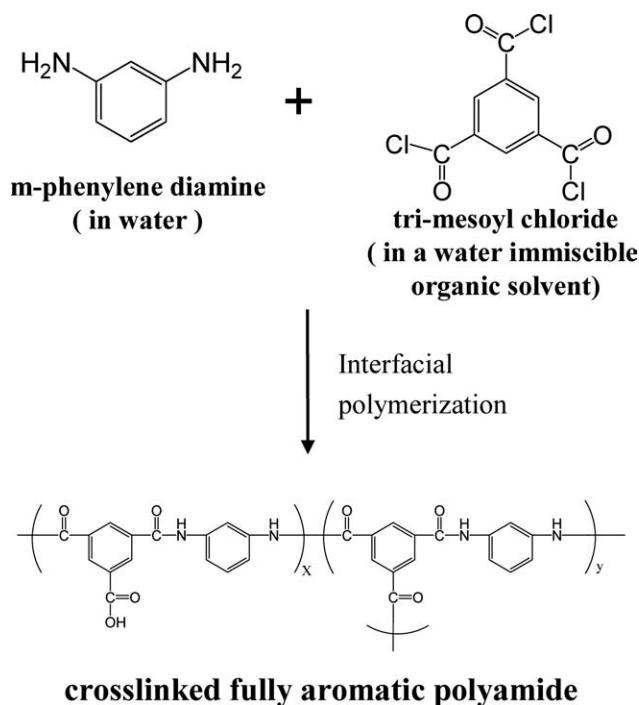

FIGURE 11 Schematic diagram of a thin film composite membrane.

FIGURE 13 Synthesis of crosslinked fully aromatic polyamide via interfacial polymerization.[9,159–162]

market for about 30 years. The success of FT-30 as an alternate material to the previous bench mark material, cellulose acetate, can be ascribed to its significantly: (a) higher flux, (b) higher salt rejection, (c) wider operational pH range, and (d) higher operational temperature.[9,154]
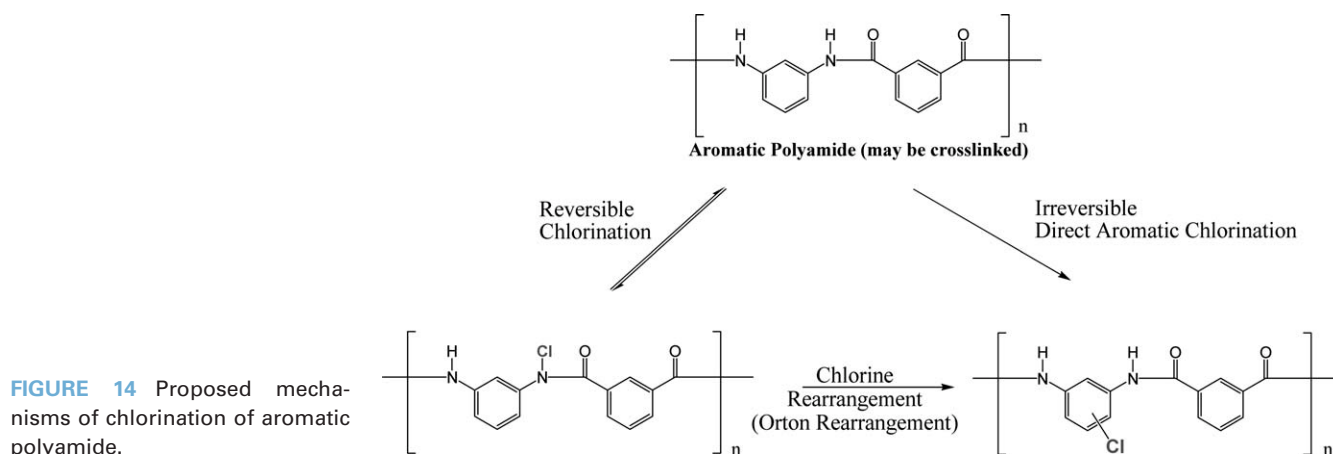
Although the aromatic polyamide TFC membranes have better resistance to hydrolysis and biological attack than cellulose acetate membranes, they are subject to oxidative degradation.[163–165] Polyamide membranes suffer significant performance degradation when exposed to trace amounts of chlorine over relatively short periods of time relative to the lifetime of a membrane element and ultimately results in membrane failure with increased passage of both salt and water. Two membrane failure mechanisms have been pro-

posed; conformational changes or cleavages of the polymer chain which are suspected to be initiated by chlorinated polyamide moieties. The proposed aromatic polyamide chlorination mechanism by Glator and Zachariah is shown in Figure 14.[166]

In the first step, the amidic hydrogen in the —NHCO— moiety is replaced by a chlorine atom. This chlorine atom is prone to a reversible reaction. The second step is a rearrangement in the position of the chlorine atom. The chlorine atom migrates into the aromatic ring via Orton rearrangement and replaces one of the hydrogen atoms on the aromatic ring which bears diamine moieties. Lowell et al. showed that the chlorine sensitivity of polyamides is pH dependent.[167] The highest chlorination was observed at pH 4.5 with a polyamide model compound. Another important factor affecting aromatic chlorination is metal residue in the feed water. It was reported that the oxidation rates by chlorine increased as the concentration of iron and aluminum in the feed water became higher.[168] Although a clear explanation was not provided, the researchers suggested a catalytic effect of these metals in the oxidation process.

Despite its destructive effects on aromatic polyamide membranes, chlorine is the most widely used biocide or disinfectant for water treatment due to its ease of use as well as its low cost.[17,169,170] There are various types of commercially available chlorine active compounds for water treatment but liquefied chlorine and hypochlorite salts (typically sodium or calcium salt) are commonly used.[17,169,170] The active chemical species responsible for the oxidizing and sterilizing properties of chlorine are hypochlorous acid (HClO) and hypochlorite ion (ClO$^-$).[171] When liquefied (compressed) chlorine is released at atmospheric condition, it immediately becomes a gas. On contact with moisture, gaseous chlorine is easily hydrolyzed to form hypochlorous acid, hydrogen ion, and chloride ion (Fig. 15). Hypochlorite ion can be produced via further ionization of hypochlorous acid or dissolution (ionization) of hypochlorite salt in water.

Since almost all natural and waste water treatment involves the use of chlorine as a biocide to prevent biofouling, the feed water should be dechlorinated before being fed to a
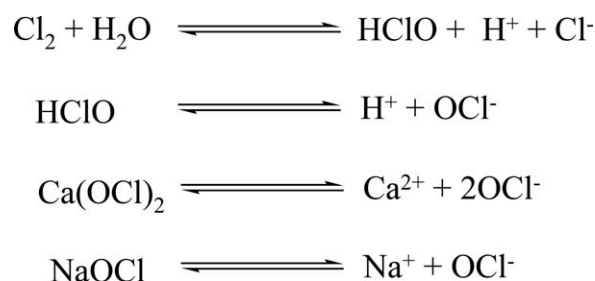

FIGURE 14 Proposed mechanisms of chlorination of aromatic polyamide.

$$Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^-$$

$$HClO \rightleftharpoons H^+ + OCl^-$$

$$Ca(OCl)_2 \rightleftharpoons Ca^{2+} + 2OCl^-$$

$$NaOCl \rightleftharpoons Na^+ + OCl^-$$

FIGURE 15 Hydrolysis and ionization of chlorine and hypochlorites.

process based on chlorine sensitive membranes.[172,173] This dechlorination can be achieved by addition of sodium bisulfite (see Fig. 1). The product water needs to be rechlorinated for disinfection before being distributed. The costly steps of dechlorination and rechlorination have triggered a quest for chlorine tolerant membrane systems. Among various attempts to develop chlorine resistant polymeric materials, the following modifications of aromatic polyamide have been considered as potential strategies.[165,174,175]

1. Replacing chlorine sensitive amidic hydrogen on the amide linkages with other moieties [e.g., methyl ($-CH_3$) or phenyl ($-C_6H_5$)].
2. Replacing the aromatic ring bonded to the amide nitrogen with aliphatic chain or cyclics.
3. Prevention of Orton rearrangement by adding protective groups at the possible chlorination sites on the aromatic rings.

Since tertiary amides do not have an amidic hydrogen, which is the most labile moiety toward chlorine attack, an enhanced chlorine tolerance is expected due to the absence of the active site. This hypothesis was confirmed by conducting chlorine degradation tests with secondary and tertiary amide model compounds. Kawaguchi and Tamura conducted a chlorine stability test with benzanilide (2° amide), N-methyl benzanilide (3° amide), and N-phenyl bezanilide (3° amide).[163] As expected, the chlorine exposed benzanilide
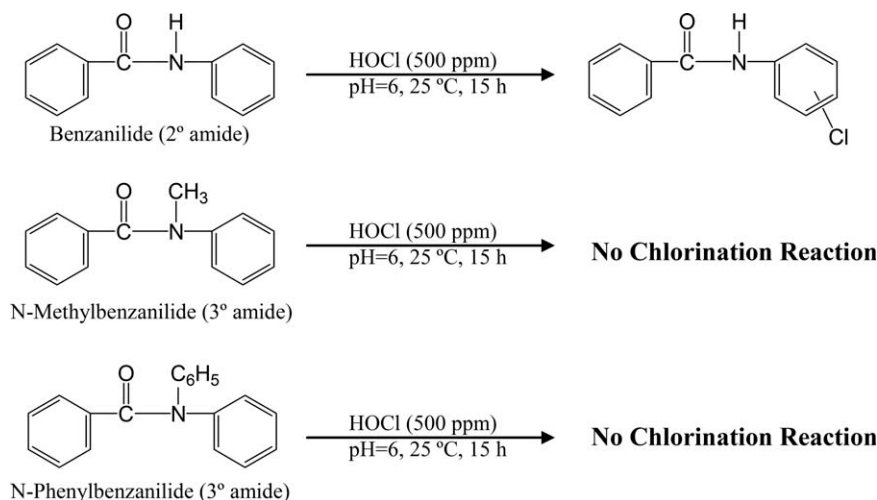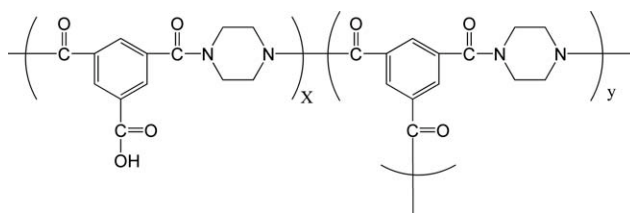

FIGURE 17 An example of polypiperazineamide.

showed significant chlorination on the aromatic ring which is presumably via Orton rearrangement while the two tertiary amide model compounds did not show any evidence of aromatic ring chlorination (Fig. 16).

Use of aliphatic diamines instead of aromatic diamines for chlorine tolerant polyamide synthesis has also been proposed.[163] As shown in Figure 14, it has been demonstrated that a chlorine atom on the nitrogen of the amide migrates to the diamine phenyl ring rather than dicarbonyl phenyl ring via Orton rearrangement. The rearrangement is believed to occur only when the amide nitrogen atom is directly connected to an aromatic ring. Consequently, polyamides which are derived from aliphatic diamines are expected to be free from aromatic ring chlorination. Several aliphatic diamine monomers including ethylene diamine, isopropyl diamine, and p-xylylenediamine (bis-1,4-aminomethylbenzene) were used to form composite reverse osmosis membranes and enhanced chlorine resistances were reported.[164]

According to various reports, the most probable aromatic chlorination site on the diamine phenyl ring via Orton rearrangement is the position ortho to the amide nitrogen.[163-165] Filling this position with substituents such as a methyl group has been proposed to prevent chlorine rearrangement.[165] Although this methodology increased chlorine tolerance, the improvements were limited.

Among numerous attempts to develop a highly chlorine tolerant polyamide material, the polypiperazineamide-based system possessing piperazine moieties is the most interesting (Fig. 17).[176,177] The polypiperazineamide composite
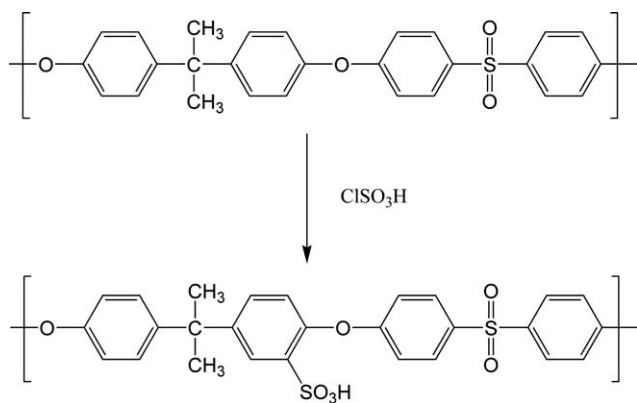

FIGURE 16 Prevention of chlorination by using tertiary amide linkages.

FIGURE 18 Postpolymerization sulfonation of polysulfone by chlorosulfonic acid.

membrane exhibited high flux (71 L m^{-2} h^{-1}) but low salt rejection (50%) with a feed of 0.5 wt % NaCl.[176,177]

The use of piperazine instead of an aromatic diamine monomer meets the former two strategies mentioned above, for example, use of a tertiary amide linkage (eliminating the amidic hydrogen) and a nonaromatic, aliphatic diamine. However, though favorable chlorine tolerance was claimed, no systematic study of chlorine tolerance was reported.[176,177]

New Membrane Approaches

Although various approaches have been explored for developing chlorine tolerant aromatic polyamide materials, the benefits have been very limited since most approaches degrade membrane separation performance. Recently, the use of polymers with robust backbones has gained much attention. The elimination of chlorine sensitive amide linkages in the membrane system may significantly enhance the chlorine resistance and many polymer platforms including polysulfones,[178–181] polyimides,[182,183] polymethacrylates,[184] polybenzimidazoles,[185,186] and styrenics[187–190] have been explored.

Most polymers with stable backbones, such as polysulfone, that exhibit excellent chlorine resistance are intrinsically hydrophobic and have extremely low water permeability. A successful approach for improving water permeability is attachment of hydrophilic ionic groups (such as sulfonate or carboxylate moieties) onto the polymer.[178–180,187–198]

Sulfonated polysulfone-based materials have been studied, and their properties, including high salt rejection and excellent chlorine tolerance, make them attractive alternatives to conventional membrane materials.[178–180] Until recently, most sulfonated polysulfone membranes were made from postpolymerization sulfonated materials. Postpolymerization sulfonation of polysulfone is an electrophilic aromatic substitution reaction and chlorosulfonic acid is the common sulfonation reagent.[178,181] An example of postpolymerization sulfonation of poly(arylene ether sulfone) based on bisphenol-A is illustrated in Figure 18.

Membranes from water soluble or water/alcohol dispersible sulfonated polysulfone materials with various ion exchange capacities (IECs) made via the postsulfonation route have been made by solution coating the polymer onto a porous polysulfone support.[176] The coated sulfonated polysulfone is then thermally cured at 100–140 °C to become water insoluble. The mechanism of sulfonated polysulfone thermal curing is not fully understood but intramolecular crosslinking via the sulfonate moiety has been proposed. Such sulfonated polysulfone-based TFC membranes have shown some promising results including excellent chlorine resistance, high flux, and good antifouling behavior.[179,199–202] However, salt rejection of these membranes is significantly reduced when the feed water has high salinity or contains moderate concentration of divalent cations such as calcium.[199]

Although sulfonatation of polysulfone is easily achieved with chlorosulfonic acid, the harsh reaction conditions cause undesirable degradation and side reactions such as chain scission, branching, and crosslinking.[179,199,200,203] To address these issues, Noshay and Robeson introduced an alternative sulfonation method by using a complex of sulfur trioxide and triethyl phosphate as a sulfonating reagent at room temperature.[180] This route minimizes possible side reactions, but the complexity of controlling the degree of sulfonation and difficulty of handling the chemicals has limited further applications.

Among the several disadvantages of the postsulfonation method, the difficulties of precise sulfonation control and the unclear reaction chemistry have become critical issues for reproducible membrane fabrication. These problems have motivated development of structurally well-defined sulfonated
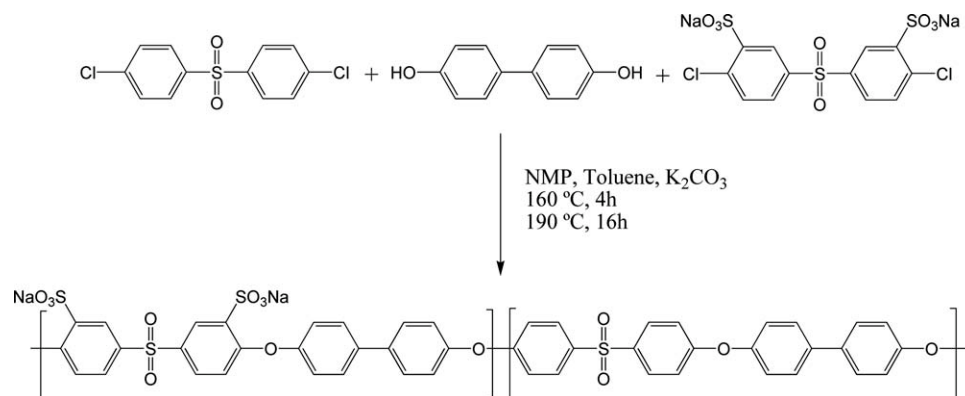

FIGURE 19 Direct copolymerization of sulfonated polysulfone by utilizing S-DCDPS monomer.
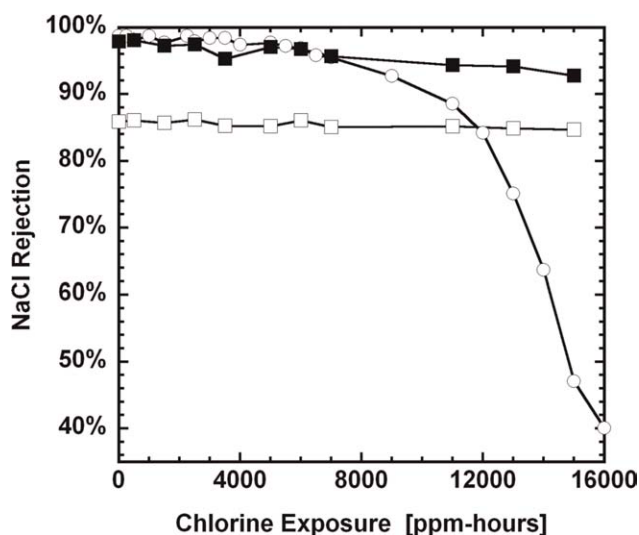
FIGURE 20 A disulfonated directly copolymerized polysulfone membrane [40% disulfonated monomer in the acid form (□) and sodium salt form (■)] exhibits high chlorine tolerance compared to a SW30HR (FilmTec) polyamide membrane (○). Experiments were performed using cross-flow geometry at pH 9.5, Δp = 400 psi, flow rate = 0.8 gal min^{-1}, 2000 ppm NaCl salt feed, 500 ppm Chlorine as NaOCl feed.

polysulfone-based materials via direct copolymerization that afford better control of the sulfonation position and degree of sulfonation in the resulting copolymer. A useful monomer for this purpose, 4,4'-dichlorodiphenyl sulfone (DCDPS), was described by Robeson and Matzner in 1982.[204] Recently, McGrath et al. have prepared wholly aromatic sulfonated poly(arylene ether sulfone)s via the direct copolymerization route, based on this monomer, and have made considerable progress by preparing these materials for ion exchange and water purification applications (Fig. 19).[205–210]

More recently, TFC membranes have been prepared from direct copolymerized sulfonated polysulfone materials; these membranes have been evaluated as potential water purification materials.[211,212] They exhibit high tolerance to chlorine over a wide pH range (from pH 4 to pH 10) as well as good antiprotein and antioily water fouling behavior without performance loss.[213] As shown in Figure 20, both salt and acid forms of sulfonated copolymers have proven to be highly chlorine tolerant with very constant NaCl rejection over continuous long-term chlorine exposure.[212] In contrast, the NaCl rejection of commercial crosslinked polyamide membranes decreases dramatically after only 10,000 ppm-hours of continuous exposure to chlorine.[212]

In addition, very precise control of both IEC and water uptake were achieved via the direct copolymerization methodology (Fig. 21). NaCl rejections ranging from 88% to >99% can be achieved. Figure 22 shows that NaCl rejection depends on the degree of sulfonation as well as the counter-ion form of the membrane. The counter-ion form of the membrane (e.g., acid form, —SO$_3$H, or salt form, —SO$_3$M
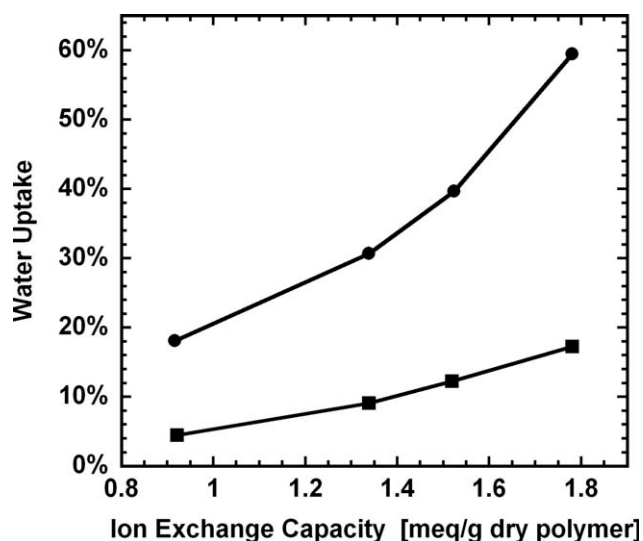

FIGURE 21 Influence of IEC on water uptake[212] of the directly copolymerized sulfonated polysulfone in the acid form (●) and the sodium salt form (■).

where M$^+$ is a cation such as Na$^+$) is known to influence the water uptake and likely the morphology of the polymer.[214–217] For the same degree of sulfonation, membranes in the acid form showed higher water permeability and lower salt rejection than those from the sodium salt form in short-term tests.[212] In longer term RO practice, the acid form should convert to the salt form.

Another system based on direct copolymerization has also been reported.[218,219] It was designed to possess both high water permeability and high salt rejection by combining a high IEC (~2.0 meq g^{-1} dry polymer) with a crosslinked architecture. A series of phenoxide terminated polysulfone-based materials with high levels of sulfonation and different molecular weights (e.g., 3–20 kg mol^{-1}) were prepared. The phenoxide telechelic end-groups were reacted with a
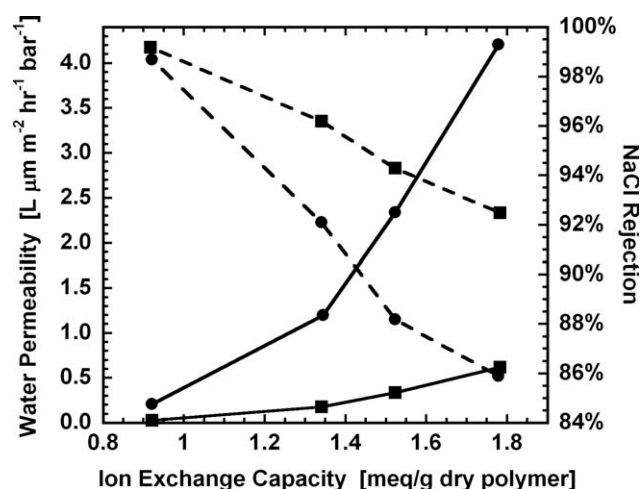

FIGURE 22 Water permeability (solid lines) and NaCl rejection (dashed lines) of the directly copolymerized sulfonated polysulfone[212] in the acid form (●) and the salt form (■).
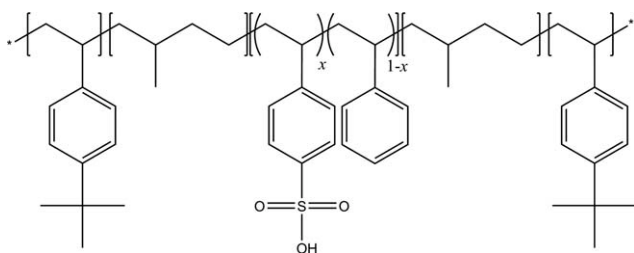
FIGURE 23 Chemical structure of Nexar^{TM} shown in the acid form with a degree of sulfonation shown here as x.

multifunctional epoxy resin and thermally crosslinked. The crosslinked membranes showed significantly higher salt rejection relative to the uncrosslinked counterparts. The salt and water permeabilities were controllable by adjusting the length of the sulfonated oligomer and curing conditions. The 20 kg mol^{-1} sulfonated sulfone oligomer was used for membrane fabrication. A water permeability of 1.4 L μm^{-1} m^{-2} h^{-1} bar^{-1} and a salt rejection of 97.5% were obtained.

Recently, Kraton Polymers LLC announced a commercially available sulfonated polymer called Nexar^{TM} (Fig. 23).[189,190] Nexar^{TM} incorporates polystyrene sulfonate in a unique pentablock copolymer architecture. Unlike previous attempts to sulfonate styrenic block copolymers where typically the end blocks of triblock poly(styrene-co-ethylene-r-propylene-co-styrene) (SEBS) copolymers were sulfonated, the sulfonation of Nexar^{TM} is restricted to the middle block of the symmetric pentablock copolymer.[189] This is made possible by choosing poly(t-butyl styrene) for the endblocks which are not sulfonated since the active para and ortho positions of the phenyl ring are blocked by the t-butyl group and by steric hindrance, respectively. Hydrogenated isoprene blocks are placed between the end and middle blocks for improved mechanical properties; these units are not reactive during the sulfonation step. Sulfonation is restricted to the middle styrene block where it occurs only at the para position of the pendant phenyl group. The result is a material with excellent dimensional stability and wet strength compared to previous attempts to sulfonate SEBS triblock copolymers.[189,220–222]

Nexar^{TM} phase separates into hydrophilic and hydrophobic domains as has been reported via small angle X-ray scattering studies.[223] This phase separation gives the material its high wet strength at high degrees of sulfonation without needing to crosslink the polymer. The degree of sulfonation of other un-crosslinked materials such as the sulfonated polysulfone-based materials discussed above is limited by the wet strength of the material in that, above a certain degree of sulfonation, the polymer will become water soluble.

As has been shown for other sulfonated materials, the hydraulic water permeability[187,188,219] and water vapor transport rate (at 50% relative humidity)[224] of Nexar^{TM} increases as sulfonation is increased due to increased hydrophilicity of the membrane as seen in Figure 24. The dimensional stability and to some extent, the water transport of Nexar^{TM} can be tuned by adjusting the block molecular weights of the base copolymer.
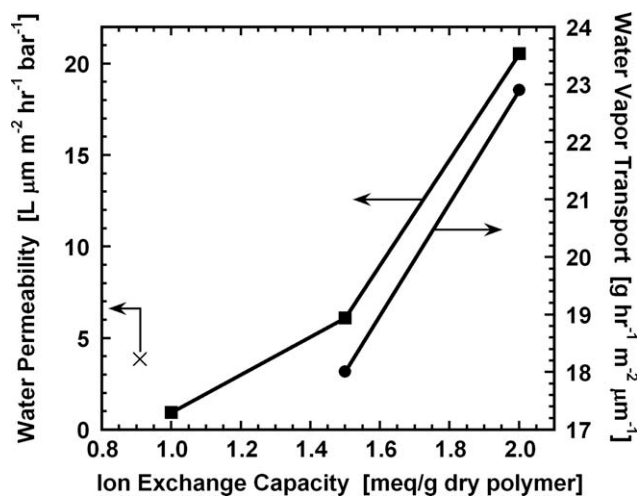
FIGURE 24 Water transport data featuring hydraulic water permeability of Nexar^{TM} (■) and Nafion® 111 (×) and water vapor transport rate for Nexar^{TM} (●).

The salt permeability of Nexar^{TM} and Nafion® is dependent on the upstream or donor cell concentration as can be seen in Figure 25.[187,224] This is believed to be due to Donnan exclusion effects resulting from the ionic sulfonate groups on the polymer backbone.[225] The fixed charge density of the polymer and, then, the salt transport rate, can be tuned by adjusting either the overall sulfonation level or the mid-block molecular weight.

Sulfonated polymers offer promise for desalination membrane technology. However, much remains to be done to
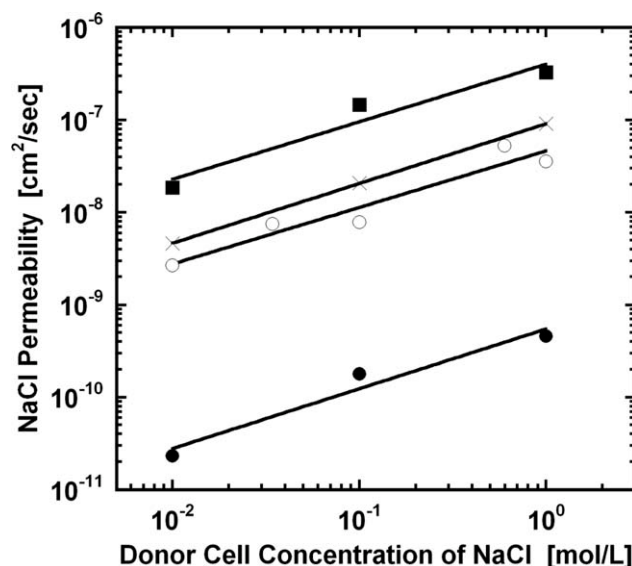
FIGURE 25 Sodium chloride permeability of Nexar^{TM} and Nafion® materials versus upstream concentration of salt shows sodium chloride permeability to be a function of salt concentration. Nexar^{TM} materials are IEC 2.0 (■), IEC 1.5 (○), and IEC 1.0 (●) whereas Nafion® 111 has an IEC of ~0.91 (×) where all IEC values are given in units of milli-equivalents per gram of dry polymer.

optimize their performance as high flux reverse osmosis membranes for both brackish water and seawater desalination. The theory of water and salt transport in this type of material is presented later.

Membranes for Removal of Other Solutes

Until this point, the focus has been on membranes for desalination; however, other water treatment applications pose opportunities for innovative polymer membrane design and optimization. These range from removal of arsenic and boron species to more macroscopic separations such as bacteria or particulates. It is beyond the scope of this article to review all of the possibilities; however, it is instructive to highlight a few examples. At the heart of all of these opportunities is the need for membranes with high flux and high rejection.

Membranes are useful for biological applications including separation of proteins and cell debris, purification of proteins, and removal or separations involving viruses and plasmid DNA.[226,227] A comprehensive review of this area has been given by van Reis and Zydney.[226,227] Key opportunities include reducing fouling in MF and UF membrane systems, increasing the separation resolution so that proteins can be size selected continuously using a membrane as opposed to size exclusion chromatography; membranes for these applications need to be highly defect free, robust, and able to resist harsh chemicals and cleaning environments.[226,227] As some bioprocess technologies move toward smaller scale operation, single-use membranes need to be high quality, inexpensive, easily produced in large quantities, and offer high product throughput.[226,227]

Wastewater effluents from chemical/pharmaceutical manufacturing plants often contain organic/biological contaminants that must be removed before wastewater discharge. These contaminants (including pesticides) have begun to make their way into groundwater requiring their removal in public drinking water treatment systems as well. Membrane treatment for removal of pharmaceuticals (including endocrine disrupters) and other low molecular weight organic contaminants has been studied and reported extensively in the literature primarily using nanofiltration membranes, though ultrafiltration and reverse osmosis membranes have been studied.[228–239] Here, a particular challenge is that these organic molecules, while present in solution at low concentration, may have high partition coefficients in the membrane which reduces rejection.[228,229,231–233,235,237,239] One possible approach for solutions of weak acid or base molecules is to modify the charge of the membrane.[237,240]

Boron[241–258] and arsenic[259–285] removal by membranes have received substantial attention since these contaminants present acute health risks.[13] The World Health Organization has recommended upper limits in drinking water for arsenic and boron of 0.01 mg L^{-1} and 0.5 mg L^{-1}, respectively.[19] Arsenic is typically found in soils and rocks,[286] and the concentration of arsenic in some groundwaters generally varies from 0.001–1 mg L^{-1}.[265,274] Boron is commonly found in seawater at concentrations from 4.5 to 6.0 mg L^{-1}.[13]

Boron exists in natural water in the form of boric acid. With a pK_a of 8.5–9.2 (depending on the ionic strength of the water), boron is essentially un-charged during a membrane filtration process.[13] NF and RO membranes typically exhibit low rejection of un-charged solutes compared to that of similarly sized charged solutes.[13,265] Thus, boron is not typically highly rejected by reverse osmosis membranes; in a typical seawater reverse osmosis single-pass system, boron rejection is typically 75–80%.[13] At these rejection levels, multiple passes are required to reduce the boron concentration in the permeate to acceptable levels.[13,19]

Arsenic, on the other hand, typically exists in natural water in two different oxidation states, As(V) as arsenate (AsO_4^{3-}), which is charged and As(III) as arsenite (AsO_3) which is not charged.[265,285] Of the two species, arsenate [As(V)] is more effectively removed from water by reverse osmosis due to its charged nature.[260,262–265,285] Using a typical reverse osmosis system, As(III) rejections are generally 40–80% and As(V) rejections are greater than 97%.[265,285] It is possible to expose the feed water to an oxidizing agent to convert As(III) to As(V), which increases total arsenic rejection.[265,266,285] As is the case with boron, pH adjustment can be used to increase arsenic rejection without using oxidizers.[263,265,285] However, increases in pH can lead to precipitation and scaling issues in RO membrane systems.[13]

Clearly, targeted removal of other solutes will continue to be an important goal of membrane development. In some cases, these challenges may be met by addressing fouling or surface charge issues. However, in other cases, specifically with uncharged solutes, other mechanisms for solute exclusion are needed.

SOLUTION-DIFFUSION MECHANISM OF TRANSPORT

Water permeates through filtration membranes by pressure gradients within the pores of the membrane. A great deal of evidence has shown that the selective layer of reverse osmosis membranes has no pores (except possibly for a very small number of defects) and should be regarded as a homogeneous structure through which water and salts are transported by molecular diffusion through the polymeric matrix.[1,12,35–40,144–147,287–295] As shown below, the role of the pressure differential Δp is to induce a concentration gradient of water within the membrane that causes a flux of water by molecular diffusion. Salt is transported by a similar diffusion process. However, unlike water, the effect of the pressure differential on salt partitioning into the membrane is generally negligible.[37,39] The following section outlines models for water and salt permeation in membranes that are swollen by water. The extent of water swelling has a significant effect on water permeation, and incorporation of fixed changes onto the polymer chains, for example, by sulfonation or carboxylation, is an effective way of controlling water sorption. Fixed charges also have a significant effect on salt sorption and transport as suggested below. However, a better understanding of these transport processes is needed to optimize membrane structures.

Fick's Law for Membranes

The diffusive flux of a species in a mixture must be expressed relative to some frame of reference. A fixed frame of reference or stationary coordinates is particularly appropriate for membrane systems. The following are two fully equivalent forms of Fick's law for binary diffusion in the z-direction[34]

$$n_1 = w_1(n_1 + n_2) - \rho D_{12} \frac{dw_1}{dz} \qquad (9)$$

$$N_1 = x_1(N_1 + N_2) - CD_{12} \frac{dx_1}{dz} \qquad (10)$$

where n_i is the mass flux of species "i" relative to stationary coordinates, N_i is the molar flux, w_i is the mass fraction of "i", x_i is the mole fraction, ρ is the mass density of the mixture, C is molar density, and D_{12} is the binary diffusion coefficient. One version can be converted to the other by simple definitions. Corresponding relations can be written for component 2 by interchanging the subscripts realizing that $D_{12} = D_{21}$. Equation 10 turns out to be more convenient for mixtures of gases since at constant pressure and temperature, the total molar density, C, is a constant at a fixed total pressure. Equation 9 is more convenient for liquids since the mass density, ρ, of such a mixture is more likely to be nearly constant than C. These relations can be adapted for diffusion of penetrants in a membrane.

First, it is useful to let the membrane component be identified with the subscript m and the penetrant with a subscript, for example, 1; this is particularly useful for the cases when there are other penetrants that can be identified as 2, 3, etc. In some cases, the binary form of Fick's law can be used when there are more than two components but not always. For all practical cases in steady state, the membrane itself is stationary, so the flux of this component is zero. Finally, it is important to recognize that for polymeric membranes molar concentrations and terms like x_i or C in eq 10 are at best ill defined and at worst not meaningful since the molecular weight of the polymer may not be unique or may even be infinite. The earliest thermodynamic treatments of polymer mixtures revealed that mole fractions were not an appropriate concentration scale in such systems.[296] Thus, eq 9 provides a more useful form of Fick's first law for membrane systems. With the simplifications noted above, it becomes

$$n_1 = -\frac{\rho D_{1m}}{1 - w_1} \frac{dw_1}{dz} = -\frac{\rho D_{1m}}{w_m} \frac{dw_1}{dz} \qquad (11)$$

This equation contains the $(1 - w_1) = w_m$ term that arises because of frame of reference considerations (i.e., a convection term). It is necessary to include this term in some cases; however, when the content of penetrant in the membrane is very small, $w_1 \ll 1$, then $w_m \cong 1$. In addition, when the mass density of the membrane-penetrant mixture, ρ, is constant (this will surely be the case when $w_1 \ll 1$), then eq 11 reduces to

$$n_1 = -D_{1m} \frac{dC_1}{dz} \qquad (12)$$

where C_1 = the mass concentration of species 1 and n_1 is the mass flux. Dividing both sides by the molecular weight of 1 leads to

$$N_1 = -D_{1m} \frac{dC_1}{dz} \qquad (13)$$

where now C_1 is the molar concentration of 1 and N_1 is its molar flux; in this simple form the flux and concentration can be written in any units so long as they are consistent.

Theory of Reverse Osmosis for Uncharged Membranes

The above framework can be applied to reverse osmosis as shown below. Water is designated as component 1 and identified by the subscript w. For uncharged membranes, it is not necessary to consider the cation and anion of the salt separately so for the time being the salt can be designated as a simple component using a subscript s.

For reverse osmosis, w_s and n_s are small so eq 11 can be used to describe the water flux. The convective term in the denominator, $(1 - w_w)$, can be ignored when w_w is small; this is sometimes done when w_w is not so small that this approximation applies but doing so results in a redefinition of the binary diffusion coefficient. Equation 11 can be written in the following differential or integrated forms when ρ and D_{wm} are independent of concentration

$$n_w = -\frac{\rho D_{wm}}{1 - w_w} \frac{dw_w}{dz} = \frac{\rho D_{wm}}{\ell < w_m >} (w_{w0} - w_{w\ell}) \qquad (14)$$

The convective term in the denominator of the differential form means the concentration profile, or w_w versus z, is not strictly linear which complicates the integration. To retain the expected form of the integration and its associated physical meaning, it is convenient to define an average value of $1 - w_w = w_m$ designated as $\langle w_m \rangle$. The thickness in eq 14 is the actual thickness of the membrane with a solvent gradient which may differ from the dry thickness when there is no solvent in the membrane or the uniformly swollen thickness. The details of computing $\langle w_m \rangle$ and ℓ are given elsewhere[39,287] and are not repeated here as they detract from our main purpose.

Next, it is necessary to show how the driving force $\Delta p = (p_0 - p_\ell)$ leads to the transport of water across the membrane by a solution-diffusion mechanism.[39] The value of $w_{w0} - w_{w\ell}$ to be inserted in eq 14 stems from the thermodynamic equilibrium the two membrane interfaces have with the upstream and downstream external phases (cf. Fig. 26). The procedure for handling this thermodynamic analysis in reverse osmosis or hydraulic permeation begins from the fact that mechanical equilibrium requires the pressure in a homogeneous, supported membrane to be constant throughout its thickness at the value imposed upstream, p_0, as schematically illustrated in Figure 26.[10,36,38,39,287–295] As also illustrated in Figure 26, the chemical potentials of water in the phases on each side of either membrane-solution interface are equal as stipulated by thermodynamics. Inside either the solution or the membrane phases, assuming these phases
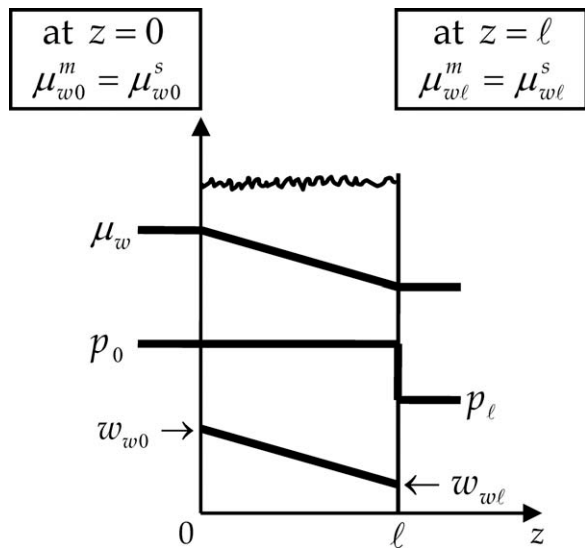
FIGURE 26 Chemical potential, pressure, and weight fraction of water profiles in a nonporous membrane as a function of membrane thickness.

are incompressible, we can write the following expression for the chemical potential of water in terms of activity (or concentration) and pressure:

$$\mu_w = \mu_w^\circ + RT \ln a_w + \overline{V}_w(p - p_r) \qquad (15)$$

where p_r is an arbitrary reference pressure (we will take this to be p_ℓ) and μ_w° is a corresponding integration constant that depends on the reference pressure chosen. From this point forward, superscripts s and m are used to make clear whether we are referring to the solution or membrane phase. In general, the partial molar volume of water may be different in the two phases and could depend on the concentration in these phases; however, in many cases, we may regard $\overline{V}_w$ as independent of composition and the same in both phases. At the upstream interface ($z = 0$), the pressure is p_0 in both the solution and membrane phases while at the downstream surface ($z = \ell$), the pressure in the membrane phase is p_0 but p_ℓ in the solution phase so there is a pressure discontinuity. These considerations lead to the following connections between the activity of water in the membrane at its surfaces to those in the external solution phases

$$a_{w0}^m = a_{w0}^s \qquad (16)$$

$$a_{w\ell}^m = a_{w\ell}^s e^{-\overline{V}_w(p_0 - p_\ell)/RT} \qquad (17)$$

By a suitable theory or by experiment, the relationship between the concentration of water and its activity in a given phase can be established. For example, the Flory-Huggins theory gives a convenient framework for polymer systems.

From eq 16, the solvent concentration in the membrane at its upstream surface in hydraulic permeation is the equilibrium swelling, w_{w0}, of the polymer in pure water ($a_{w0}^s = 1$)

or the upstream solution for the general case. On the other hand, eq 17 shows that the pressure discontinuity decreases the activity of water (hence, its concentration) in the membrane at the downstream surface, that is, water is "squeezed" out leading to a concentration gradient within the membrane. This is the origin of the diffusional flux induced by the pressure applied upstream.

The general results above can be expressed in some commonly used forms by using the definition of osmotic pressure in the external liquid phases, eq 1, and an assumption of ideality in the membrane phase, that is, $a_w^m = w_w/w_w^*$ where w_w^* is the equilibrium swelling of the membrane in pure water. With these simplifications, eqs 16 and 17 can be used to obtain

$$w_{w0} - w_{w\ell} = w_{w0}\left(1 - e^{-\overline{V}_w(\Delta p - \Delta\pi)/RT}\right) \qquad (18)$$

where $\Delta\pi = \pi_0 - \pi_\ell$. When the exponent is small enough, a series expansion of the exponential term is justified such that

$$(w_{w0} - w_{w\ell}) \cong \frac{w_{w0}\overline{V}_w(\Delta p - \Delta\pi)}{RT} \qquad (19)$$

Equations 14 and 19 can be combined to get

$$n_w = \frac{D_{wm}C_{w0}^m\overline{V}_w(\Delta p - \Delta\pi)}{\ell RT} = \frac{P_w C_w^s\overline{V}_w(\Delta p - \Delta\pi)}{\ell RT} \qquad (20)$$

which is the classic result for water flux in reverse osmosis when $\langle w_m \rangle \sim 1$ and $C_w^m = \rho w_w$.[1,39] The extreme right hand version of eq 20 makes use of the definition of the water permeability

$$P_w \equiv D_{wm}\frac{C_{w0}^m}{C_w^s} = D_{wm}K_w \qquad (21)$$

where C_w^s is the concentration of water in the solution phase (essentially a constant) and K_w is the water partition coefficient.

To develop a relation for salt flux from Fick's law, it has been correctly argued for desalination purposes that the pressure should have a negligible effect on salt partitioning into the membrane.[37,39] For uncharged polymers, a constant distribution coefficient for salt (or solute), K_s, between the solution and membrane phases appears to be adequate. Thus, we can write

$$n_s = -D_{sm}\frac{dC_s^m}{dz} \cong D_{sm}\frac{\Delta C_s^m}{\ell} = D_{sm}K_s\left(\frac{C_{s0}^s - C_{s\ell}^s}{\ell}\right) \qquad (22)$$

Here, the salt permeability can be defined as

$$P_s = D_{sm}K_s \qquad (23)$$

and eq 22 can be simplified to

$$n_s = D_{sm}K_s\left(\frac{C_{s0}^s - C_{s\ell}^s}{\ell}\right) = P_s\left(\frac{C_{s0}^s - C_{s\ell}^s}{\ell}\right) \qquad (24)$$

Using the definition of solute rejection, eq 7, and a mass balance, eqs 20 and 22 can be combined to obtain the familiar result[1,39]

$$\mathbf{R} = \left[1 + \frac{D_{sm} K_s RT C_{w\ell}^s}{D_{wm} C_w^m \overline{V}_w (\Delta p - \Delta \pi)} \right]^{-1} \qquad (25)$$

The limitations of the simple theory embodied in eqs 20 and 25 have been described previously.[39]

Salt Partitioning in Charged Membranes

As seen above, addition of ionic groups to the polymer chain, for example, by sulfonation, provides a useful way to tune water sorption and makes it possible to obtain high water permeability with polymers that are more chemically robust or more chlorine resistant. Although the water sorbed into charged polymers may be bound in certain ways, for example, by hydration to immobile ions, it may be possible as a first approximation to use the total water uptake in the theory for water permeation given in the previous section without accounting for such details. However, salt uptake and diffusion in charged polymers membrane will certainly not be adequately described by the simple treatment given earlier where the ionic nature of the salt was not explicitly considered. The fixed charges on the polymer will certainly affect the salt uptake by the membrane, that is, Donnan exclusion, and probably the diffusion through the membrane. These issues will be explored here.

Depending on pH, polyamides like those used in thin film composite membranes can be charged, and this plays some role in their performance. The focus of this section, however, is on polymers having strongly charged units, like $-SO_3^-$, affixed to the backbone. Such materials can be prepared in "acid" or "salt" forms.[180,297] However, in a reverse osmosis application ion exchange with the feed solution will occur so that the "salt" form should be favored. It is well known that the ionic units in ionomers can self-associate to form clusters or "domains."[298–303] This possibility and how it may affect membrane performance has not been explored enough to give any comments here. The following discussion considers the ideal limit where the charged units are homogeneously distributed in the polymer matrix.

In the theory for reverse osmosis given above, it is assumed that salt partitions into the polymer with a simple constant partition coefficient that can be used to calculate the salt concentration in the membrane at its surfaces resulting from equilibration with the external solutions. For charged polymers, the fixed or immobile ions attached to the polymer chain tend to exclude mobile ions of the same charge and, thus, the salt itself, that is, Donnan exclusion. Helfferich[225] gives a good physical description of how this affects salt sorption in ion exchange polymers. Imagine a polymer containing strongly charged groups (e.g., $A^- = -SO_3^-$) immersed in a large volume of a relatively dilute solution of a strong electrolyte (see Fig. 27); for simplicity only monovalent salts, that is, $M^+ X^-$, are considered here. The polymer initially contains counterions, for example, H^+ (acid form) or M^+ (salt form), but no other anions or mobile electrolyte. Of course, the
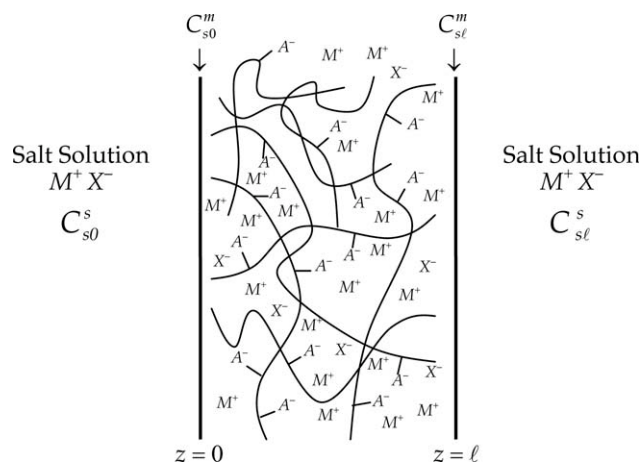

FIGURE 27 Sorption of salt into an ion-exchange membrane.

polymer will sorb water owing to the presence of the hydrophilic ionic groups on its backbone. If the polymer is initially in the acid form, the H^+ ions will eventually be exchanged for M^+ ions, that is, converted to the salt form, owing to the large quantity of solution relative to the membrane. Thus, it is simpler to think of the membrane in the salt form in the first place. The cation concentration in the membrane will be higher than in the solution, but the concentration of mobile anions in the external solution phase will be higher than in the membrane. If these ions carried no charge, diffusion would tend to level out these concentration differences. However, migration of cations into the solution and anions into the membrane would set up an electrical charge difference, or an electrical potential, between these phases. This Donnan potential tends to pull the cations back into the membrane and the anions back into the solution. An equilibrium is eventually established whereby the tendency to equalize the concentrations is balanced by the electric field. The literature contains various quantitative approaches to such an analysis, and one of these is summarized here.[225,304]

The charge density of ion containing materials is often specified in terms of ion exchange capacity, IEC, typically expressed as milliequivalents per gram of dry polymer. As the membrane is swollen by water, it is necessary to account for this to get equivalents per unit volume of membrane, C_A^m, as follows

$$C_A^m = \rho_m \, \text{IEC} = w_m \, \rho \text{IEC} \qquad (26)$$

The ion exchange literature often also expresses mobile ion content per mass of dry polymer, but for diffusion consideration, it is more appropriate to express the content per unit volume of the swollen membrane. The molar concentrations of mobile anions C_X^m and cations C_M^m at any point in the membrane phase are related by the following

$$C_A^m + C_X^m = C_M^m \qquad (27)$$

owing to local charge neutrality. Thus, the "salt" concentration at that point is given by

$$C_s^m = C_X^m = C_M^m - C_A^m \qquad (28)$$

Using this nomenclature, the relationship between the salt concentration in the membrane and in the external solution phase C_s^s at equilibrium can be expressed as follows[1]

$$C_s^m = \left[\frac{1}{4}(C_A^m)^2 + (C_s^s)^2\left(\frac{\gamma_\pm^s}{\gamma_\pm^m}\right)^2\right]^{1/2} - \frac{1}{2}C_A^m \qquad (29)$$

where the $\gamma_\pm$ are the mean activities of the ions in the solution or membrane phase as indicated by the superscript. An alternate approach to the formulation includes addition of terms attributed to "swelling" pressure effects;[225,304] however, this appears to be incorrect. It is useful to express eq 29 in terms of the salt partition coefficient

$$K_s \equiv \frac{C_s^m}{C_s^s} = \left[\frac{1}{4}\left(\frac{C_A^m}{C_s^s}\right)^2 + \left(\frac{\gamma_\pm^s}{\gamma_\pm^m}\right)^2\right]^{1/2} - \frac{1}{2}\frac{C_A^m}{C_s^s} \qquad (30)$$

while the activity coefficients are surely dependent on salt concentration, their ratio may be less so. In the limit of very high salt concentrations in the solution, eq 30 reduces to

$$K_s \rightarrow K_\infty = \frac{\gamma_\pm^s}{\gamma_\pm^m} \qquad \text{when} \qquad C_s^s \gg C_A^m \qquad (31)$$

where K_∞ may be interpreted as the salt partition coefficient that would be observed for a noncharged polymer of equal water uptake. For very low salt concentrations in the solution, the salt partition coefficient predicted by eq 30 becomes

$$K_s \rightarrow \frac{C_s^s}{C_A^m}(K_\infty)^2 \qquad \text{when} \qquad C_s^s \ll C_A^m \qquad (32)$$

To interpret eq 30, it is instructive to discuss reasonable values for C_A^m and K_∞. For materials with promising desalination performance characteristics, such as those discussed earlier, the fixed charge concentrations, C_A^m, fall in the range of 0.8–1 mol L^{-1}. Strictly speaking, the optimal value of C_A^m will depend on the targeted application and the polymer. However, we will consider $C_A^m \cong 1$ mol L^{-1} to be a reasonable value for this parameter. In considering reasonable values for K_∞ different approaches may be taken. Recalling the definition of K_∞ in eq 31, it may be possible to determine values for the activity coefficients in the membrane, $\gamma_\pm^m$, via modeling approaches. Determination of the solution phase activity coefficient, $\gamma_\pm^s$, is more straightforward and both models[305] and published data[306–311] exist. Another approach is to consider K_∞ to be the salt partition coefficient that would be observed for a noncharged polymer with comparable water uptake. Using this approach, the experimental salt partition coefficients for cellulose acetate[35,312] provide an estimate of K_∞ as 0.03. With these approximations, eq 30 can be plotted in the form shown in Figure 28.

Considering that the concentration of NaCl in seawater is approximately in the range of 0.6–0.7 mol L^{-1}, it is reasonable to assume that operation of many desalination processes
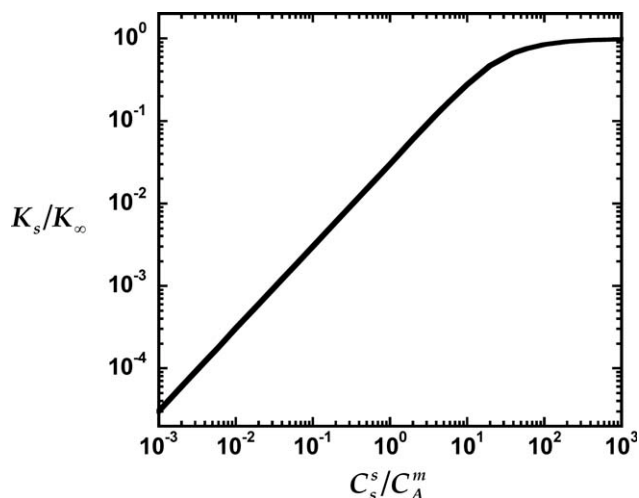

FIGURE 28 When $K_\infty = 0.03$ and $C_A^m = 1.0$ mol L^{-1} normalized partition coefficient K_s/K_∞ can be plotted versus C_s^s/C_A^m using eq 30.

will occur at $C_s^s/C_A^m < 1$ though it is important to note that C_s^s on the feed side of the membrane will be elevated somewhat by concentration polarization and by removal of the product water.

Thus, the theory gives expected scaling laws for the membrane salt concentration and the salt partition coefficient. For dilute salt solutions C_s^m varies as $\left(C_s^s\right)^2$ and inversely with C_A^m. And, for reasonable values of C_A^m, C_s^s, and K_∞, the salt partition coefficient, K_s, can be expected to vary as C_s^s. These scaling laws assume that the fixed charge character of the polymer is homogeneously distributed throughout the volume of the polymer. In practice, deviations from these scaling laws have been observed for ion exchange polymers and attributed to nonhomogeneous charge distribution throughout the volume of the polymer.[313–316]

The equilibrium relationship given by eq 29 should be evaluated at C_{s0}^s to give the concentration in the membrane at $x = 0$ and at $C_{s\ell}^s$ for the concentration in the membrane at $x = \ell$. That is, these relations define the boundary conditions for the diffusion of salt through the membrane suggested in Figure 27. Of course, an important issue is how to quantify these relationships, and there is very limited literature to use as a guide. Molecular simulation techniques might be a valuable source of insight and perhaps quantitative information.

Salt Transport in Charged Membranes

The simple diffusion equations used earlier do not provide a basis for dealing with the electrical forces that affects ions nor do they allow a means for dealing with the multicomponent nature of even the simplest case where there are four components; that is, polymer, water, one cation, and one anion. The Maxwell-Stefan equations, originally derived from kinetic theory to describe multicomponent diffusion in low-density gas mixtures[34,317] provide a useful framework for liquid and polymeric systems.[34,318,319] A general form of the

one-dimensional Maxwell-Stefan equations for isothermal multicomponent mixtures can be written as

$$d_i = -\sum_{j \neq i} \frac{x_i x_j}{Ð_{ij}}(v_i - v_j) \qquad (33)$$

where the $Ð_{ij}$ are multicomponent diffusion coefficients,[34] x_i is the mole fraction of i in the mixture, and v_i is the velocity of i in the z-direction relative to stationary coordinates. The term d_i is a generalized force (in the z-direction) for component i that causes it to diffuse relative to other species. Its general form is[34]

$$CRT d_i = C_i \frac{d\mu_i^m}{dz} - w_i \frac{dp_m}{dz} + C_i z_i F \frac{d\phi}{dz} \qquad (34)$$

where

$$\frac{d\mu_i^m}{dz} = RT \frac{d \ln a_i^m}{dz} + \overline{V}_i \frac{dp_m}{dz} \qquad (35)$$

In these equations, C is the molar density of the mixture, C_i is the molar concentration of i (note $x_i = C_i/C$), z_i is the charge on species i (+ for cations, − for anions), F is the Faraday constant, ϕ is the electrical potential, μ_i^m is the chemical potential of i in the membrane, a_i^m in the activity of i in the membrane, and p_m is the pressure in the membrane. For nonporous supported membranes, the pressure throughout the membrane is constant[36,38,39,287–295] as discussed earlier. So, for the cases of interest here, $dp_m/dz = 0$. As a result, eq 33 simplifies to

$$-\sum_{j \neq i} \frac{x_i x_j}{Ð_{ij}}(v_i - v_j) = x_i \left[\frac{d \ln a_i^m}{dz} + z_i \frac{F}{RT} \frac{d\phi}{dz} \right] \qquad (36)$$

The pressure that drives transport by the solution-diffusion process does not appear in the flux law but comes in via the boundary conditions used in the integration of these equations as seen earlier.

Equation 36 can be expressed in forms more useful for describing diffusion in membranes. At steady state, the velocity or flux of the membrane material is zero relative to stationary coordinators, that is, $v_m = n_m = 0$. Penetrant velocities can be converted to either molar fluxes $N_i = x_i C_i v_i$ or mass fluxes $n_i = w_i \rho v_i$ where ρ is the mass density of the membrane-penetrants mixture. As noted earlier, mole fractions are not useful for membrane systems; this issue can be resolved by converting to volume or mass fractions as discussed in recent articles.[39,320,321] Mass fractions and fluxes will be used here, and the conversion can be accomplished by the following

$$x_i = \frac{M}{M_i} w_i, \quad M = \left[\sum \frac{w_j}{M_j} \right]^{-1} \qquad (37)$$

where M_i is the molecular weight of i and M is the number average molecular weight of the mixture. It could be said that M is ill defined because of the ambiguity of the molecu-

lar weight of the membrane material; however, this potential complication appears to be resolved by redefining the diffusion coefficients. In the end, these diffusion coefficients must be determined experimentally. With the conversion to mass fractions, it becomes useful to redefine the diffusion coefficients in the following way

$$D_{ij} = Ð_{ij} \frac{M_j}{M} \qquad (38)$$

since they always appear in these combinations;[39,320] similar redefinitions in terms involving molar volumes are needed when expressing eq 36 in terms of volume fractions.[321]

For simplicity, only 1–1 electrolytes $M^+ X^-$, such as sodium chloride, are considered in the following. It is useful to begin with the analysis of simple salt diffusion in water where there is no electric current flow.[34] The salt is considered to be fully dissociated and the two ions have different mobilities; however, the molar flux of the two ions will be equal to preserve charge neutrality and no current flow. This is assured by the electrical potential terms in the Maxwell-Stefan equations that can be written for the M^+ and X^- species as follows[34]

$$\frac{1}{CÐ_{Mw}} [x_w N_M - x_M N_w] = -x_M \frac{d \ln a_M^m}{dz} - \frac{x_M F}{RT} \frac{d\phi}{dz} \qquad (39)$$

$$\frac{1}{CÐ_{Xw}} [x_w N_X - x_X N_w] = -x_X \frac{d \ln a_X^m}{dz} + \frac{x_X F}{RT} \frac{d\phi}{dz} \qquad (40)$$

These are equivalent to the Nernst-Planck equations.[225] The terms involving the potential gradient can be eliminated between the two equations using the simplifications $N_M = N_X = N_s$ and $x_M = x_X = x_s$. The gradient in electric potential can be eliminated between these two equations to obtain the following expression for salt flux

$$N_s = \left[\frac{1}{CÐ_{Mw}} + \frac{1}{CÐ_{Xw}} \right] \left(\frac{d \ln a_s^m}{dz} \right) + x_s (N_s + N_w) \qquad (41)$$

where $a_s \equiv a_M a_X$. For dilute solutions, this can be recast into the following form with the aid of eq 38

$$N_s = -C \left[\frac{D_{Mw} D_{Xw}}{D_{Mw} + D_{Xw}} \right] \left(\frac{d \ln a_s^m}{d \ln x_s} \right) \left(\frac{dx_s}{dz} \right) + x_s [N_s + N_w] \qquad (42)$$

which is identical to Fick's law, eq 10, with

$$D_{sw} = \left[\frac{D_{Mw} D_{Xw}}{D_{Mw} + D_{Xw}} \right] \frac{d \ln a_s^m}{d \ln x_s} \qquad (43)$$

The Maxwell-Stefan equations correctly account for the convection terms; however, when these terms can be ignored, eq 42 can be expressed as

$$N_s = \left[\frac{D_{Mw} D_{Xw}}{D_{Mw} + D_{Xw}} \right] \left(\frac{d \ln a_s^m}{d \ln C_s^m} \right) \left(\frac{dC_s^m}{dz} \right) = -D_{sw} \frac{dC_s^m}{dz} \qquad (44)$$

The effective diffusion coefficient for salt in water includes a contribution from the thermodynamics of the salt-water

mixture. The two ions with their hydration layers generally have different mobilities, that is, $D_{Mw} \neq D_{Xw}$;[322,323] as may be seen, the species with the lower mobility dominates the salt diffusion rate owing to the electrical potential forces that force them to move at the same rate.

A similar analysis can be made for salt permeation through a water-swollen membrane. Of course, the inclusion of the membrane as a component adds to the number of terms that must be considered and for reasons explained earlier, it is necessary to move away from mole fractions to express composition of water and ions in the membrane. To simplify the analysis somewhat, it is convenient to set the flux of water through the membrane N_w equal to zero. This is not a serious limitation for a simple salt permeation experiment. After much algebra, the Maxwell-Stefan equations can be used to obtain the salt flux, $N_s = N_M = N_X$, expressed in similar form as eq 44

$$N_s = - \left[\frac{D_M D_X}{D_M + D_X} \right] \left(\frac{d \ln a_s^m}{d \ln C_s^m} \right) \frac{dC_s^m}{dz} \qquad (45)$$

where

$$\frac{1}{D_M} = \frac{w_m}{D_{Mm}} + \frac{w_w}{D_{Mw}} \qquad (46)$$

$$\frac{1}{D_X} = \frac{w_m}{D_{Xm}} + \frac{w_w}{D_{Xw}} \qquad (47)$$

The essential difference here is the accounting for the frictional forces diffusing ions experience with the polymer in addition to those with the water.

Finally, a similar analysis can be made for ion diffusion in a charged polymer. As before, the water flux is neglected which is only a small limitation for a salt permeation experiment but this simplification needs to be examined more carefully when using the results to analyze reverse osmosis experiments. For a water-swollen membrane containing C_A^m equivalents of strong acid units per unit volume in the salt form, a Maxwell-Stefan analysis leads to the following expression for salt flux

$$N_s = - \frac{C_M^m C_X^m D_M D_X}{C_M^m D_M + C_X^m D_X} \frac{d \ln a_M^m a_X^m}{dz} \qquad (48)$$

where the diffusion coefficients are the same as defined by eqs 46 and 47. As we can set $C_X^m = C_s^m$ and $C_M^m = C_A^m + C_s^m$, the flux expression can be rewritten as

$$N_s = - \frac{\left(C_A^m + C_s^m \right) D_M D_X}{\left(C_A^m + C_s^m \right) D_M + C_s^m D_X} \left(\frac{d \ln a_M^m a_X^m}{d \ln C_s^m} \right) \frac{dC_s^m}{dz} \qquad (49)$$

This equation differs from the corresponding result for an uncharged polymer in several regards. As $C_M^m \neq C_X^m$, this affects how the D_M and D_X terms appear in the effective diffusion coefficient; the mobile ion in the lowest concentration (X) tends to dominate the diffusion process. The activity derivative is now more complex for the same reason, and there

is little guidance from the literature on how this will compare to the corresponding term for the uncharged membrane, see eq 44. Of course, the salt concentrations at the membrane surface are lower than in the case of the uncharged membrane which will have the effect of reducing salt flux or improving rejection.

It is instructive to consider the limit when $C_s^m \ll C_A^m$. The flux equation becomes

$$N_s = -D_X \left(\frac{d \ln a_M^m a_X^m}{d \ln C_s^m} \right) \frac{dC_s^m}{dz} \qquad (50)$$

Thus, the salt diffusion is entirely determined by the mobility of the anion X^- in the membrane. If we can assume the salt content in the downstream solution is negligible compared to the upstream value, then the concentration gradient can be approximated as C_{s0}^m / ℓ and using eq 32 when $C_s^s \ll C_A^m$, the salt permeability becomes

$$P_s = \frac{N_s \ell}{C_{s0}^s}$$
$$= D_X \left(\frac{d \ln a_M^m a_X^m}{d \ln C_s^m} \right) \frac{C_{s0}^s}{C_A^m} \left(\frac{\gamma_\pm^s}{\gamma_\pm^m} \right)^2 = D_X \left(\frac{d \ln a_M^m a_X^m}{d \ln C_s^m} \right) \frac{C_{s0}^s}{C_A^m} (K_\infty)^2 \qquad (51)$$

If the thermodynamic terms are effectively constant, the salt permeability varies with the upstream salt concentration. Since Donnan exclusion results from fixed charge groups bound to the polymer backbone, increased fixed charge concentration (related to the polymer's IEC) results in decreased salt partitioning. Thus, salt permeability is inversely related to the polymer's fixed charge concentration. As the salt content in the feed increases, Donnan exclusion will diminish.[324–326]

OTHER MEMBRANE PROCESSES

Forward Osmosis for Desalination
Water can also be purified by a process known as forward osmosis whereby water from the feed solution is driven through the membrane by a draw solution of a lower solvent chemical potential; thus, the driving force for water transport is the osmotic pressure difference across the membrane.[327] One such example is the so called ammonia-carbon dioxide forward osmosis desalination process where an ammonium bicarbonate draw solution extracts water from a saline feed solution.[328–330] The ammonium bicarbonate can then be removed as ammonia and carbon dioxide to yield the pure water product by heating the draw solution; in this system, the ammonia and carbon dioxide can then be recycled back as fresh draw solution.[328–330]

Forward osmosis can be applied to a wide variety of applications including water treatment, food processing, controlled drug release devices, and desalination as discussed in the literature.[327] In desalination via forward osmosis, the draw solution must be chosen such that the water collected from the salinated feed can be easily purified.[327,328,331] Several draw

solutions have been studied, and these have been reviewed in the literature.[327,328] As long as an effective, easily removable, and recyclable draw solvent can be used, forward osmosis desalination could potentially be less energy intensive than reverse osmosis desalination.[330]

One critical challenge facing forward osmosis technology is the design of the membrane itself. Specifically, the challenge is to design a membrane that reduces both internal and external concentration polarization where the former is believed to be the greater challenge.[327,332–336] When a typical asymmetric or composite membrane is used in forward osmosis, internal concentration polarization can occur in the porous support layer of the membrane, greatly reducing the driving force for transport and, thus, the flux of solvent.[327] Cath et al. indicated that the ideal forward osmosis membrane would consist of a thin and dense selective layer with a thin support layer that has necessary mechanical strength and a low porosity to minimize internal concentration polarization while not impeding membrane flux.[327] Of course, as is the case with most membrane-based separations, membranes with high flux and high rejection are required. Furthermore, fouling issues, as discussed previously, also apply to forward osmosis systems. These issues represent areas where developments in polymer science and membrane design could aid the development of forward osmosis technology.

Power Generation

Purification of water by any process consumes energy; however, in principle, it is possible to turn this around and generate power using the difference in salinity of two bodies of water. This concept was first proposed by Loeb[337–339] and was termed pressure-retarded osmosis. The idea is to capture some of the free energy of mixing contained in an aqueous salt solution. To do this requires a membrane-based power generating system where there is a supply of salt water and of fresh water, for example, where a river flows into the sea. If fresh water and the salt water streams are allowed to flow past a reverse osmosis membrane, there will be a tendency for the fresh water to permeate through the membrane into the salt water (osmosis) at a flux equal to $-A\Delta\pi$ according to eq 4 or the $\Delta p = 0$ intercept in Figure 2. If the salt solution is pressurized to $\Delta p < \Delta\pi$, osmosis still occurs, but the volume flow across the membrane acting against this pressure can do work. This work can be converted into electrical power via a turbine generator.[335–338,340–343]

The theoretical power generation per unit area of membrane is given by

$$\text{Theoretical Power} = \text{Flux} \cdot \Delta p = A(\Delta p - \Delta\pi)\Delta p \quad (52)$$

The potential power generation will be of a parabolic form when plotted versus Δp and goes to zero when $\Delta p = 0$ or $\Delta p = \Delta\pi$, and the maximum power generation possible occurs when $\Delta p = \frac{1}{2}\Delta\pi$ and is $A(\Delta\pi)^2/4$. There are, of course, inefficiencies in both the membrane and the turbine.

Clearly, the best membrane is one capable of a very large flux, that is, large A in eq 4 and with high salt rejection. However, it has been shown that a significant limitation is the resistance to salt transport in the porous substructure.[327,332–336] The skin surface would be placed on the salt water side where concentration polarization can be managed by fluid mechanics. However, there is a significant polarization of the salt passing through the membrane that does not exist in reverse osmosis. In the latter, the water flow sweeps this salt out by convection; however, in pressure-retarded osmosis the water flow is in the opposite direction and cannot assist with this problem. This has been a major limitation, that, in the past, has prevented this process from being economical.[335,336,338,340] This problem could be reduced by membranes that intrinsically have lower salt permeability while at the same time having high water flux.

In addition, some redesign of the porous support to help minimize this problem may be possible. Although this technology has not been economically attractive in the past, the current high costs for energy plus the prospect for improved membranes has caused at least one company, Statkraft of Norway, to relook at this technology.[341,342,344,345]

Electrodialysis

Both desalination and power generation can be accomplished using electrodialysis[346–350] and reverse electrodialysis,[335,351–359] respectively. It is generally accepted that electrodialysis, as a desalination process, is limited to brackish or ultra-high purity water applications due to the high level of energy that would be required to use the technology in seawater applications—though some seawater systems have been proposed.[346–348,350]

Electrodialysis and reverse electrodialysis rely on the implementation of both cationic and anionic membranes where cationic membranes have negative fixed charge groups and anionic membranes have positive fixed charge groups. In these technologies, alternating series of cationic and anionic membranes form flow channels as shown in Figure 29.
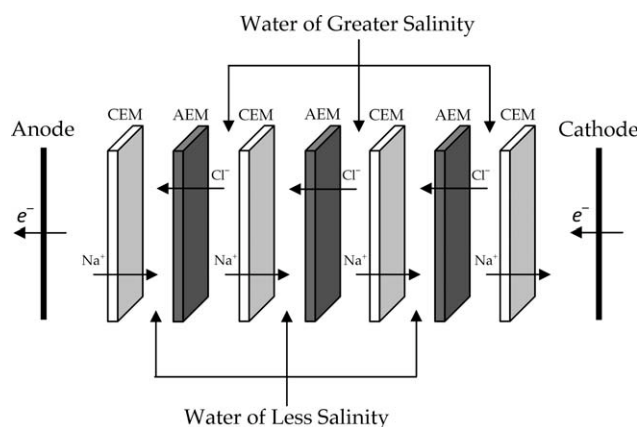

FIGURE 29 Diagram of an electrodialysis system showing alternating cation exchange membranes and anion exchange membranes and the alternating flow of ions through those membranes.

When solutions of different salinity are passed in countercurrent flow through alternating flow channels as seen in Figure 29, cations can preferentially pass through the cation exchange membranes and anions can preferentially pass through the anion exchange membranes.[350,352,357] Electroneutrality is maintained in electrodialysis by applying a potential across the series (or stack) of membranes and flow channels.[346–350] In reverse electrodialysis, electroneutrality is maintained by charge collectors on either side of the system.[352,357] An electric potential is established as a driving force to pass current through an external circuit.[352,357]

Electrodialysis for desalination may have advantages over technologies such as reverse osmosis in that electrodialysis may be less sensitive to feedwater quality—thus reducing need for pretreatment steps, it may be possible to run electrodialysis at a higher recovery compared to reverse osmosis, and the electrodialysis system may be easier to clean than an RO module.[346]

Power generation by reverse electrodialysis was suggested as early as 1954,[360] and has received considerable attention in years since.[335,351–354,356–358,361–364] Many studies have been conducted to show that reverse electrodialysis could be a viable option for power generation if the process can be suitably optimized—these have been reviewed recently in the literature.[357]

Membranes for both electrodialysis and reverse electrodialysis must be able to transport individual ions with very high selectivity to either purify water or generate electric power efficiently.[352,357] Membranes must have low electrical resistance and high ion selectivity; both of these characteristics have been shown to be dependent on membrane charge density.[352,357] It has been suggested that the spacers used to separate the membranes and, thus, create flow channels in the system could be incorporated into the membrane itself—thereby increasing system efficiency.[365] The membranes for these applications should be robust and relatively easily and reproducibly manufactured at large production scales.[352] Water permeability or flux is not as important in these applications as in the others mentioned in this review. However, the same issues relating to fouling, scaling, and chemical resistance (including chlorine tolerance) apply to electrodialysis and reverse electrodialysis membranes.

SUMMARY AND CONCLUSIONS

The global challenge of providing safe water for human use, agriculture, and manufacturing for an ever growing and shifting population poses an opportunity for innovations in polymer chemistry, physics, and engineering. In many ways, the supply of energy is intimately connected to that of water as pointed out here. Because of their energy efficiency and other advantages, membrane processes will become the dominant technology for water purification. However, to meet the needs of the future, better membranes and membrane processes must be developed.

These goals will be facilitated by building a stronger scientific understanding of the structure-property relationships of polymers of interest as membranes for water purification and how these materials are formed into functional and efficient membranes. A key part of this is a better understanding of how water and the solutes, especially salts, and particulate matter that need to be removed interact with the polymer and are transported within the membrane structure.

In nearly all cases, water purification processes would benefit from membranes with higher productivity and selectivity; both are determined by membrane structure. The physical morphology of all practical membranes is complex. Better ways are needed to control and analyze their structure and to assess its impact on transport of water, solutes, and particulate matter. For membranes that function by pore flow mechanisms, the selectivity of the membrane is determined by the size, distribution, and interconnectivity of these pores plus surface and charge interactions. For membranes that function by a solution-diffusion mechanism, there must be an extremely thin dense layer to achieve a high flux but with few defects to realize the intrinsic selectivity of the polymer. There is a dearth of systematic studies of the relation between transport behavior and polymer molecule structure. The polymer literature has not addressed at any level the fundamental issue of characterization and behavior of thin films with thickness of the order of 100 nm or less[366] in an aqueous environment. These layers must be supported on some form of porous substrate made of the same or a different polymer. Understanding and optimizing polymer morphology of these types could pay huge dividends.

The understanding of the partitioning of solutes, particularly ionizable salts, from an aqueous phase into a water swollen polymer has not been studied with sufficient depth. When the polymer is charged, as many membranes for water purification are, the only guide to its sorption of ions is the ion exchange literature which, at best, is lacking in adequate experimental data, a sound theoretical framework, and any clear understanding of how the nature of the polymer influences this important behavior. The understanding of salt transport in such cases is largely devoid of systematic experimental or theoretical analysis. This is in stark contrast to the very detailed exploration of how gases permeate through polymers that has been motivated by membrane-based gas separations.[367]

Membranes used to process aqueous feed streams are prone to fouling via a variety of mechanisms; biofouling processes are among the most troublesome. Solving, or at least managing, these problems would have a huge impact for society. Contemporary approaches include grafting polymer chains to the membrane surface, addition of highly permeable coatings, manipulation of surface charge, etc. Innovations in these or other approaches are critically needed.

Increased membrane durability or life-time is another key to affordability. The polymer used must be robust enough to survive aggressive environments for many years. This includes operating over a wide range of pH and conditions where hydrolysis reactions are favored and many forms of

undesirable biologically driven chemistries are possible. One particular problem receiving much attention today is improving the resistance to chlorine used to disinfect water and curb biofouling.

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