

Water and Salt Transport Behavior through Hydrophilic-Hydrophobic Copolymer Membranes and Their Relations to Reverse Osmosis Membrane Performance

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INTRODUCTION

Sulfonated copolymers are one of the most attractive areas of research due to their versatile applications. More recently, sulfonated polymers have received significant attention related to their use as fuel cell membranes¹. Sulfonated polymers have also been considered as interesting membrane materials for ultrafiltration (UF)², nanofiltration (NF)³ and reverse osmosis (RO)⁴. These materials exhibit good resistance properties to bio-, protein-, and oily water-fouling due to their hydrophilic nature and negative surface charge. They also exhibit high tolerance to chlorine⁵, which is a problem with current commercial polyamide RO membranes. However, in previous work, the widespread use of sulfonated polymer membranes was hindered by the fact that they were prepared using post-polymerization sulfonation employing very strong sulfonating agents (i.e., chlorosulfuric acid and sulfuric acid). These sulfonation techniques resulted in undesirable chain scission, branching and crosslinking. That is, their stability and performance characteristics as membranes for water purification were not sufficient for commercial practice. Fortunately, a promising development in this area has been achieved via the synthesis of tailor-made sulfonated copolymer membranes via direct copolymerization of disulfonated monomer⁶. These sulfonated copolymer membranes can be reproducibly prepared with different morphologies, and they exhibit excellent hydrolytic and thermo-oxidative stability⁷. Therefore, in the present study, these sulfonated copolymers have been highlighted as potential membranes for RO. The current work includes studies of antifouling properties and chemical stability against free chlorine attack, as well as fundamental RO separation performance (e.g., water permeability and salt rejection at various operating conditions (i.e., feed concentration, feed pressure, and feed flow-rate)). Intrinsic properties of the membranes, such as salt partition coefficient and diffusivity, will be discussed as will the tradeoff relationship between water flux and salt rejections in this family of materials.

EXPERIMENTAL

Synthesis. The synthesis of sulfonated copolymers was carried out as previously reported⁶. The basic chemical structure of the sulfonated copolymers used in this study is shown in Figure 1. Usually, the copolymers contained approximately 20-40 mol% of the disulfonated monomer.

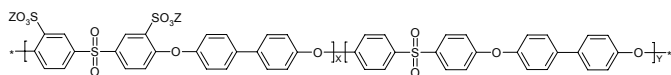


Figure 1. Chemical structure of representative sulfonated copolymer membranes (disulfonated poly(arylene ether sulfone) copolymer (BPS); X=0.20, 0.30, 0.35, 0.40; Y=1-X; Z= H⁺ or Na⁺)

Membrane Preparation. The sulfonated copolymer membranes were prepared by casting a 10% (w/w) solution of the copolymer in *N,N*-dimethylacetamide (DMAc, Aldrich) onto a clean glass plate. The copolymer solution, filtered through a 4.5 μ m porous steel filter, was cast onto a glass plate. The cast membranes were dried in a vacuum oven at 110-120 °C overnight. Membranes were removed from the

glass plate by immersing them in deionized water (Millipore). For acidification, the membranes were refluxed in 0.5M sulfuric acid for 2h. Membranes were then removed from the acid solution, rinsed with deionized water and refluxed with deionized water for 2h. The resulting membranes were stored in deionized water before use for RO test and salt permeability measurements.

RO Membrane Test Unit. A laboratory-scale RO test unit was used for the membrane studies. The system utilizes a Lesson motor coupled with a Hydra-Cell pump capable of providing pressures up to 500 psi (3447 kPa) and a maximum crossflow of 3.8 liter per minute (1 gallon per minute). Temperature control was achieved by passing chilled water through a cooling coil submerged in the feed tank. Membrane coupons (effective membrane area: 22cm²) were mounted in custom-made crossflow test cells.

Kinetic Desorption Measurement. The diffusivity of salt (i.e., NaCl, CaCl₂, Na₂SO₄) in the membranes was determined from the salt desorption rate into deionized water bath from a membrane previously equilibrated with the salt solution of interest⁸. The membranes used for kinetic desorption experiments were equilibrated with 5 wt.% salt solution (50mL) at 25 °C for at least 48h while slowly stirring the solution at or less 100 rpm. Then, the films were blotted with tissue paper to remove excess surface water and sorbed salt and introduced into the extraction (i.e., desorption) bath containing already air-saturated deionized water to minimize the effect of atmospheric carbon dioxide on conductivity. The temperature of the deionized water (50mL) in the extraction bath and in the conductivity cell was maintained at 25 °C. A conductivity cell with a cell constant of 0.1 cm⁻¹ (LR 325/01, WTW, Germany) and a conductivity meter (Inolab Cond 730, WTW) were used to record the conductivity in the extraction baths as a function of time.

Direct Transport Measurement. The salt permeability through the membranes was determined from direct transport measurement using a custom-made two-chamber diffusion cell (9mm Horizontal Cell, PermeGear). The volume of each chamber is 3 mL. A membrane is clamped between two chambers, and one side of the cell is filled with the salt solution of interest (i.e., 0.1M NaCl solution) and the other side is filled with deionized water. The concentration of salt in receiving cell was measured using an ion-selective electrodes (sodium or calcium, as appropriate) and/or a conductivity cell. The salt permeability (P_s) was obtained from the following equation:

$$\ln(1-2C_R(t)/C_D(0)) \cdot (-Vd/2A) = P_s t \quad (1)$$

Where $C_R(t)$ and $C_D(0)$ are receiver and donor cell concentrations (M), respectively, V is receiving solution volume (cm³), d is membrane thickness (cm), and A is effective membrane area (cm²).

RESULTS AND DISCUSSION

In general, a study of the water sorption suggests possible application of the sulfonated copolymer membranes. Basically, current sulfonated copolymer membranes are available in two different forms; acid and sodium salt forms. The water uptake (%) of the sulfonated polymer membranes increased with the content (mol%) of sulfonated monomer (3,3'-disulfonated 4,4'-dichlorodiphenyl sulfone) or ion exchange capacity (IEC, meq/g). As shown in Figure 2, the water permeability of the acid form was higher than that of sodium salt form because, in the case of sodium salt form, sodium ions are strongly bound to the sulfonate groups via Coulombic forces, leading to a slightly basic or neutral state for the polymer. Irrespective of acid or salt form, water permeability through the membranes increased with water uptake so that water permeability is strongly dependent upon water uptake in these polymers. At above 40 mol% of sulfonated monomer, the sulfonated polymer membranes in the acid form tend to be excessively water-swollen, which results in high water permeability but low salt rejection and poor mechanical properties in fully hydrated state.

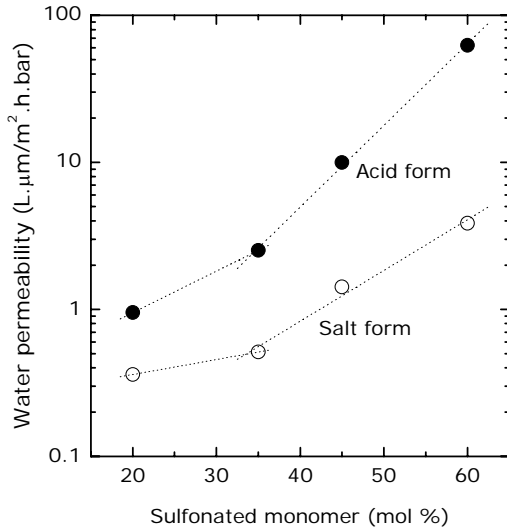


Figure 2. Water permeability of sulfonated copolymers in acid and salt form at 25 °C as a function of sulfonated monomer content.

In this study, sodium chloride (NaCl) was used as a primary solute for monovalent ion rejection studies. The salt rejection experiments were performed in the cross-flow system using feed solutions containing 2000 mg/L of NaCl (2000 ppm). The salt rejection (R) describes the fraction of the depletion of salt in the permeate compared with that in the feed²:

$$R(\%) = (1 - C_p/C_f) \times 100 \quad (2)$$

where C_p is the salt concentration in the permeate, and C_f is the salt concentration in the feed water. Both C_p and C_f were measured with a conductivity meter. Generally, salt rejection (%) of the sulfonated polymers decreased with the content of sulfonated monomer at the same operating conditions (pressure difference and temperature). This might be caused by the increase of hydraulic permeability with increasing sulfonation degree. The sulfonated polymer membranes often showed good rejection toward dilute salt solution such as tap water or 0.1 wt.% aqueous NaCl solution. However, salt rejection levels decreased with a rapid fall off at increasing salinities. That is, in sulfonated aromatic polymer membranes, Donnan ion exclusion might be a dominant factor in their RO performance. In dilute feed waters, these negatively charged membranes exclude feed water anions (i.e., Cl⁻) from entering the membranes by charge repulsion effects, thus inhibiting salt passage. In more concentrated feed salt solutions, the charge repulsion effects are shielded by the high ionic activity of the feed water. That is, with increasing feed concentration, this exclusion becomes less effective because the concentration of the co-ion in the membrane is very low. In every case, the sodium salt-form showed higher salt rejection than the acid form, as shown in Table 1.

Thermodynamic partitioning (solubility, S) and molecular diffusivity (D) within the membrane are the most important factors to explain molecular scale separation in RO membranes. It is believed that the water flux is proportional to the applied feed pressure but that salt passage is independent of pressure in RO membranes. Therefore, the salt permeability of the membranes in the fully hydrated state can be regarded as a good barometer of the tradeoff between water permeability and salt rejection in RO membrane materials. For instance, although the solubility of NaCl in polyamide (PA) membranes is higher than that in cellulose acetate (CA) membranes, PA membranes will reject salt better than CA membranes because the diffusivity of NaCl through the PA membranes is considerably lower,

and the permeability of water through them is higher than that in CA membranes¹⁰.

Table 1. Water Permeability and Salt Rejection of BPS 40 series (Crossflow Experiment at 25 °C)

Sample	BPS 40 (acid form)	BPS 40 (salt form)
Water uptake (%)	38.6	16.7
Water permeability (L·µm/m²·h.bar)	4.2	0.6
Water permeability in salt solution (NaCl 2000 ppm)	4.1	0.5
NaCl rejection (%) (NaCl 2000 ppm, 400 psi)	88.6	98.2

The solubility and diffusivity for NaCl in sulfonated copolymer membranes have been determined. Typical results for acid and sodium salt forms obtained from kinetic desorption measurements are shown in Figure 3. The plots are usually linear at early times, and the diffusivity of NaCl, D_2 (cm²/sec), can be calculated as follows:

$$D_2 = (\pi/16)((M_t/M_{inf})/(t^{1/2}/d)) \quad (3)$$

where M_t and M_{inf} are the conductivity (µS/cm) at time t and at equilibrium, respectively, t is time (sec), and d is thickness (cm).

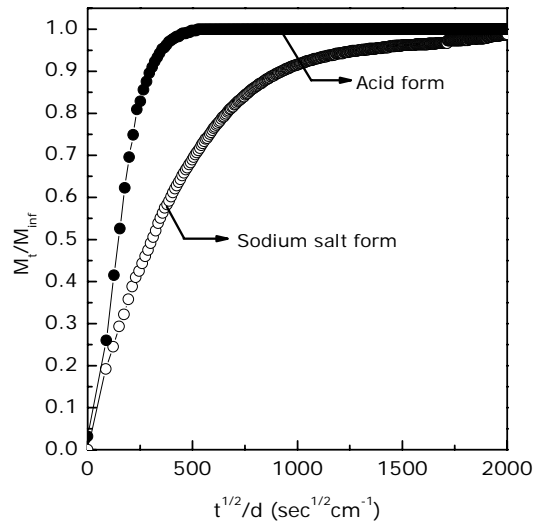


Figure 3. Desorption of NaCl from acid and sodium salt forms of a sulfonated copolymer membrane at 25 °C (40 mol% sulfonated monomer).

The amount of NaCl removed from the sample was calculated from the equilibrium conductivity value of the extracting solution. The partition coefficient, K_2 , was obtained from the amount of salt extracted and the concentration of the original soaking solution. Finally, the salt permeability (P_2) was calculated from the product of D_2 and K_2 . From these measurements, the intrinsic transport properties of these polymers have been calculated. From the results so far, the current sulfonated copolymer membranes showed higher salt diffusivity and similar (to PA) or larger salt solubility than CA or PA membranes (cf. Table 2). The higher salt diffusivity was expected to be related to the higher water content and the state of water in these sulfonated copolymer membranes.

Table 2. Diffusivity, Solubility, and Permeability Coefficients of NaCl in CA, PA, and Sulfonated Polymer Membranes

	CA ^a (Acetyl content = 39.8%)	PA ^b	BPS 30 ^c (acid form)	BPS 30 (salt form)
D_2 (cm ² /sec)	9.4×10^{-10}	1.5×10^{-10}	1.2×10^{-6}	4.2×10^{-7}
K_2	0.04	0.2	0.03	0.02
P_2 (= D_2K_2) (cm ² /sec)	3.3×10^{-11}	3.0×10^{-11}	3.4×10^{-8}	9.7×10^{-9}

(a: reference 11; b: reference 10; c: 30 mol% sulfonated monomer)

These new sulfonated copolymer membranes are compared with commercial polyamide membranes in terms of salt rejection and product flux in Figure 4. For the sulfonated copolymer membranes, the flux is calculated from measured permeability coefficients and a presumed membrane thickness of 1 μm . Although commercial polyamide membranes (open circles) show excellent RO performance, low chlorine stability can reduce the membrane life time. On the other hand, the sulfonated copolymer membranes in the acid and salt forms show a strong tradeoff relationship between salt rejection and flux, and this tradeoff depends upon sulfonation degree and membrane structure. Considering that polyamide composite membranes consist of very thin selective layers (on the order of several tens of nanometers), the sulfonated copolymer membranes exhibit high water flux and reasonable salt rejection. While commercial polyamide membranes have suffered from low chlorine tolerance over a broad pH range (4-10), these sulfonated copolymer membranes show excellent chlorine tolerance as well as good fouling resistance against protein and oily water.

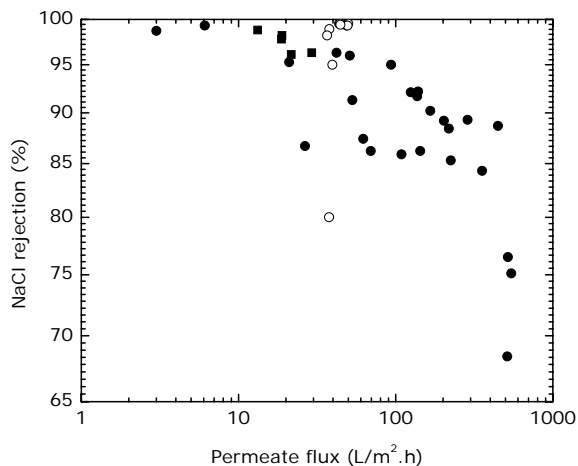


Figure 4. Comparative data of sulfonated copolymer membranes with commercial polyamide RO membranes at 25 °C (feed concentration: NaCl 2000 ppm). (○): polyamide membranes (feed pressure = 225 psi); (●): sulfonated copolymer membranes in acid form (400-800 psi); (■): sulfonated copolymer membranes in salt form (400 psi).

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