A Study of Reverse Osmosis Separation and Permeation Rate for Sulfonated Poly(2,6-dimethyl-1,4-phenylene oxide) Membranes in Different Cationic Forms

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SYNOPSIS

Thin film composite membranes were prepared by coating a thin layer of sulfonated poly(1,4-dimethyl-2,6-phenylene oxide) polymer on the surface of a polysulfone ultrafiltration membrane. The membrane performance was studied when the sulfonate was either in the hydrogen form or loaded fully with an alkali metal cation. It was found that the permeation rate was greater than the pure water permeation rate, when the sulfonate was in the hydrogen form and the feed solution contained an alkali metal chloride solute. The permeation rate increased with an increase in the ionic radius of the alkali metal cation. With respect to membranes in which the sulfonate was loaded with an alkali metal cation, the pure water permeation rate was found to increase with a decrease in the ionic radius of the alkali metal cation. The permeation rate was the same as the pure water permeation rate when the membranes of the latter form were tested for reverse osmosis of aqueous solutions involving either sodium chloride or an organic solute. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, a number of charged thin film composite membranes have been developed. These membranes exhibit high water flux and are resistant to chlorine, high and low pH, and high temperature.[1,2] The performance of these membranes are primarily controlled by the electric charge of the thin selective layer at the membrane surface. The ionic groups present at the surface layer of the composite membrane show electric repulsion to solutes having the same charge as that of the surface layer. This repulsive force is effective over a range longer than the dielectric repulsive force working between the charged solute and the neutral surface. Therefore, a larger pore size is allowed at the surface of the charged membrane than at the neutral membrane to maintain a given level of rejection of the charged solute. Together with the thinness of the selective surface layer, the charged thin film composite membrane features a higher flux or a lower operating pressure than that of the neutral membranes.[2,3] The above principle has been applied industrially for the development of nanofiltration membranes whose performance data are between those of reverse osmosis and ultrafiltration membranes.

Studies on the rejection of different electrolyte solutes by a number of charged composite membranes have already been reported.[2] Normally, the membranes are negatively charged, and electrolyte solutes with higher anionic charge densities and/or with lower cationic charge densities are rejected more effectively. On the other hand, the rejection of solutes without electric charge is less effective and, as a result, the charged thin film composite membrane can reject ions with radii much smaller than the membrane pore radii but cannot reject solute molecules when the solutes do not carry any electric charge and their sizes are as small as ions.[4-6] Studies have also been made on the interactions between membranes and water-organic solvent mixtures when the membranes were loaded with different counterions.[7]

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Little has been mentioned so far about the dependence of the permeation rate on the nature of the electrolyte solute present in the feed solution. We have observed, recently, that the membrane permeation rate in the presence of the electrolyte solute in the feed increases significantly from that in the absence of the electrolyte solute.

It was the objective of this work, therefore, to study the dependence of the permeation rate on the nature of the electrolyte solute systematically. Two series of experiments were conducted for this purpose: In the first series, the sulfonate in the membrane was maintained in the hydrogen form. The permeation rate was determined in the presence of an alkali metal chloride as the solute in the feed solution. The alkali metal ion was changed systematically from lithium to cesium. In the second series, the proton in sulfonic acid was replaced by an alkali metal ion and the pure water permeation rate in the absence of the solute was determined. The alkali metal ion was changed again systematically from lithium to potassium. The experimental results are reported and discussions are made on the basis of the experimental results.

EXPERIMENTAL

Materials

The flat sheet membrane used for the substrate of the composite membrane was a polysulfone membrane provided generously by Osmonics, Inc. The poly(phenylene oxide) [poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)] polymer was provided by General Electric Co. Chlorosulfonic acid, chloroform, and methanol were provided by BDH Co.

Preparation of Sulfonated Poly(phenylene oxide) (SPPO)

PPO polymer was used without any further treatment. A 10 wt % PPO solution was prepared by dissolving PPO polymer in chloroform. Then, a stoichiometric quantity of chlorosulfonic acid was added dropwise to the above PPO solution according to the method described in Ref. 8. As sulfonation progressed, SPPO precipitated from the solution since SPPO is not soluble in chloroform. The precipitate was dissolved in methanol and washed thoroughly with distilled water until the wash water showed a pH value higher than 4. The precipitate was further dried exhaustively for 2 days under vacuum at room temperature. The ion-exchange capacity (IEC) of the SPPO polymer so prepared was measured by the acid–base titration method and was 2.0 meq/g of dry polymer.

Preparation of Composite Membranes

The skin side of the substrate ultrafiltration membrane was contacted with 1 wt % SPPO solution in methanol. The solution on the membrane surface was drained by holding the membrane vertically, leaving a thin layer of the SPPO solution. The coated layer was then dried for 0.5 h at room temperature. The above coating procedure was repeated three times, which was followed by drying overnight under ambient conditions. The membranes so prepared were considered to be in hydrogen form and kept in distilled water.

The membrane containing an alkali metal cation was prepared by equilibrating a membrane of hydrogen form in 0.5*N* hydroxide solution of the respective cation. The excess caustic was then removed by immersing the membrane in distilled water.

Reverse Osmosis Experiments

The reverse osmosis experiments were conducted using six high-pressure permeation cells with an effective membrane area of 13.2 cm^2, the details of which were described elsewhere.[9] The details of the experimental procedure were also described. The experiments were conducted at the operating pressure of 1000 kPa gauge and at room temperature. The solute concentration was either 0.01 or 0.04 mol/L for electrolyte solutes and 100 ppm for organic solutes. The feed solution was circulated through the feed chamber of the permeation cell at a flow rate of 27.6 L/h. For each experiment, the pure water permeation rate (PWP) (g/m^2 h), the permeation rate (PR) (g/m^2 h) in the presence of the solute in the feed, and the solute separation, defined as

$$\text{Solute separation} = (\text{feed solute concentration} - \text{permeate solute concentration}) / \text{feed solute concentration}$$

were determined. The permeation rate was converted to that at 25°C using the density and viscosity data of water. The concentration of the electrolyte solutes was determined conductometrically, whereas the concentration of the organic solutes was determined by using a Total Carbon Analyzer (Beckman 915B).

RESULTS AND DISCUSSION

Reverse Osmosis Results When Sulfonate Is in the Hydrogen Form

Table I shows the reverse osmosis performance of the SPPO composite membranes, where the sulfonate is maintained in the hydrogen form. As the table indicates, the permeation rate (PR) in the presence of the electrolyte solute in the feed is greater than the pure water permeation rate (PWP) with the exception of lithium chloride solute, for which the PR is nearly equal to the PWP. These results are significant, since it is normally believed that the PR is either equal to or less than the PWP in reverse osmosis.

The above results can be interpreted by the proton (H^+)-alkali metal cation (Me^+) exchange written as

$$-\mathrm{SO_3H} + \mathrm{Me^+hy} = -\mathrm{SO_3^-Me^+} + \mathrm{H^+hy}$$

The energy involved in the above exchange reaction is governed by a quantity defined as the binding energy of $-\mathrm{SO_3^-Me^+}$ minus the hydration energy of Me^+. The latter quantity is lowered as the radius of the cation increases,[10] particularly when the anion is as large as the SO_3^- ion. Thus, the right side of the above reaction becomes more favored as the cationic radius increases from Li^+ to Cs^+. Table II shows the ion-exchange equilibrium constant K_0, defined as $[(-\mathrm{SO_3^-Me^+})(\mathrm{H^+})]/[(-\mathrm{SO_3H})(\mathrm{Me^+})]$ of polystyrene sulfonate.[11] Clearly, K_0 increases from Li^+ to Cs^+. The same tendency is expected to be valid for PPO sulfonate.

Comparing $-\mathrm{SO_3H}$ with $-\mathrm{SO_3^-Me^+}$, a cation is associated with a sulfonate anion in both cases; however, their properties are different. In $-\mathrm{SO_3H}$, a covalent bond is formed between a proton and one of the oxygen atom in $-\mathrm{SO_3}$. Ionic properties of the proton and the sulfonate ion disappear completely. On the other hand, $-\mathrm{SO_3^-}$ and Me^+ retain their ionic properties, although they are associated with each other. Hence, the number of molecular and/or ionic species increases from two to three as the reaction progresses from the left to the right side of the exchange reaction. As a result, more water molecules are drawn into the membrane due to the osmotic pressure effect as the exchange reaction proceeds. Since the increase in the cationic size enhances the progress of ion exchange, more water is drawn into the membrane with an increase in the cationic size, which further results in a higher permeation rate. The decrease in solute separation with an increase of the cationic size is also understandable, since more cations are in the membrane as the counterion of the fixed negative charge as the exchange reaction is enhanced.

Table I Reverse Osmosis Performance of the SPPO–H Composite Membrane in the Presence of Alkali Chloride Solutes

Salt Present in the Feed	PWP × 10^{-3} (g/m^2 h)	PR × 10^{-3} (g/m^2 h)	Solute Separation (%)
LiCl	62.6	60.8	87.8
NaCl	62.6	76.8	86.5
KCl	62.6	88.1	83.5
CsCl	62.6	91.2	77.0

Operating pressure, 1000 kPa (gauge); operating temperature, 25°C; feed concentration, 0.01 mol/L.

Table II Ion-exchange Equilibrium Constant K_0 of the Sulfonated Polystyrene Polymer for Different Alkali Metal Cations

Cations	log K_0
Li^+	−0.1
Na^+	0.17
K^+	0.37
Cs^+	0.38

Reverse Osmosis Results When Sulfonate Is Loaded with Alkali Metal Cation

The PWP and the separation data, when the sulfonate ion in the surface layer is loaded with the alkali metal cation, Me^+, are shown in Table III. Interestingly, the tendency is completely reversed from that of membranes where the sulfonate ions were kept in hydrogen form, i.e., PWP is the highest

Table III The Effect of Different Counterions in the SPPO–Me$^+$ Composite Membrane on Separation and Flux of Reverse Osmosis

Counterions	PWP × 10^{-3}	PR × 10^{-3}	Solute Separation
Li^+	89.7	91.3	64.0
Na^+	83.0	89.6	67.0
K^+	69.4	76.2	74.0

Feed, aqueous sodium chloride solution; operating pressure, 1000 kPa (gauge); operating temperature, 25°C; feed concentration, 0.04 mol/L.

Table IV Effect of Counterion on the Separation of Glucose Solute by the SPPO–Me$^+$ Composite Membrane

Counterions	Solute Separation
Li$^+$	65.0
Na$^+$	66.0
K$^+$	71.8

PWP and PR are nearly equal to Table III. Operating pressure, 1000 kPa (gauge); operating temperature, 25°C; feed concentration, 100 ppm.

Table VI Effect of Counterion on the Separation of Raffinose by the SPPO–Me$^+$ Composite Membrane

Counterions	Solute Separation
Li$^+$	80.0
Na$^+$	86.0
K$^+$	92.0

PWP and PR are nearly equal to Table III. Operating pressure, 1000 kPa (gauge); operating temperature, 25°C; feed concentration, 100 ppm.

whereas the separation is the lowest for Li$^+$ form. The PR in the presence of the electrolyte solute in the feed was slightly higher than the PWP.

The above results can be interpreted in the following way: All sulfonate ions are now in the —$SO_3^-Me^+$ form. Assuming hydrated water molecules are not totally stripped off from the alkali metal cation when the —$SO_3^-Me^+$ ion pair is formed, the largest amount of water molecules is drawn into the membrane when the cation is Li$^+$, since its hydration number is the greatest. This is evidenced by the highest degree of swelling of the polymer when the sulfonate is in the Li$^+$ form.[12] Thus, the PR becomes the highest, and the solute separation, the lowest, since the swelling results in an increase of the membrane pore size.

Separation of Organic Solutes

Separation experiments were carried out with respect to glucose, sucrose, and raffinose solutes. The membranes in the Li$^+$, Na$^+$, and K$^+$ forms were used for these experiments. As the results in Table IV–VI show, the separation was the lowest when the membrane was in the Li$^+$ form. The PWP and PR were practically the same for all experiments involved. The separation increased with an increase of the molecular weight of the organic solute. A separation experiment was also carried out with respect to FC & D #40 dye (Red Dye) solute. The separation of the latter dye solute was nearly equal to 100% for every cationic form, which was higher than that of raffinose due to the anionic nature of the dye molecule.

Table V Effect of Counterion on the Separation of Sucrose by the SPPO–Me$^+$ Composite Membrane

Counterions	Solute Separation
Li$^+$	70.0
Na$^+$	77.0
K$^+$	83.0

PWP and PR are nearly equal to Table III. Operating pressure, 1000 kPa (gauge); operating temperature, 25°C; feed concentration, 100 ppm.

CONCLUSIONS

The thin film composite membrane prepared by coating a thin layer of SPPO polymer on the surface of a polysulfone ultrafiltration membrane shows a high water flux with reasonable rejections for both inorganic electrolyte solutes and organic solutes. Thus, the membrane has practical usefulness as a nanofiltration membrane. The unusually high permeation rate of this membrane for a given level of solute rejection is due to the ionic nature and the thinness of the selective layer. The permeation rate of the membrane is the function of various factors including the ionic radius of the electrolyte solute involved and the ionic radius of the counterion combined to the fixed anionic charge of the membrane.

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