Study of Reverse Osmosis Separation and Permeation Rate for Sulfonated Poly(2,6-dimethyl-1,4-phenylene oxide) Membranes of Different Ion Exchange Capacities

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SYNOPSIS

The reverse osmosis performance of thin-film composite membranes prepared from sulfonated polyphenylene oxide polymer with different ion-exchange capacities was studied using various electrolyte solutes. The effect of the solvent used for the preparation of the polymer solution for surface coating was also studied. It was found that the preparation of thin-film composite membranes with high selectivities and high fluxes was possible by adjusting properly the ion-exchange capacity and the solvent. It was also found that the membrane performance was governed primarily by the ion-exchange reaction between the solute cation and the proton in SO_3H and the Donnan equilibrium. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In the 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 selectivity of these membranes is primarily controlled by the electric charge of the thin selective layer at the membrane surface. Because of the thinness of the selective surface layer, the charged composite membrane is also featured by a higher flux or a lower operating pressure than those of neutral membranes.[2,3] This principle has been applied industrially for the development of nano-filtration membranes whose performance characteristics are between those of reverse osmosis and ultrafiltration membranes.

Studies on the performance of charged composite membranes have been reported by a number of authors.[3-5] 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 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.[6-8]

Little has been mentioned so far, however, about the dependence of the permeation rate on the nature of the electrolyte solute present in the feed solution. We have reported recently that the membrane permeation rate in the presence of the electrolyte solute in the feed may increase significantly from that in the absence of the electrolyte solute.[9]

Studies on the effect of the conditions of the membrane preparation on the membrane performance are also few in the literature. Huang et al. studied the preparation and performance of polyphenylene oxide membranes and attributed the change in performance mostly to the change in the ion-exchange capacity (IEC) of the polymer.[10,11]

The objective of this work is to study the effect of IEC values on the reverse osmosis performance of sulfonated polyphenylene oxide membranes when the membranes are in contact with electrolyte solutions of different valences and ionic radii. The effect of the solvent used for the preparation

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of polymer solutions for membrane coating is also reported.

EXPERIMENTAL

Materials

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

Preparation of Sulfonated Polyphenylene 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 PPO solution according to the method described in Ref. 12. As sulfonation progresses, SPPO precipitated from the solution since SPPO is not soluble in chloroform. The precipitate was dissolved in methanol or a chloroform–methanol mixture and cast into a film. The SPPO film was then dried and cut into small pieces, which were further washed thoroughly with distilled water until the wash water showed a pH value higher than four. The polymer was then dried exhaustively for 2 days under vacuum at room temperature. The IEC of the SPPO polymer thus prepared was measured by the acid–base titration method.

Preparation of Composite Membranes

The skin side of the substrate ultrafiltration membrane was contacted with a 1 wt % SPPO solution. The solvent used to prepare the SPPO solution depended on the IEC value of the SPPO polymer, as indicated in the following:

For IEC value of 1.29, chloroform–methanol mixture (chloroform 47 wt %)

For IEC value of 1.41, chloroform–methanol mixtures (chloroform 61 or 15 wt %)

For IEC value of 1.98, chloroform–methanol mixture (chloroform 56 wt %) or methanol

For IEC value of 2.60, 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 half an hour 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 in hydrogen form and stored in distilled water.

Reverse Osmosis Experiment

The reverse osmosis experiments were conducted by using six high-pressure permeation cells with an effective membrane area of 10.2 cm^2, the details of which were described elsewhere.[13] The details of the experimental procedures were also described. The experiments were conducted at the operating pressure of 1379 kPa gauge (200 psig) and at room temperature. The solute concentration was 0.05 mol/L for all electrolyte solutes. The feed solution was circulated through the feed chamber of the permeation cell at a flow rate of 30 L/h. For each experiment pure water permeation rate (PWP), the product permeation rate (PR) in the presence of the solute, both in m^3/m^2 s, and the solute separation, defined as solute separation = (feed solute concentration − permeate solute concentration)/feed solute concentration were determined. The permeation rate was converted to that at 25°C by using the density and viscosity data of water. The concentration of the electrolyte solutes was determined conductometrically.

RESULTS AND DISCUSSION

Effect of IEC Values of SPPO Polymers

Figure 1 illustrates the change in the separation of sodium chloride and product rate with a change in the IEC value of the SPPO composite membrane. Regarding IEC values of 1.41 and 1.98, data correspond to membranes prepared with solvent mixtures containing less chloroform, i.e., the membrane with IEC value of 1.41 with chloroform content of 15 wt % and the membrane with IEC value of 1.98 with methanol. The figure indicates a decrease in solute separation from IEC value of 1.29–1.98 and an increase from IEC value of 1.98–2.60, although all separation data were found in a narrow range. Correspondingly, the product rate data showed a maximum at the IEC value of 1.98. The change in product rate was, however, more spectacular, i.e., there was more than a threefold change when the IEC value increased from 1.29 to 1.98. These results indicate the possibility to prepare a membrane of
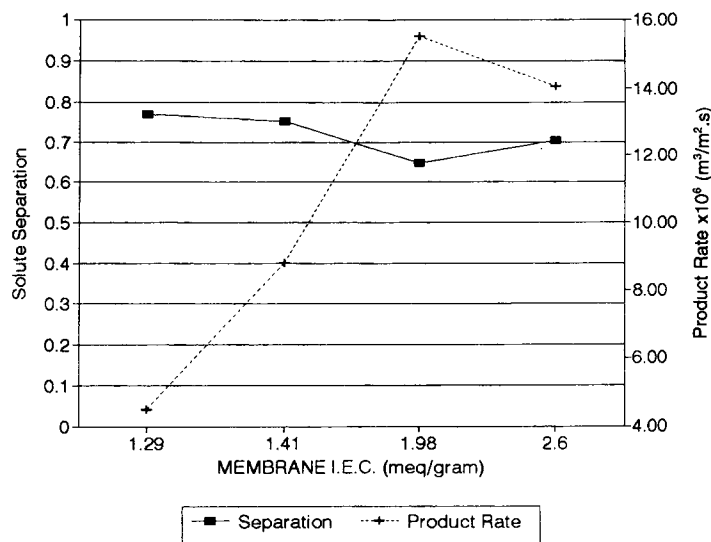
Figure 1   Effect of the IEC value of SPPO membrane on the reverse osmosis performance. Operating pressure, 1379 kPa gauge (200 psig); feed sodium chloride concentration, 0.05 mol/L.

higher productivity without much sacrifice in the separation by properly adjusting the IEC value.

Effect of Solvents Used in the Preparation of Casting Solutions

As explained in the experimental section, the SPPOs of different IEC values were dissolved in different solvents to prepare a polymer solution for coating, i.e., SPPOs with IEC values of 1.29 and 1.41 are more hydrophobic and were dissolved in chloroform–methanol mixtures, whereas SPPO with IEC values of 1.98 and 2.60 are more hydrophilic and could be dissolved in methanol. Then, it is not entirely clear if we have observed in the above experiment the effect of the IEC value or the effect of the solvent. In order to investigate the effect of the solvent, two membranes were prepared from the SPPO polymer with an IEC value of 1.41 meq/g using chloroform–methanol mixtures of 15 wt % chloroform and 61 wt % chloroform and reverse osmosis performance of each membrane was examined. The solute separation and the product rate with respect to four alkali metal halide salts are summarized in Figure 2. The figure indicates a slight decrease in the solute separation and an about 55% drop in the product rate with a change in chloroform content from 15 to 61 wt %. Similarly, SPPO polymer with an IEC value of 1.98 was dissolved in two different solvents; one methanol and the other chloroform–methanol mixture with 56 wt % chloroform, and reverse osmosis membranes were prepared. The performance of

these reverse osmosis membranes are summarized in Figure 3. The figure indicates a slight increase in the solute separation and an about 50% drop in the product rate with a change in solvent from methanol to chloroform–methanol mixture.

Since the same polymer was used for the preparation of the coating layer, these results clearly indicate the effect of the morphological change of the coated polymer layer when different solvents were used to prepare coating solutions. This conclusion was further substantiated by the following experiments. Three substrate ultrafiltration membranes, which are the same as the one used for the preparation of composite membranes, were contacted with methanol, a chloroform–methanol mixture (chloroform 46 wt %), and a chloroform–methanol mixture (chloroform 56 wt %), separately, and dried after draining the solvent from the membrane surface. The contacting with a solvent and drying were done in a way similar to that of SPPO coating membrane preparation. Then, the pure water permeation (PWP) rate was determined for each membrane after 6 h of compaction at 689 kPa gauge (100 psig) under water. The results were 20, 27, and 28 $\times$ 10^{-6} m^3/m^2 s, respectively, for the first, second, and the third membrane. These results indicate that the permeability of the substrate membrane *increases* with an increase in the chloroform content in the solvent. The permeability of the SPPO-coated membranes, on the other hand, *decreases*, with an increase in the chloroform content in the solvent. Therefore, the effect of the solvent on the membrane flux of the
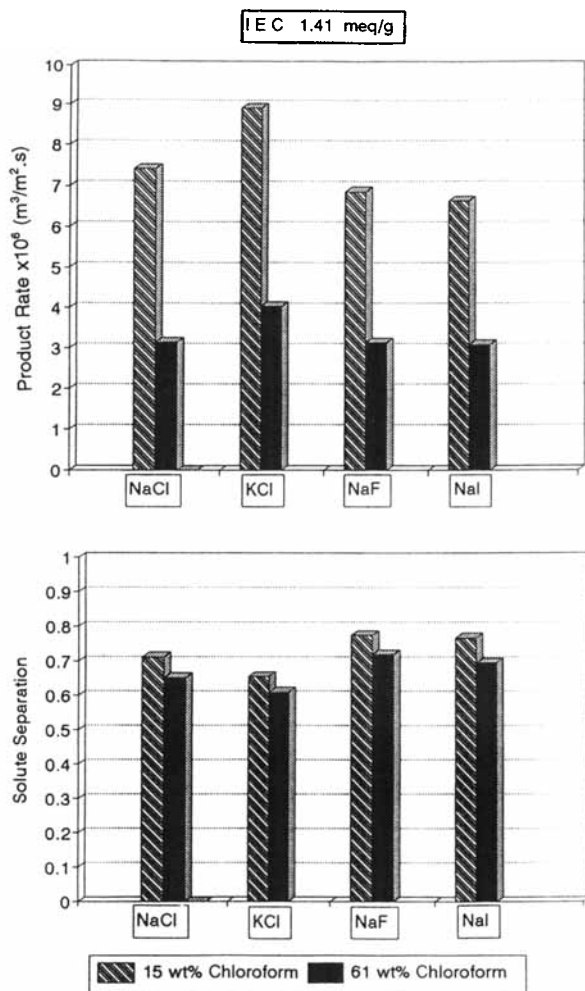
Figure 2 Effect of solvent in coating solutions on the reverse osmosis performance of SPPO membrane with an IEC value of 1.41 meq/g. Operating pressure, 1379 kPa gauge (200 psig); feed electrolyte concentration, 0.05 mol/L.

SPPO-coated membranes is not due to the change of the substrate membrane but due to the morphological change of the coated SPPO layer. Apparently, the use of a more hydrophilic solvent with a higher methanol content created a more open structure in the charged polymer and such an open structure was retained even after drying and subsequent contact of the coated layer with the feed aqueous solution. Interestingly, the open structure affected more on the product rate than the solute separation.

It can be concluded, therefore, that the effect of IEC values shown in Figure 1 is in fact a result of the superimposition of two different effects, one the effect of the IEC value and the other the effect of the solvent. As the IEC value increases from 1.29 to 1.98, the chloroform content in the solvent mix-

ture should be decreased (or the methanol content should be increased), and as a result the product rate increases without much sacrifice in the solute separation. A further increase in IEC value from 1.98 and 2.6 does not necessarily lead to an increase in the product rate.

These observations are very important in the design of composite reverse osmosis membranes with a SPPO-coated layer. They indicate that the IEC value should be properly adjusted and the solvent should be properly chosen for the preparation of the coating solution.

Effect of Cations on the Performance of Reverse Osmosis Membrane When the Anion is Chloride

Reverse osmosis separation of various metal chlorides were investigated and the results summarized
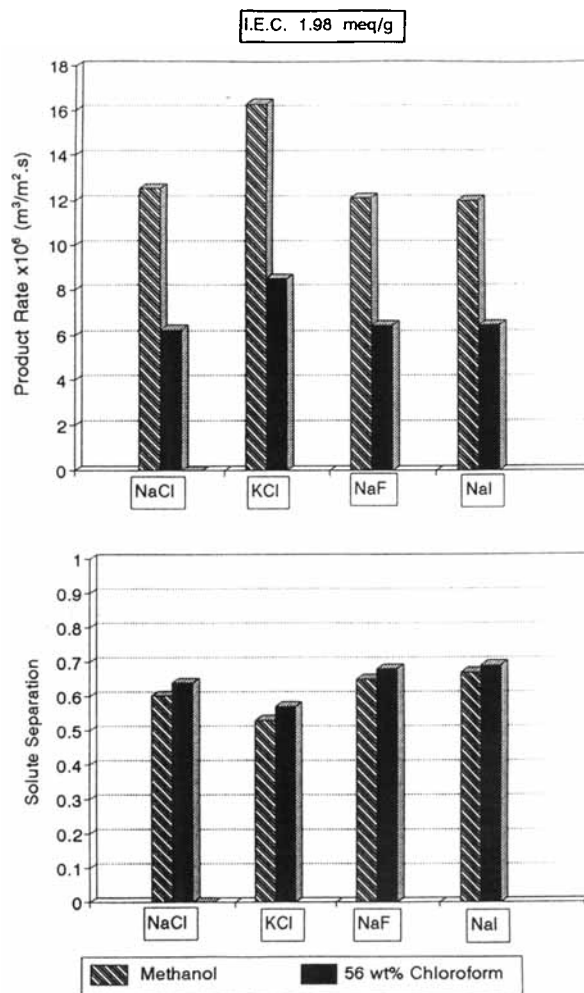

Figure 3 Effect of solvent in coating solutions on the reverse osmosis performance of SPPO membrane with an IEC value of 1.98 meq/g. Operating conditions same as Figure 2.

in Table I. The ionic radii of the cations are also included in the table. There are two effects involved in this table. One is the effect of the ionic radius and the other is the effect of the ionic valence.

Regarding the effect of the ionic radius, the following tendency can be observed for ions of the same valence.

1. The product rate (PR) can become greater than pure water permeation (PWP) rate and increases with an increase in the ionic radius.
2. The solute separation decreases with an increase in the ionic radius with only one exception, i.e., the separation of $CaCl_2$ is greater than that of $MgCl_2$, even though the radius of Ca^{2+} ion is larger than that of Mg^{2+} ion.

Exactly the same tendency was observed in our previous work on the reverse osmosis performance of SPPO membranes with respect to alkali metal chloride solutes.[9] This observation was explained by the change in the free energy of the following exchange reaction:

$$-SO_3H + Me^+hy = -SO_3^-Me^+ + H^+hy \quad (1)$$
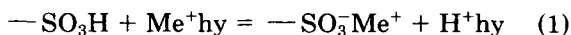
The free energy of the above exchange reaction decreases as the ionic radius of Me^+ cation increases,[14]

favoring the right side of the equation.[15] The number of species in the membrane increases from one to two for each conversion of $-SO_3H$ to $-SO_3^-Me^+$. Then, more water flows into the membrane phase due to an increase in the osmotic pressure effect. As a result, the product rate increases with an increase in the ionic radius and simultaneously the solute separation decreases. The same explanation may be valid for the ion of other valences.

Regarding the effect of the valence, the following tendency is observed in Table I: comparing Li^+, Mg^{2+}, and Fe^{3+}, whose ionic radii are close to each other [Li^+ (0.60), Mg^{2+} (0.65), Fe^{3+} (0.64)], the product rate either increases or decreases from Li^+ to Mg^{2+} and always decreases from Mg^{2+} to Fe^{3+}. The solute separation, on the other hand, has a minimum at Mg^{2+}.

Considering the following exchange reaction,

$$n(-SO_3H) + Me^{n+}(hy)_n$$

$$= (-SO_3^-)_nMe^{n+} + nH^+hy \quad (2)$$
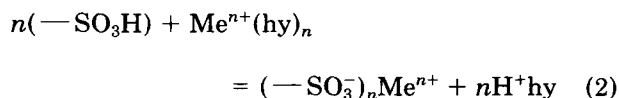
the free energy of reaction becomes smaller as the valence of cation, n, increases from 1 to 2 due to an increase in electrostatic force between ($-SO_3^-$) and Me^{n+}. Therefore, the intake of electrolyte into the membrane phase is enhanced, resulting in the lower

Table I   Reverse Osmosis Performance of SPPO-H Membranes[a]

Solute	Ionic Radius of Cation $\times 10^{10}$ m	Membrane Performance	IEC 1.29	IEC 1.41	IEC 1.98	IEC 2.60
		PWP	3.49	6.74	11.74	10.71
LiCl	0.60	PR	3.40	6.70	11.65	10.56
		Separation, f	0.80	0.79	0.69	0.76
NaCl	0.95	PR	4.48	8.82	15.52	14.05
		Separation, f	0.77	0.75	0.64	0.70
KCl	1.33	PR	5.85	11.37	20.09	18.53
		Separation, f	0.73	0.71	0.59	0.65
NH$_4$Cl	1.43	PR	5.52	10.28	19.38	17.17
		Separation, f	0.71	0.69	0.58	0.64
MgCl$_2$	0.65	PR	3.49	6.27	13.11	11.55
		Separation, f	0.38	0.33	0.25	0.27
CaCl$_2$	0.99	PR	3.77	7.03	14.86	13.16
		Separation, f	0.40	0.37	0.31	0.32
		PWP	3.40	6.18	12.69	11.18
AlCl$_3$	0.51	PR	1.93	3.25	7.83	6.98
		Separation, f	0.58	0.60	0.37	0.42
FeCl$_3$	0.64	PR	1.98	3.40	7.31	7.22
		Separation, f	0.48	0.45	0.39	0.40
		PWP	1.56	2.59	5.85	5.33

[a] PWP and PR $\times 10^6$ (m^3/m^2 s).

Table II Reverse Osmosis Performance of SPPO-H Membranes

Solute	Membrane Performance	IEC 1.29	IEC 1.41	IEC 1.98	IEC 2.60
Na_2SO_4	PR $\times$ 10^6 (m³/m³ s)	4.01	7.45	13.63	12.64
	Separation, f	0.95	0.94	0.84	0.91
K_2SO_4	PR $\times$ 10^6 (m³/m² s)	5.09	9.34	17.45	16.32
	Separation, f	0.93	0.92	0.78	0.87
$MgSO_4$	PR $\times$ 10^6 (m³/m² s)	3.30	5.94	12.55	11.13
	Separation, f	0.65	0.63	0.43	0.47
$Al_2(SO_4)_3$	PR $\times$ 10^6 (m³/m² s)	2.22	3.82	8.02	7.26
	Separation, f	0.61	0.61	0.39	0.42

solute separation. The change in the number of species at the conversion of $2(-SO_3H)$ to $(-SO_3^-)_2Me^{2+}$, is from 2 to 3 when $(-SO_3^-)_2Me^{2+}$ is dissociated, whereas it is 2 to 1 when $(-SO_3^-)_2Me^{2+}$ is associated. Therefore, the osmotic pressure effect may increase or decrease, depending on the degree of association. Consequently, the product rate may also increase or decrease.

When the cationic valence, n, increases further to 3, the metal cation is very strongly bound to sulfonate anion, causing the crosslinking of SPPO polymer. The polymeric coating layer becomes denser, resulting in the lower product rate and higher solute separation than $n = 2$. The densification of the polymer is permanent and the initial pure water permeation rate can no longer be recovered.

Effect of Cations on the Membrane Performance When the Anion Is Sulfate

Table II summarizes the effect of cations on the membrane performance when the anion is sulfate. Exactly the same tendency is observed as in the case of chloride anion; i.e., the solute separation decreases and the product rate increases when the cation changes from sodium to potassium. Both solute separation and product rate decrease when the cation changes from Na^+ to Mg^{2+}. There is only a small

change in solute separation but the product rate decreases significantly when the cation changes from Mg^{2+} to Al^{3+}.

Effect of Anions on the Membrane Performance When the Cation Is Sodium

Table III summarizes the effect of anions on the membrane performance when the cation is sodium. It is obvious that the separation increases whereas the product rate decreases slightly as the valence of the anion increases. This is difficult to explain by considering the exchange reactions (1) and (2) alone, since the above equations do not include anions. When considering the Donnan equilibrium expressed by

$$K = \{(Na^+)_{mem}[(-SO_3^-)_{mem}$$

$$+ (X^{m-})_{mem}]\}/\{(Na^+)(X^{m-})\} \quad (3)$$

where ( ) and ( )$_{mem}$ indicate the concentration in the solution phase and in the membrane phase, respectively, the equilibrium constant K should decrease as the anionic valence m increases because of the stronger electrostatic repulsion between $(-SO_3^-)$ and X^{m-} for larger m. The intake of the electrolyte solute $(Na^+)_m X^{m-}$ into the membrane

Table III Reverse Osmosis Performance of SPPO-H Membranes

Solute	Membrane Performance	IEC 1.29	IEC 1.41	IEC 1.98	IEC 2.60
NaCl	PR $\times$ 10^6 (m³/m² s)	4.48	8.82	15.52	14.05
	Separation, f	0.77	0.75	0.64	0.70
$NaHCO_3$	PR $\times$ 10^6 (m³/m² s)	4.43	8.54	15.28	13.87
	Separation, f	0.85	0.83	0.71	0.76
Na_2CO_3	PR $\times$ 10^6 (m³/m² s)	3.87	7.36	13.11	12.22
	Separation, f	0.93	0.91	0.81	0.87

phase, therefore, should decrease in order to maintain electroneutrality. Thus, the solute separation increases as anionic valence increases. The effect of anionic valence on product rate and the effect of anionic radius on solute separation and product rate are more difficult to explain.

Effect of Solute Concentration on the Performance of Reverse Osmosis Membrane

Figure 4 illustrates the effect of feed sodium chloride concentration on the solute separation and product rate. The figure indicates that the solute separation decreases significantly with an increase in sodium chloride concentration. For example, with respect to the membrane with an IEC value of 1.41, the solute separation changed from 95 to 71%. This is in contrast to the membranes without electric charge such as cellulose acetate membranes, for which the solute separation depends only little on sodium

chloride concentration. The strong dependency of the solute separation on the concentration of electrolyte solutes is a well-known phenomenon for charged reverse osmosis membranes and explained by the fact that the intake of electrolyte solutes to the membrane phase is more favored at a higher electrolyte concentration according to the Donnan equilibrium.[16]

Figure 4 also indicates that the product rate is little affected by sodium chloride concentration. This is also reasonable since the sodium chloride concentrations involved in this study are so low that the effect of osmotic pressure on the product rate can be ignored.

CONCLUSIONS

The following conclusions can be drawn from the above experimental results.

1. Thin-film composite membranes of high selectivities and high fluxes can be prepared from SPPO polymer by properly adjusting the IEC value and the solvent used for the preparation of the polymer solution for surface coating.
2. When the anion of the electrolyte solute is fixed, the membrane performance is a rather complicated function of the cationic valence and radius. In particular, the separation of alkali metal chloride solutes decreases with an increase in the radius of, or the decrease in the charge density of, the alkali metal cation. These results are unexpected considering the electrostatic interaction between a solute cation and a membrane surface charged anionically by $-SO_3^-$.
3. These results, however, can be interpreted by considering the ion exchange between the solute cation and the proton in $-SO_3H$.
4. When the cation of the solute electrolyte is sodium, the solute separation increases, whereas the product rate decreases as the valence of the anion increases. This phenomenon can be interpreted by the Donnan equilibrium.
5. The solute separation decreases with an increase in the electrolyte concentration. This also can be explained by the Donnan equilibrium.
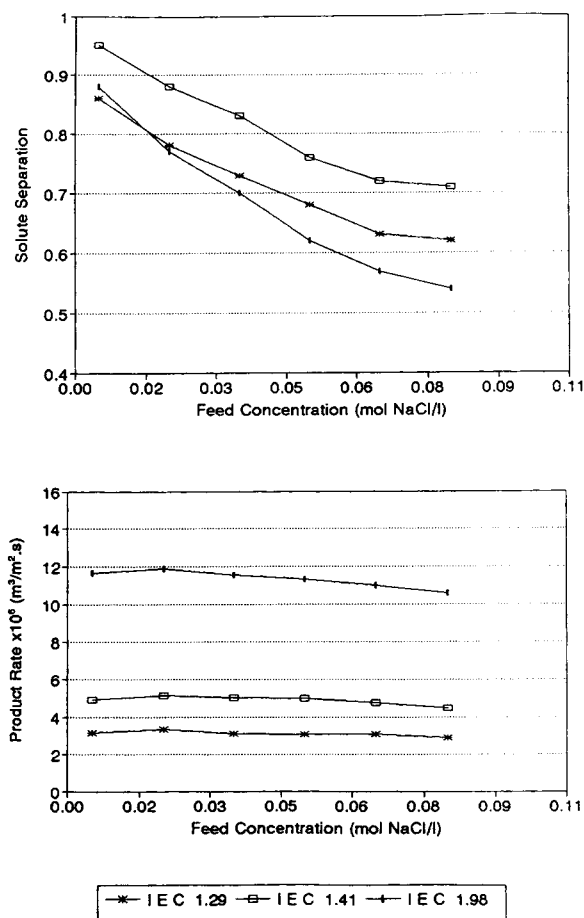

Figure 4   Effect of feed sodium chloride concentration on SPPO membranes with various IEC values. Operating pressure, 1379 kPa gauge (200 psig).

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