Ionically Crosslinked Poly(acrylic Acid) Membranes. IV. Composite Reverse Osmosis Membranes*

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Synopsis

Composite reverse osmosis membranes of ionically crosslinked poly(acrylic acid) (PAA) have been prepared. The process consists of coating a porous polysulfone membrane with a thin layer of dilute solution of PAA, drying the thin liquid layer, and ionically crosslinking the PAA in solutions of different salts. The influence of some important preparation parameters on the properties of these membranes was investigated. It was found that all these membranes possessed ion exchange properties and could be ion exchanged; some of them have been found to be suitable for the desalination of low concentration salt solutions. By comparison to cellulose acetate (CA) membranes, higher rejection of phenols may be an interesting property of these membranes.

INTRODUCTION

Since Loeb and Sourirajan made the first high flux reverse osmosis membranes of cellulose acetate (CA),[1] research on membrane materials suitable for reverse osmosis and on membrane-making technology has been extensively carried out.

In ionically crosslinked PAA, the main chain $(CH_2–CH)_n$ is hydrophobic and stable, the pendant groups (COOH) are strongly hydrophilic, while the crosslinking metal ions have the function of making water molecules fairly clustered, and the hydrogen atoms at the α-site in PAA molecules are properly activated—all of these factors contribute to making the membrane permselective to water and salt transport. Furthermore, ionically crosslinked PAA possesses many improved properties: higher mechanical strength (especially creep strength), higher glass transition temperature (better thermal stability), insolubility in water (excellent hydrolytic stability), and resistance to many chemicals. According to the preferential sorption mechanism,[2] hydrogen bonding mechanism,[3] and water clustering principle,[4] ionically crosslinked PAA could be a candidate for a reverse osmosis membrane material.

On the basis of previous work carried out in this laboratory,[5–9] this paper focuses on the preparation and properties of composite reverse osmosis membranes of ionically crosslinked PAA on a polysulfone support. The former work on ionically crosslinked PAA membranes, which was begun in 1973, had developed a qualitative rate model of ionically crosslinked PAA; this was followed by membrane synthesis using wet and dry techniques, and demonstrated the po-

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tentiality of ionically crosslinked PAA for reverse osmosis. Composite membrane technology was adopted in this research to improve the membrane flux, salt rejection, and stability. The technological process and main variables, such as species of crosslinking ions, concentration, pH, and temperature of crosslinking bath, etc., have been studied in detail.

EXPERIMENTAL

Material

The polysulfone (PS) used in this work was obtained from Polyscience Inc. The poly(acrylic acid) (PAA) used was obtained from Rohm and Haas (25% by weight) or synthesized in this laboratory by free radical polymerization of the monomer as described previously.[7] The average molecular weight of PAA was about 10^5. All the other chemicals, such as organic solvents, organic and inorganic compounds as well as inorganic metal salts, were Baker Analytical Reagent grade materials.

Membrane Preparation

Preparation of Porous Polysulfone Membrane.[10] A solution containing 12.5 wt% PS and 12.5 wt% methyl cellosolve in dimethylformamide was cast onto a clean glass plate using a Gardner casting knife in the thickness of 0.3 mm. After the casting, the coated liquid film was immersed into a 15 wt% NaCl quenching bath immediately. The film gelled very quickly, was then washed with water, and cut into the required size with a membrane die and immersed into 10% NaOH solution for neutralization to give hydrophilic property. Finally it was put into deionized water for at least 24 h.

Preparation of Ionically Crosslinked PAA Composite Membranes. A solution containing 1.0–2.5 wt% of PAA (or PAA–Na) was prepared by diluting the 25 wt% of PAA solution (or after neturalizing with NaOH for the PAA–Na case). A porous PS support membrane prepared as described above (about 6.4 cm in diameter) was placed and stuck onto a glass plate. The PAA (or PAA–Na) liquid film (with thickness of about 0.3–0.5 mm) was cast onto the surface of above PS support membrane. It was then put into an oven and dried at 50–60°C for about 0.5 h. When the PAA (or PAA–Na) composite layer was formed, the composite membrane was then immersed into the crosslinking bath at constant temperature.

Transport Properties of Composite Membrane. The reverse osmosis test was conducted in six high-pressure cells, which have been described in detail in many previous papers on reverse osmosis.[11] The effective membrane area was 18.1 cm^2 (4.8 cm in diameter). The experiments were conducted at 300 psig, at a room temperature of approximately 25°C, and with a sodium chloride and other organic compound feed solution of 0.1 wt% circulated during the experiments. The pure water permeability was determined by measuring the flux of water under a pressure of 300 psig. Sodium chloride and organic compound concentrations were determined using a Water Associates Differential Refractometer Model R403, which showed good linearity in refractive index vs. concentration tests. The pH was determined using a Model 28 pH Meter, Radiometer Co-

TABLE I
Preparation and Reverse Osmosis Results of Ionically Crosslinked PAA Composite Membranes[a]

Membrane no.	Crosslinking solution		XLT ($°C$)	XLt (h)	PWP (gfd)	Rejection (%)
	Metal salt	pH				
920-7	$0.25M$ $ZnCl_2$	5.6	60	8	231.0	16.0
927-2	$0.25M$ $ZnSO_4$	5.3	70	4	420.0	10.2
930-1	$0.25M$ $Ba(OH)_2$	13.3	70	2	58.7	17.4
1001-2	$0.25M$ $BaCl_2$	7.0	70	4	244.4	13.8
917-1	$0.25M$ $CrCl_3$	1.9	60	1	401.4	7.4
922-5	$0.25M$ $Cr_2(SO_4)_3$	1.1	70	24	748.4	2.9
929-5	$0.25M$ $Cr(NO_3)_3$	1.5	70	4	560.0	3.9
916-3	$0.25M$ $AlCl_3$	3.6	60	4	41.7	43.5
923-3	$0.25M$ $Al_2(SO_4)_3$	2.3	70	4	133.6	13.3
924-2	$0.25M$ $AlK(SO_4)_2$	2.8	70	2	17.6	36.7
927-6	$0.25M$ $Al(NO_3)_3$	2.6	70	6	121.5	15.6
916-5	$0.25M$ $ZrCl_4$	1.0	60	2	60.8	29.0
923-10	$0.25M$ $Zr(SO_4)_2$	2.1	70	24	1098.0	7.6
923-3	$0.25M$ $ZrO(NO_3)_2$	1.2	70	6	60.8	32.4
G812-4	sat. $Zr(NO_3)_4$	0.3	70	—	15	85
1029-1	$0.25M$ $UO_2(NO_3)_2$	2.1	70	1	11.7	79.5
1101-6	$0.25M$ $UO_2(NO_3)_2$	2.1	25	3	21.5	51.2

[a] Casting solution on PS membrane: 2.5 wt % PAA, pH 2.5/25°C ($\alpha = 0$), applied pressure = 300 psig, feed solution: 0.1 wt % NaCl, XLT = crosslinking temperature, XLt = crosslinking time, PWP = pure water permeability, gfd = gal/ft²·day.

penhagen, Denmark. The thickness of two layers of the PAA composite membrane was measured with the aid of a microscope after the membrane was dyed with a water-soluble blue dye. Both the water and metal contents of the membrane were determined by means of gravimetrical methods. The ion exchange capacity (IEC) of the sample was obtained by using the acid–base backtitrimetric method.

RESULTS AND DISCUSSION

Various metal salts have been investigated as crosslinking agents for poly (acrylic acid). Initial membrane synthesis was aimed at evaluating the effects of variables such as divalent, trivalent, and tetravalent metal cations, pH, concentration of aqueous crosslinking solution, crosslinking temperature, and crosslinking time.

Effect of pH

Quantitative results for unneutralized PAA composite membranes coated on a porous PS membrane support and crosslinked with several kinds of metal salts are summarized in Table I. It can be seen from this table that the salt rejections for most cases were very poor excepting Zr^{4+} and U^{4+}, so that the major conclusion was that the degree of crosslinking was very low for all the cations tested excepting for Zr^{4+} and U^{4+}.

In order to test this conclusion, liquid phase homogeneous ionic crosslinking of PAA was carried out with several metal salts at room temperature, and the results are shown in Figure 1. The dependence of ionic crosslinking or precipi-
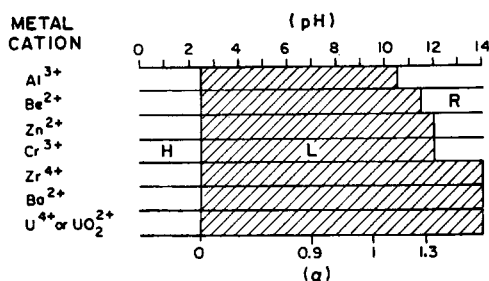
Fig. 1. Effect of pH on the liquid phase homogeneous ionical crosslinking of PAA (at 25°C): H = precipitation at high salt concentration nearly saturated; L = precipitation at low salt concentration; R = redissolution of precipitant; α = degree of neutralization with NaOH (salt-free concentration of PAA = 2.5 wt%, α = 0 and pH 2.5). In acidic solution, $UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$.[13]

tation on degree of neutralization (α) of PAA or pH was in accord with the results obtained by Ikegami and Imai.[12] The precipitation of uncharged PAA at α = 0 or at low pH occurred only at high salt concentrations (nearly saturated), while at intermediate degrees of neutralization there were precipitants at low salt concentrations, and these results did not agree with the predominance diagram for polyvalent metals.[13] It was also found that there was redissolution of ionically crosslinked precipitants such as in the cases of Al^{3+}, Be^{2+}, Zn^{2+}, and Cr^{3+} at very high pH ($\alpha \gg 1$). This redissolution seems to occur because the concentration

TABLE II
Preparation and Reverse Osmosis Results of Ionically Crosslinked PAA Composite Membranes with Neutralized PAA (pH 7.0, α = 0.9)[a]

Membrane no.	Crosslinking solution Metal salt	pH	XLT (°C)	XLt (h)	PWP (gfd)	Rejection (%)
G812-1	sat. Ba(OH)$_2$	13.3	70	—	—	30
G812-2	sat. ZnSO$_4$	5.3	70	—	48	40
G812-3	sat. AlK(SO$_4$)$_2$	2.8	70	—	27	80
930-6	0.25M AlK(SO$_4$)$_2$	3.0	70	6	11.7	42.8
1006-2	0.5M AlK(SO$_4$)$_2$	2.8	70	4	6.8	60.8
1013-3	0.5M AlK(SO$_4$)$_2$	2.8	70	22	7.4	64.3
1020-2	0.5M Al(NO$_3$)$_3$	2.3	70	4	21.9	34.0
1018-4	1M Al(NO$_3$)$_3$	2.1	70	6	8.6	81.0
1015-6	2M Al(NO$_3$)$_3$	1.5	70	6	4.7	63.3
1004-4	0.25M AlCl$_3$	3.6	70	2	2.7	67.7
1018-2	0.5M AlCl$_3$	3.1	70	4	3.9	84.9
1015-2	1M AlCl$_3$	2.6	70	4	2.2	77.5
1006-6	2M AlCl$_3$	1.7	70	6	2.8	70.0
1013-4	2M AlCl$_3$	1.7	70	7	2.7	80.6
1004-2	0.25M ZrCl$_4$	1.0	70	4	102.9	48.7
1007-1	1.5M ZrCl$_4$	0.6	70	2	15.6	72.3
1001-5	0.25M ZrO(NO$_3$)$_2$	1.2	70	4	106.6	34.8
1007-7	2M ZrO(NO$_3$)$_2$	0.3	70	2	22.7	49.1
1029-4	0.25M UO$_2$(NO$_3$)$_2$	2.1	70	1	89.9	6.8
1029-6	0.25M UO$_2$(NO$_3$)$_2$	2.1	70	3	328.5	1.9

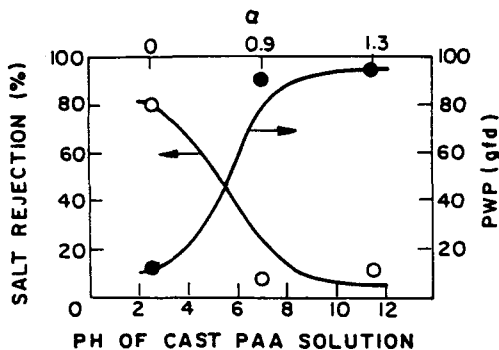[a] See footnote to Table I for abbreviations.

Fig. 2. Neutralization effect of cast PAA solution crosslinked with U^{4+} on the salt rejection. XL solution = $0.25M$ $UO_2(NO_3)_2$ aq, XLt = 1 h, XLT = 70°C.

of Na^+ is very high and the concentration of polyvalent cation is relatively low, since most states of the carboxylate groups are water-soluble $COO-Na$,[12] and because Al^{3+}, Be^{2+}, Zn^{2+}, and Cr^{3+} are mor hydrophilic than Zr^{4+}, Ba^{2+}, and UO_2^{2+}.

From these results, a thin layer of neutralized PAA with NaOH was coated on a porous PS membrane, dried, and ionically crosslinked in solutions of different metal salts. The preparation and reverse osmosis results of these membranes are presented in Table II. As expected, there was ionic crosslinking and these membranes showed much improved salt rejection properties excepting for the case of U^{4+}.

To test the neutralization effect in the case of U^{4+}, several kinds of PAA were coated on a PS membrane and crosslinked, and the results are presented in Figure 2. It can be seen from these results that the salt rejection decreased with increasing degree of neutralization.
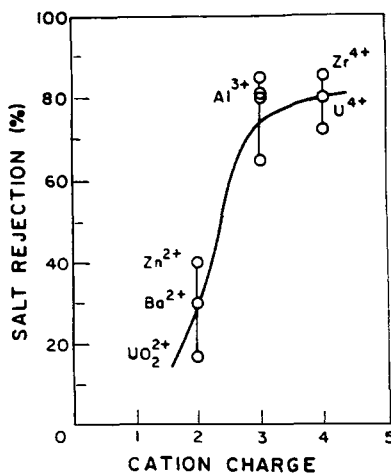

Fig. 3. Effect of polyvalent cation charge on the salt rejection. Cast PAA solution: pH 2.5–11.6 (α = 0–1.3), concentration of crosslinking solution = 0.25–2M aq, XLT = 70°C, XLt = 1–24 h.

TABLE III
Physical Properties of Metal Ions[a]

Metal cation	z	r (Å)	z/r	$z \cdot r$	Class	K_{ex} (s^{-1})
K$^+$	1	1.33	1.33	1.33	H	10^9
Na$^+$	1	0.95	1.05	0.95	H	10^9
Be^{2+}	2	0.31	6.45	0.62	H	10^2
Zn^{2+}	2	0.74	2.60	1.48	BL	5×10^8
Ba^{2+}	2	1.35	1.48	2.70	H	2×10^9
UO$_2^{2+}$	2	0.75	2.67	1.50	H	
Cr^{3+}	3	0.69	4.35	2.07	H	3×10^{-6}
Al^{3+}	3	0.50	6.00	1.50	H	1
Zr^{4+}	4	0.80	5.00	3.20	H	
U^{4+}	4	0.97	4.12	3.88	H	

[a] z = cation charge, r = Pauling ionic radius,[13,18] class = Pearson's hard (H)–soft (S) classification of metal ions,[15,16] K_{ex} = ligand H$_2$O exchange rate.[17]

Effect of Charge of the Polyvalent Cation

In Figure 3 are shown the results of reverse osmosis with several ionically crosslinked PAA composite membranes varying the charge of the metal cations. From these results, it is evident that the salt rejection increased with the increasing charge and also increased with the degree of crosslinking.

To compare the effects of other properties of cations on the ionic crosslinking, some physical properties of metal cations are listed in Table III. However, there appears to be no clear-cut relation between these properties excepting for the charge of cation, and it seems that coulombic forces are the major factor in this type of ionic crosslinking.[14] The x/r value, Pearson's hard–soft acid–base principle (HSAB),[15,16] or Cotton and Wilkinson's exchange rate of ligand H$_2$O[17] do not appear to be the major factors.

Effect of Concentration of Crosslinking Solution

Figure 4 shows the effects of concentration of aqueous crosslinking AlCl$_3$ solution on the salt rejection.
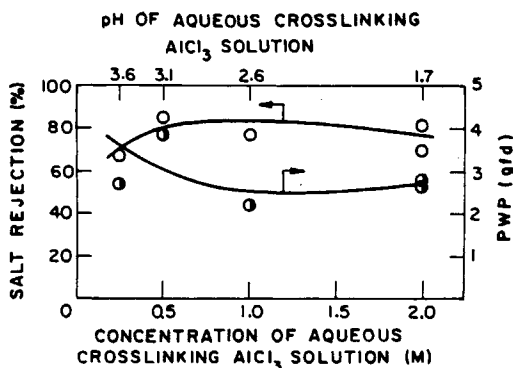

Fig. 4. Effect of concentration of crosslinking solution on the salt rejection and pure water permeability. XLT = 70°C, XLt = 2–7 h, cast PAA solution, pH 7.0 (α = 0.9).

TABLE IV
Some Properties of Ionically Crosslinked Composite PAA Membranes[a]

Membrane no.	Type of membrane[b]	Thickness top layer/ matrix (μm)	Water content (g/g wet film)[c]	Metal content[d]	Ion exchange (IEC)[e] (meq/g dry resin)
1124-1,2	PAA–Zr	15–20/90–100	0.515	0.364	7.23
1124-3,4	PAA–Al	10–15/90–100	0.569	0.228	15.45
1124-5,6	PAA–U	15–20/90–100	0.506	0.528	4.16
1124-7,8	PAA–Na–Zr	10–15/90–100	0.540	0.428	5.10
1124-9,10	PAA–Na–Al	10–15/90–100	0.560	0.265	9.84
1124-11,12	PAA–Na–U	10–15/90–100	0.501	0.582	4.08
1124-13,14	PAA–Na–Zn	10–15/90–100	0.567	0.412	7.38
1124-15,16	PAA–Na–Ba	10–15/90–100	0.563	0.676	8.46

[a] Crosslinking temperature and time: 70°C and 6 h.

[b] PAA–membrane, cast with unneutralized PAA ($\alpha = 0$, pH 2.5); PAA–Na–membrane, cast with neutralized PAA ($\alpha = 0.9$, pH 7.0); crosslinking solutions, $1.5M$ $ZrCl_4$ (pH 0.10), $0.25M$ $UO_2(NO_3)_2$ (pH 2.05); $2M$ $AlCl_3$ (pH 1.75), $0.25M$ $ZnSO_4$ (pH 5.25) and $0.25M$ $Ba(OH)_2$ (pH 13.3).

[c] Wet composite membrane at 100% relative humidity.

[d] Dried at 0.05 mm Hg and 55°C for 2 h, calcinated at 950°C for 1 h.

[e] The composite membrane was neutralized with a measured excess of $0.1N$ NaOH and with excess NaCl, it was maintained overnight and backtitrated with $0.1N$ HCl during a 2-week period since the neutralization of carboxylic groups in the crosslined poly(acrylic acid) took a relatively long time.

As shown previously in Figure 1, since the ionical crosslinking occurred at very low concentration if the pAA casting solution was neutralized (critical salt concentration c_s for the precipitation of the PAA with aqueous $AlCl_3$ solution was nearly zero[12]), for this case the concentration of crosslinking solution did not have much influence on the salt rejection, but only affected the crosslinking rate and in turn the optimum crosslinking time.

However, if the PAA casting solution was not neutralized, since the ionic crosslinking occurred at very high concentration (nearly saturated concentration), the concentration of crosslinking solution had a considerable influence. Several kinds of PAA membranes and their main structural and characteristic properties are listed in Table IV.

Table V shows the relationship between concentration and pH of $Zr(NO_3)_4$ solution, as well as their effect on metal content and IEC of crosslinked membranes.

TABLE V
The Effect of Concentration and pH of $Zr(NO_3)_4$ Solution

Concentration of $Zr(NO_3)_4$ solution (wt%)	pH	Metal content (g/g dry resin)	IEC (meq/g dry resin)
7.0	0.35	0.131	11.32
1.8	0.72	0.328	7.90
0.9	1.00	0.467	5.06
0.58	1.21	—	5.06

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TABLE VI
The Effect of Temperature of Crosslinking Bath[a]

Temperature of crosslinking bath (°C)	pH of crosslinking bath	Metal content of cross- linked PAA	Water content of the compos- ite membrane
25	0.72	0.45	0.62
50	0.72	0.46	0.26
75	0.72	0.46	0.23

[a] $Zr(NO_3)_4$ solution.

Effect of Crosslinking Temperature and Time

The temperature did not have much influence on the pH of the crosslinking bath and final extent of reaction between the carboxyl group and the metal ion. It did, however, change the rate of reaction between the carboxyl group and the metal ion, and water content of the composite membrane obtained. Some effects of temperature of crosslinking bath are listed in Table VI.

As shown in Figure 6, salt rejection increased with the crosslinking time at crosslinking temperature 25°C, while the degree of crosslinking increased, and both the rate of diffusion of metal cation and the rate of crosslinking reaction agreed with the qualitative rate model, as previously reported from this labo-
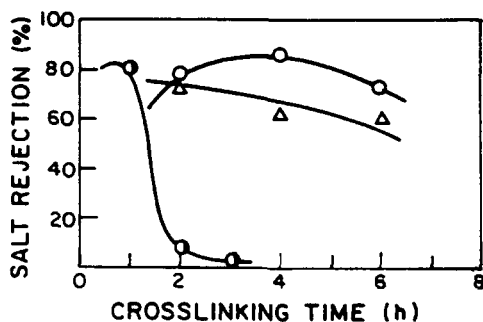

Fig. 5. Effect of crosslinking time on the salt rejection: (O) $0.5M$ $AlCl_3$, $\alpha = \overline{0.9}$ (pH 7); (△) $1.5M$ $ZrCl_4$, $\alpha = 0.9$ (pH 7); (●) $0.25M$ $UO_2(NO_3)_2$, $\alpha = 0$ (pH 2.5), XLT = 70°C.
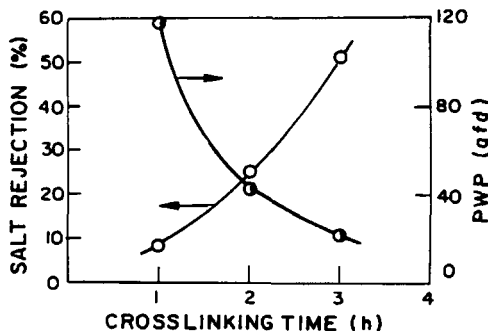

Fig. 6. Effect of crosslinking time on the salt rejection and pure water permeability: Crosslinking solution: $0.25M$ $UO_2(NO_3)_2$, aq. Cast PAA solution pH: 2.5 ($\alpha = 0$), XLT = 25°C.

TABLE VII

Separation and Permeability Characteristics of Ionically Crosslinked Poly(acrylic Acid) Composite Reverse Osmosis Membranes for Some Organic Solutes in Aqueous Solutions[a]

Membrane[b] no.	Film type[c] (on PS support)	Crosslinking solution[d] Metal salt	pH	Solute rejection (%) PEG200	Phenol	Urea	PWP[e] (gfd)	Product Rate (gfd) PEG200	Phenol	Urea
1110-1	PAA–Zr	1.5M ZrCl$_4$	0.1	71.8	66.6	46.3	2.9	1.7	1.3	1.4
2	PAA–Zr	1.5M ZrCl$_4$	0.1	50.5	58.1	39.6	3.4	2.2	1.6	1.6
5	PAA–Al	2M AlCl$_3$	1.7	54.8	62.6	47.5	3.5	2.3	1.7	1.6
7	PAA–Na–Zr	1.5M ZrCl$_4$	0.1	72.0	57.4	40.4	3.1	2.2	1.7	1.8
10	PAA–Na–Al	2M AlCl$_3$	1.7	82.9	79.5	52.4	1.0	1.0	0.9	1.2

[a] Solute concentration: 0.1 wt %; applied pressure and temperature: 300 psig, 20°C.

[b] Solution separation order: PEG200 → phenol → urea → ethanol → acetic acid.

[c] PAA–Me: cast with unneutralized PAA aq solution ($\alpha = 0$) before crosslinking; PAA–Na–Me: cast with neutralized PAA aq solution ($\alpha = 0.9$) before crosslinking.

[d] Crosslinking temperature and time: 70°C, 6 h.
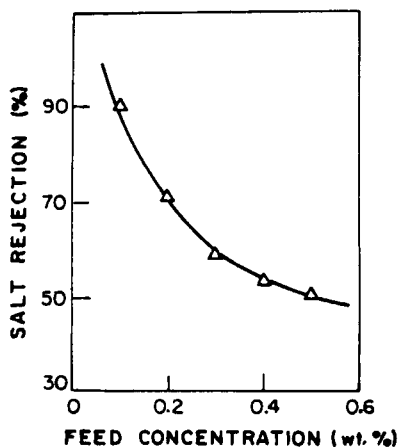
[e] PWP: pure water permeability (gal/ft^2-day).

Fig. 7. The effect of external salt concentration on the salt rejection of ionically crosslinked PAA membranes. Temperature 20°C; 350 psig.

ratory.[7,8] At crosslinking temperatures 60°C and 70°C, it was found that the results were similar to the case of 25°C excepting for the higher rate of cross-linking.

As shown in Figure 5, if the crosslinking time was much longer than the optimum period, the degree of crosslinking became excessive and thus the crosslinked PAA composite membrane structure became more dense to become undesirably brittle, thereby allowing the passage of more bulk solution and causing a decrease in selectivity. These results agreed well with the fact that there was an optimum AA/Al mole ratio for the maximum salt rejection, as previously reported from this laboratory.[9]

The Separation of Some Organic Compounds

The separations of some organic compounds by using ionic crosslinked PAA membranes were tested under reverse osmosis conditions. The related data are summarized in Table VII.

The membrane has one interesting separation property, which is the higher rejection for phenol than the CA membrane as reported by Sourirajan and Matsuura.[11] Phenol is negatively adsorbed at the interface and mostly rejected. Perhaps the negatively charged surface of ionically crosslinked PAA membrane repels the polar molecules of phenol or phenolic groups.

The decrease of salt rejection of the membrane with the concentration of feed: When the membrane was tested with salt solutions of different concentrations, it was found that the salt rejection of all the ionically crosslinked PAA membranes decreased with the increase of the feed concentration, as shown in Figure 7. This phenomenon is a typical characteristic of charged membranes. This strong dependence of salt rejection on the salt concentration can be interpreted by the Donnan equilibrium and expressed by many equations. One of the simplified equations has been given by Kedem as follows[19]:

$$R_\infty = 1 - \frac{1}{t_1 + t_2(K')^2} K'$$

The maximum salt rejection (R_∞) is related to the salt distribution coefficient (K') and the transport numbers of counterion and co-ion (t_1, t_2). K' is simultaneously dependent on concentration of external solution (C_s). The smaller the C_s, the larger is the value of R_∞.

CONCLUSIONS

Composite reverse osmosis membranes of ionically crosslinked poly(acrylic acid) coated on a porous polysulfone membrane as a mechanical support showed improved desalting properties under proper pH conditions of cast poly(acrylic acid) solution. The salt rejection increased with the increasing charge of the ionically bound polyvalent metal cation. The concentration of crosslinking solution did not have much influence on the salt rejection if poly(acrylic acid) casting solution was neutralized, but, if unneutralized, it had considerable influence. For maximum salt rejection there was an optimum period of crosslinking at high temperature such as 70°C, depending on the crosslinking metal salt solutions used. An interesting property of the membranes were the higher rejection of phenols when compared to cellulose acetate membranes.

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