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Characteristics of Reverse Osmosis Membranes Prepared from Schiff Bases of Polyallylamine in Aprotic Solvents and Separation of Inorganic and Organic Solutes through the Membranes

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Abstract

Four different aprotic solvents, *N,N*-dimethylformamide, dimethylsulfoxide (DMSO), *N,N*-dimethylacetamide, and *N*-methyl-2-pyrrolidinone, were used for the preparation of crosslinked membranes of polyallylamine Schiff base derived from 2-pyridinecarboxaldehyde and salicylaldehyde. The membrane from DMSO showed performances quite different from those of the membranes from three other solvents. This was attributable to the reduced solvating power of DMSO leading to a porous membrane, from the comparison of viscosity, turbidity, and surface tension of the polymer solutions, the swelling degree of the membranes, and SEM observation. Cobalt(II) salt-complexed membranes were very hydrophilic and water permeated preferentially from aqueous solutions of organic substances. The separation factor strongly depended on the molecular size of the solute. Cobalt(II) chloride had a higher complex stability and hydrophilicity, and it showed a better performance than cobalt(II) sulfate.

INTRODUCTION

Polyallylamine (PAAm) is a useful raw material as one of reactive polymers, and some applications for chelating use, photosensitive resins, and so on have already been reported (*1–3*). We have prepared Schiff bases of PAAm with several kinds of aldehydes (*4*) and demonstrated that the crosslinked membranes of the Schiff bases were useful for the separation of inorganic solutes like sodium chloride and cobalt(II) chloride and for the separation of those salts from a mixed feed (*5*, *6*). In particular, the ethylene glycol diglycidyl ether (EGE) crosslinked membranes prepared by casting the dimethylsulfoxide (DMSO) solution of hybrid Schiff bases

(PS) derived from both 2-pyridinecarboxaldehyde (P) and salicyl aldehyde (S) showed a large difference in rejection *R* between NaCl and $CoCl_2$ (*4*, *6*). Aprotic solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), and *N*-methyl-2-pyrrolidinone (NMP) can also dissolve PS and be used as a casting solvent. The PS membranes prepared by using DMSO were found to have a different performance of solute separation from that of the membranes from those solvents. In the present study, therefore, properties of the PS membranes from the respective solvent were compared with each other in relation to solute separation behavior, and their separation performances for organic solutes have been investigated.

EXPERIMENTAL

PAAm was supplied from Nitto Boseki Co., Ltd. (Japan) as the salt of hydrogen chloride, and its free base was used after treatment with an anion exchanger. Aldehydes, solvents, and EGE were distilled under reduced pressure before use.

The hybrid Schiff bases were prepared from P and S as in a previous report (*6*): to a 10% methanol solution of PAAm, a DMF solution containing 56 mol% P and then 24 mol% S based on a PAAm unit were added and stirred at 40°C for 3 h after the addition of each aldehyde. The polymer was precipitated in ether.

Preparation of membranes crosslinked with stoichiometric amounts of EGE by casting, drying, and reverse osmosis (RO) were carried out in the same manner as in earlier reports (*5*, *6*). NaCl feed was supplied first, and then $CoCl_2$ feed was used after the membrane was washed with water. The concentration of the permeate was estimated conductometrically for inorganic salts and with a Shimazu total organic carbon analyzer TOC-500 for organic solutes.

The solute rejection *R* and hydraulic permeability K_1 were obtained from the following equations, respectively:

$$R = (c - c')/c \tag{1}$$

$$J_1 = K_1 (\Delta P - \Delta\pi)/\Delta x \tag{2}$$

where c and c' are the feed and product concentrations, respectively, J_1 is the volumetric flux, ΔP is the pressure difference, $\Delta\pi$ is the osmotic pressure difference between feed and product solution, and Δx is the membrane thickness.

Separation factor α with respect to water in the separation of organic solutes was determined from

$$\alpha = (Y_w/Y_o)/(X_w/X_o) \tag{3}$$

where X and Y denote the weight fraction of the feed and product, respectively, and the subscripts w and o represent water and organic solute, respectively.

The tensile strength of membranes was expressed relative to the strength of the cellulose acetate membrane prepared by Manjikian's method (7), and the water content in a wet membrane was measured as before (5).

The swelling degree Q of a membrane was estimated from the following equation after immersion of the dry membrane in the solvent for 2 days at room temperature:

$$Q = 1 + (\rho_m/\rho_s)(W_2 - W_1)/W_1 \tag{4}$$

where W_1 is the weight of the dry membrane and W_2 is that of the swollen blotted one. ρ_m and ρ_s are the densities of the membrane and solvent, respectively. ρ_m was measured in a pycnometer at 25°C. The membranes were prepared by casting a 8% solution and drying at 80°C for 2 h.

Turbidity was expressed as a water volume added to a 4 wt% solution of the Schiff base in an aprotic solvent until the cloudiness in the solution persisted for 5 minutes under magnetic stirring.

Surface tension γ was calculated according to the following equation by measuring the capillary rise h of solvents and solutions at 25°C:

$$\gamma = rhdg/2 \tag{5}$$

where r is the radius of the capillary used, d is the density of the sample liquid, and g is acceleration due to gravity.

A scanning electron micrograph of the cross section of membranes was recorded with a Joel JSM-T 100 after the following treatment: immersion of the cast membrane in water for 5 days, drying in an ambient atmosphere for 2 days and under reduced pressure for 10 h, and breaking of the liquid nitrogen-frozen membrane.

RESULTS AND DISCUSSION

Influence of Aprotic Solvents on Membrane Performance

The Schiff base samples employed in this study are listed in Table 1. They were prepared repeatedly under the same reaction conditions, and

TABLE 1
Preparation of Schiff Bases of Polyallylamine

Polymer code	Yield (%)	Composition[a] [NH$_2$]	[P]	[S]	[η][b]
PS-4	52.8	15.6	60.3	24.1	—
PS-5	75.9	17.7	59.4	22.9	—
PS-6[c]	61.8	14.7	59.0	26.3	1.320
PS-8	94.7	15.8	56.8	27.4	0.299
PS-9	78.2	18.1	58.3	23.6	0.290
PS-10	48.6	18.4	57.1	24.5	0.323
PS-14	26.2	21.9	61.5	16.6	—
PS-15	33.8	16.9	59.9	23.2	0.376
PS-17[c]	32.2	18.1	60.6	21.3	0.650
PS-18	48.6	22.7	59.1	18.2	0.334
PS-19	54.5	20.6	57.6	21.8	0.298
PS-20[c]	46.5	20.2	59.8	20.0	0.313

[a] Molar ratio determined by NMR.

[b] In DMF solution at 25°C.

[c] A sample of $\overline{M}_w$ = 50,000–83,000 was used after removal of a high molecular weight portion by fractional precipitation. The $\overline{M}_w$ of the others was 50,000–65,000.

the polymer code represents the run number. The intrinsic viscosity tended to increase with a decrease in yield, probably due to the loss of lower molecular weight portions in ether precipitation (*6*). Other discussions were described in a previous paper (*6*).

The dependence of R and K_1 on drying time is shown in Figs. 1, 2, and 3 for membranes cast from DMF, DMA, and NMP, respectively. The difference in R and K_1 between PS-4 and -5 membranes at 50 min is so small in Fig. 1 that it is very unlikely that the difference in the composition, as much as about 2% between them and among other code polymers in Table 1, brings about only small differences in R and K_1. The performances in Figs. 1–3 resemble to each other except for the membranes with a short drying time. However, previously reported R and K_1 of membranes cast from DMSO (*4*) are quite different, as is depicted by dashed lines in Fig. 3. Outstanding are the differences in R between NaCl and $CoCl_2$ at 90 and 120 min. A similar large difference in R was observed at 10 min in Fig. 1, but it disappeared with a little longer drying period. The relatively shorter drying times in Fig. 1 are due to the higher volatility of DMF compared with DMA and NMP. At the shorter drying time of 60 min in Figs. 2 and 3, the R of NaCl is higher than the R of $CoCl_2$, unlike other membranes with a longer drying time. This is because the membrane swollen in contact

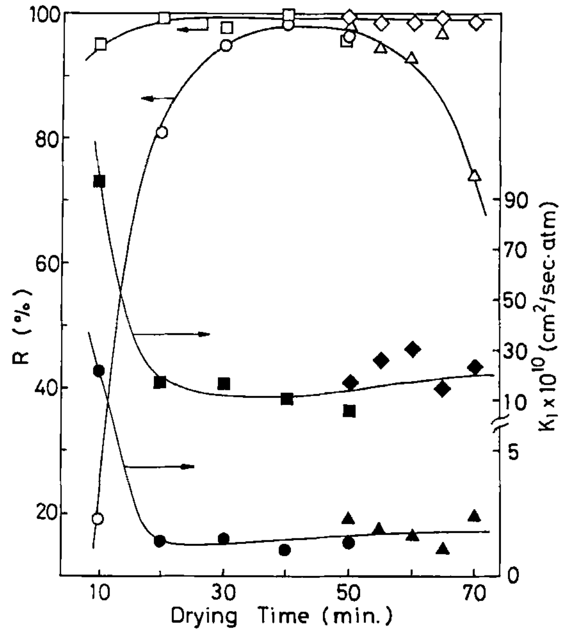

FIG. 1. R and K_1 vs drying time for PS-4 and -5 membranes cast from 19 wt% DMF solution. (△, ▲) NaCl feed for PS-4; (○, ●) NaCl feed for PS-5; (◇, ◆) $CoCl_2$ feed for PS-4; (□, ■) $CoCl_2$ feed for PS-5.

with $CoCl_2$ became weak, probably forming channels for solute passage under the applied pressure. The swelling in contact with $CoCl_2$ is clearly shown in Fig. 4; it is due to the difference in water content before and after contact with the $CoCl_2$ feed. The other three aprotic casting solvents gave analogous results.

Figure 5 shows the relative strength and water content for the membranes used in Fig. 1. The relative strength was measured before the RO test because the swollen membranes reduced their strength so much as to be hardly measurable. Both increased gradually and reached a maximum at about 60 min, indicating the progress of the crosslinking reaction. A longer drying may bring about interstices in the membrane matrix due to excessive contraction which leads to reductions of both strength and water content. The difference in these two properties, which depends on the kind of casting solvent, is illustrated in Fig. 6. The strength decreased in the order NMP > DMA > DMF at 60 min and MNP > DMA > DMSO at 100 min. The same order is followed for the water content as estimated after the RO

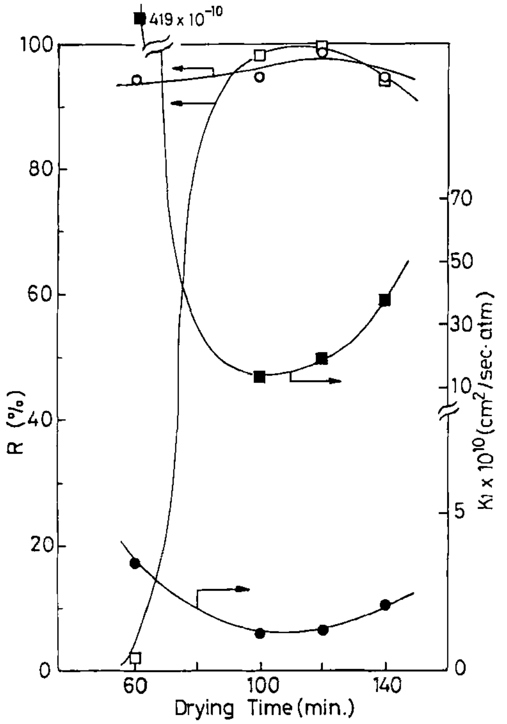

FIG. 2. R and K_1 vs drying time for PS-9 membranes cast from 19 wt% DMA solution. (○, ●) NaCl feed; (□, ■) $CoCl_2$ feed.

test. This difference may represent the difference in the morphological structure or the fabricated state of PS polymer chains, and elastic recovery from compression under applied pressure, provided that the degree of crosslinking is similar in the four solvents.

Comparison of Membrane Charcteristics

The membranes cast from DMSO solution behave very differently from those from DMF, DMA, and NMP as shown Figs. 1–3 and 6. Moreover, a DMSO casting solution with a high concentration was hard to prepare; it tended to give translucent or opaque membranes. They sometimes broke during the RO test under an applied pressure of 80 kg/cm^2. It is conceivable that those unique behaviors stem from the state of PS molecules in the solution. Therefore, the difference in the four solvents was investigated through such solution properties as viscosity, turbidity (which corresponds

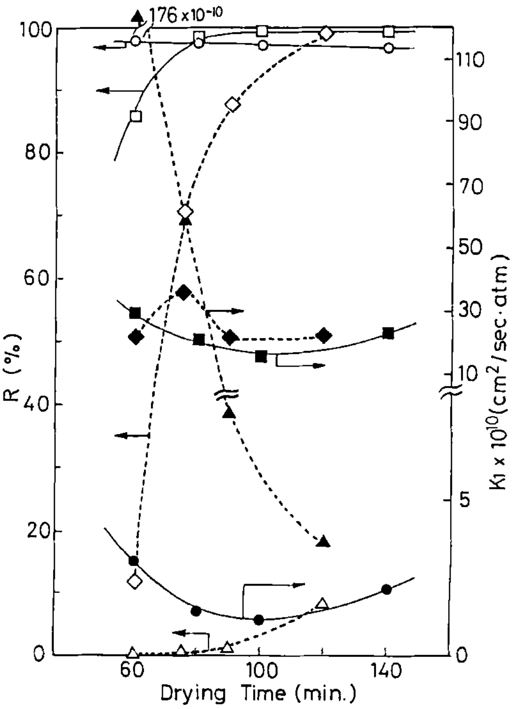

FIG. 3. R and K_1 vs drying time for PS-10 membranes cast from 19 wt% NMP solution and PS-3 membranes (dashed lines) cast from 10 wt% DMSO solution. (○, ●) NaCl feed PS-10; (△, ▲) NaCl feed for PS-3; (□, ■) $CoCl_2$ feed for PS-10; (◇, ◆) $CoCl_2$ feed for PS-3.

to solubility), and the degree of swelling of membranes cast from the four different solvents. The results are shown in Fig. 7. The order of inherent viscosity was NMP > DMA > DMF > DMSO; that is, PS polymer chains are more extended in NMP while they are more coiled in DMSO. The turbidity was in the same order. NMP has the highest affinity and solubility for PS polymer, and DMSO has the lowest values. The degree of swelling gave the same order when a membrane sheet was prepared from each solvent and a fraction of each membrane was separately immersed in the four solvents. Again, NMP exhibited the highest value and DMSO had the lowest: MNP > DMA > DMF > DMSO. The reason why the membrane cast from DMF showed an especially high degree in each swelling solvent may be due to the occurrence of interstices in the membrane matrix after 2 h drying, which agrees with the fact that the relative strength decreased in 70 min drying, as shown in Fig. 5. These interstices may contain the swelling solvent. This order of solvents coincides with that in Fig. 6.

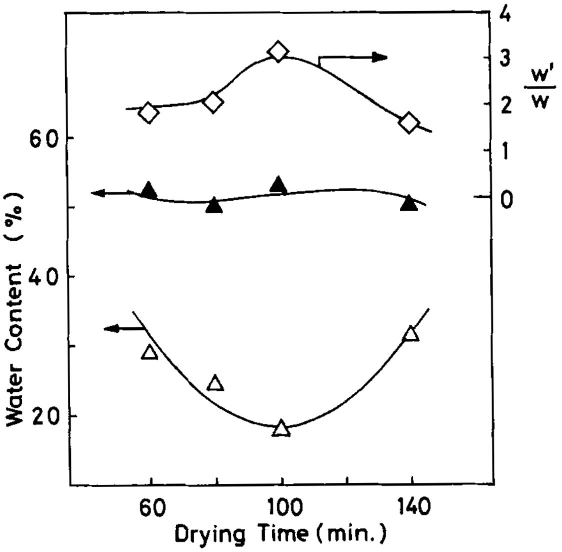

FIG. 4. Water content vs drying time for PS-10 membranes cast from 19% NMP solution. (△) Before the test, *w*; (▲) after the test, *w*′.

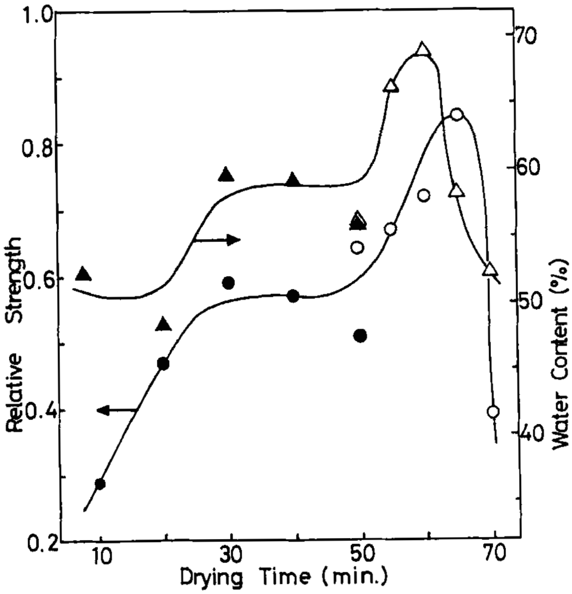

FIG. 5. Relative strength (before the test) and water content vs drying time for PS-4 and -5 membranes cast from 19 wt% DMF solution. (○, △) PS-4; (●, ▲) PS-5.

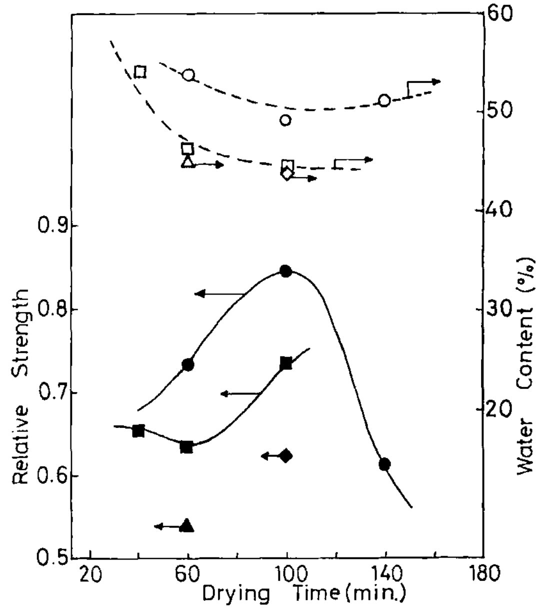

FIG. 6. Relative strength (before the test) and water content vs drying time for PS-8 membranes. (●, ○) NMP; (■, □) DMA; (▲, △) DMF; (◆, ◇) DMSO.

Entanglement of more extended chains appears to contribute to the strength to a greater degree.

All these experimental facts indicate that DMSO has the lowest affinity to PS polymer and to its crosslinked membrane. Kesting discussed the oxygen permeability $P(O_2)$ of polysulfone hollow fiber in relation to the molar size of the casting solvent, and he attributed the difference in $P(O_2)$ to the template effect, i.e., the size of interchain displacement derived from the different solvent sizes (*8*). DMSO is the smallest of the four solvents in molar size (see Table 2). However, this is not the case for our results. The difference in surface tension between the casting solution and the solvent is related to the structure of the asymmetric membrane (*10*, *11*). However, any particular relationship could not be drawn from our estimated values of the solvents and the solutions, as shown in Table 2. The solubility parameters can be ruled out because any peculiarity in DMSO is not seen.

The difference in solution properties and in an affinity to the crosslinked polymer, as shown in Fig. 7, may influence the membrane structure and, consequently, the membrane performance. SEM photographs of the cross section of the membranes are shown in Fig. 8. Small pores, such as those

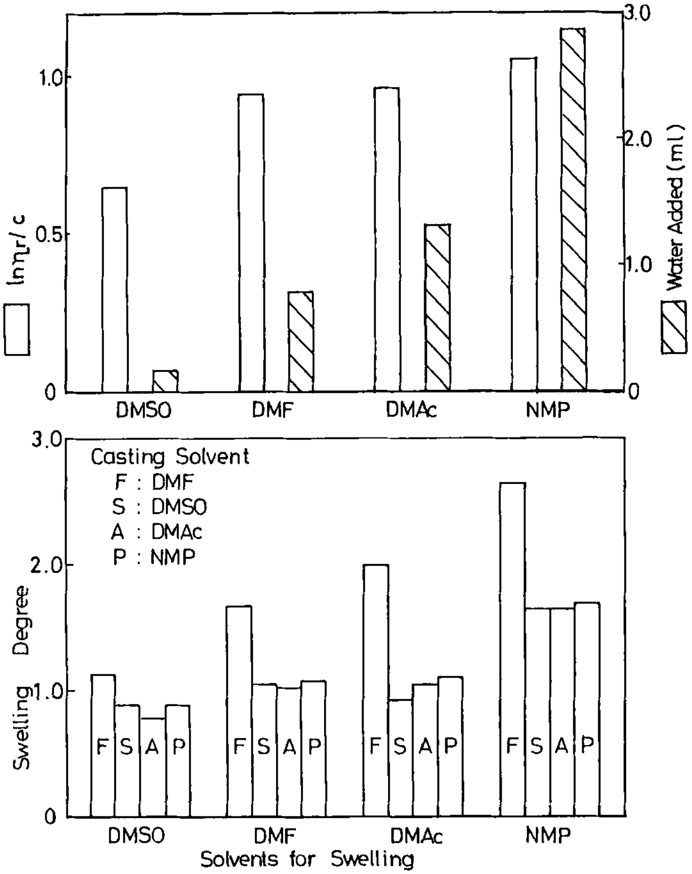

FIG. 7. Viscosity and turbidity of PS-6 solutions, and swelling degree of EGE–crosslinked PS-6 membranes cast from each solvent.

shown in Fig. 8(a), are observed in membranes dried for 45 min (and even for 90 min) while no pores or cavities, such as those of Fig. 8(a), are seen in the membranes prepared from other solvents (Fig. 8b). It is therefore apparent that the unique performance depicted by the dotted lines in Fig. 3 is derived from the morphological structure. The coiled conformation in DMSO solution is probably responsible for the occurrence of such porous membranes and the lower relative strength.

Separation of Organic Solutes through a Cobalt Salt-Coordinated Composite Membrane

A single PS membrane prepared by casting on a glass plate drastically loses strength after contact with $CoCl_2$ feed because of swelling due to the

TABLE 2
Some Physical Constants of the Solvents and Surface Tensions

Solvent	MW	Density (d)[a]	Molar volume MW/d (mL/mol)	bp (°C)	Solubility parameter[b]	γ (dyn/cm)		Difference in γ (solution − solvent)
						Solvent	Solution[c]	
DMF	73.1	0.9421	77.59	153.0	12.1	35.79	36.38	0.59
DMSO	78.1	1.0964	71.23	189	12	43.32	42.27	−1.05
DMA	87.1	0.9326	93.39	165	10.8	35.09	35.12	0.03
NMP	99.1	1.0304	96.18	202	11.3	40.44	39.71	−0.73

[a] Measured at 25°C.
[b] Ref. *9*.
[c] For a 3% solution of PS-15.

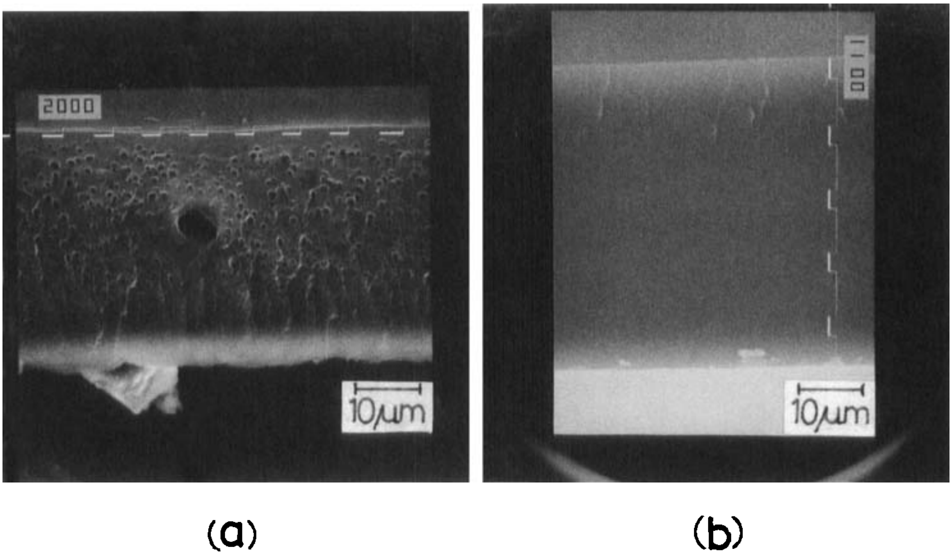

FIG. 8. Scanning electron micrographs (SEM) of the cross sections of PS-18 membranes dried at 80°C for 60 min. (a) Cast from DMSO solution. (b) Cast from NMP solution. The bottom is the glass plate side.

complexation of PS polymer with $CoCl_2$. However, reinforcement by a porous sheet such as membrane filter and filter paper was successful, and a composite membrane cast on a sheet of filter paper enabled continuous and repeated RO operations for a long period (*6*). Since the complexed membrane has a charged and hydrophilic character (*12*), such increased hydrophilicity seems favorable for preferential permeation of water in organic solute-containing feed. Therefore, the $CoCl_2$-complexed composite membrane was used in order to separate water-soluble organic solutes. Flux and separation factor are shown in Figs. 9 and 10 versus the concentration of the solute. Acetic acid partly decomposed the complex, giving a reddish permeate due to $CoCl_2$. The tendency of increasing flux with increasing water composition in the feed in Fig. 9 manifests the hydrophilic character of the membrane. The orders in the magnitude of J_1, Q, molar volume, and viscosity are listed in Table 3. The order of J_1 at 50% solute is mostly parallel to that of Q except with acetone whose viscosity is extraordinarily low. Molecular size is also closely related to J_1 based on the order of molar volume. The difference in α among three alcohols is remarkable. The larger the size of the solute, the higher is α. High α values for *t*-butanol appear to have some relationship with particularly high vis-

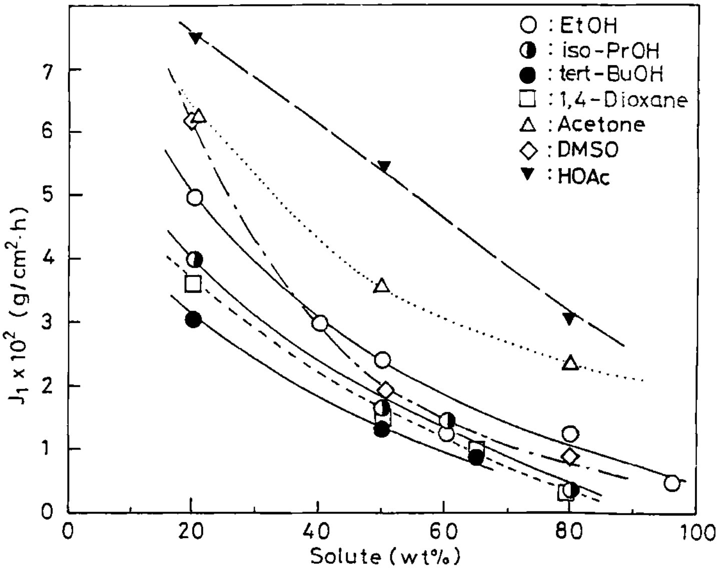

FIG. 9. J_1 vs solute concentration for $CoCl_2$-complexed PS-14EGE50F composite membrane. Thickness Δx of coated polymer = 88.5 μm.

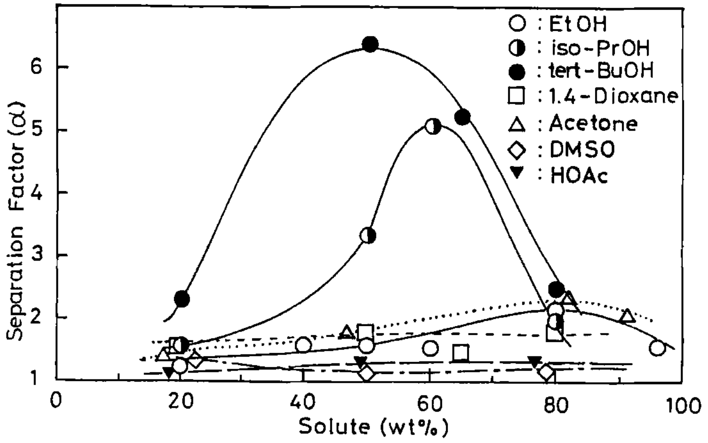

FIG. 10. Separation factor α vs solute concentration for $CoCl_2$-complexed PS-14EGE50F composite membrane. The same Δx as in Fig. 9.

TABLE 3
The Order of J_1 and the Swelling Degree (Q) of PS-17 Membrane, and the Molar Volume (MV) and Viscosity (η) of Solvents

$J_1^{a,b}$:	Water >	acetic acid >	acetone >	ethanol >	DMSO >	isopropanol >	1,4-dioxane >	*t*-butanol
Q^c:	Water >	acetic acid >	DMSO >	isopropanol >	ethanol >	*t*-butanol >	1,4-dioxane >	acetone
	2.66	2.12	1.36	1.18	1.13	1.07	1.01	1
MV^d:	Water <	acetic acid <	ethanol <	DMSO <	acetone <	isopropanol <	1,4-dioxane <	*t*-butanol
	18.0	57.2	58.4	70.9	73.5	76.4	85.2	94.2
η^e:	Acetone <	water <	ethanol <	acetic acid <	1,4-dioxane <	DMSO <	isopropanol <	*t*-butanol
	0.32	1.00	1.17	1.26	1.31	2.20	2.43	3.35(30°C)

[a] The solution was supplied in the order: water, ethanol, isopropanol, *t*-butanol, 1,4-dioxane, acetone, DMSO, and acetic acid.

[b] At 50% solute concentration.

[c] Relative values based on acetone for a single membrane which was soaked in 0.06 *M* $CoCl_2$ solution for a week, washed with water, and dried on a Teflon sheet under reduced pressure.

[d] Molecular weight/density at 20°C.

[e] Centipoise at 20°C (*13*).

cosity. For an 80% *t*-butanol solution, no permeate was obtained. That the permeation occurred in a wide range of feed concentrations and α over unity in Fig. 10 for all the solutes suggests that the preferential penetration of water into the very hydrophilic membrane exceeds the osmotic difference between feed and product.

It has been reported that the addition of a trace amount of $CoSO_4$ to the aqueous ethanol feed markedly increases the separation factor through a cuprophane membrane, which was attributed to the complexation of $CoSO_4$ with cellulose molecules (*14*). In this study, PS membrane was complexed in advance with $CoSO_4$ by feeding $CoSO_4$ solution under the applied pressure for about 100 h. The $CoSO_4$-complexed PS membrane exhibited the results shown in Fig. 11. In spite of thinner membranes, the J_1's of three alcohols in Fig. 11 did not exceed those in Fig. 9, and the α's were not higher than those in Fig. 9 except for a little higher α for *t*-butanol at 50%. These facts indicate that water penetrates into the $CoSO_4$-complexed membrane to a degree less than the $CoCl_2$-complexed membrane. This is supported by a low swelling degree Q and the water content of the former compared with a high degree of the latter as seen in Table 4. R, J_1, and the complexed amount of cobalt salt are also higher in the $CoCl_2$-complexed membrane than in the $CoSO_4$-complexed membrane. pH values of the feed solutions are irrelevant to the difference between the two salts.

Table 5 shows the desalination results of $CoSO_4$ feed followed by $CoCl_2$. R decreased with time with comparable fluxes and recovered when the

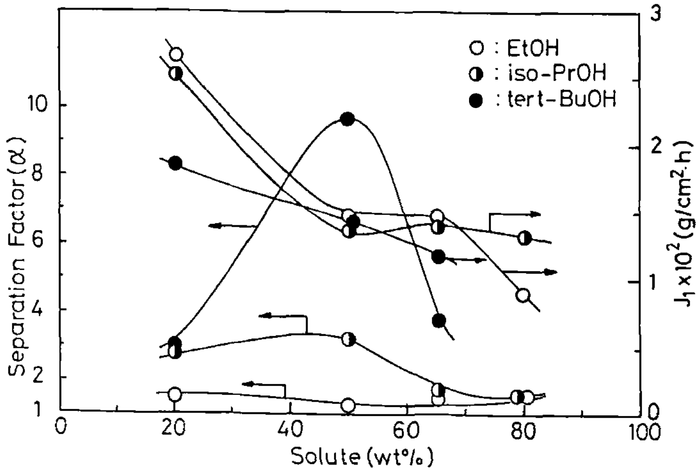

FIG. 11. J_1 and separation factor α vs solute concentration for $CoSO_4$-complexed PS-19EGE50F membrane. Δx of coated polymer = 62.3 μm.

TABLE 4

Performance and Properties of Cobalt Salt-Complexed Membranes[a]

Salt	Thickness as prepared (μm)	R[b] (%)	J_1[b] (g/cm²·h)	Q	Water content (%)	Complexed salt in membrane[c] (M)
$CoCl_2$[d]	24.5	99.8	2.98	2.66	50.1	0.174
$CoSO_4$[d]	23.5	95.4	1.31	2.29	44.0	0.099

[a] PS-20 cast from 12 wt% DMF solution and dried at 80°C for 90 min.

[b] At 24 h.

[c] Extracted with aqueous HCl and titrated by the chelating method after the RO test and water washing.

[d] pH of the feed solution: 5.70 ($CoCl_2$), 5.55 ($CoSO_4$), 5.50 (deionized water).

TABLE 5

Desalination of Cobalt Salts by RO with a Composite Membrane PS-19EGE50F[a]

Salt	$CoSO_4$	$CoSO_4$	$CoSO_4$	$CoSO_4$	$CoCl_2$[b]
Time elapsed (h)	20	54	93	112	>112
R (%)	97.1	92.3	92.2	90.8	97.7
$J_1 \times 10^2$ (g/cm²·h)	3.13	4.24	3.92	4.99	6.64

[a] The thickness (Δx) of polymer coated by casting DMSO solution on filter paper was 107.7 μm.

[b] When the feed was replaced by $CoCl_2$ feed after 112 h.

feed was replaced by $CoCl_2$. This fact indicates that the coordinating power of $CoSO_4$ is smaller than that of $CoCl_2$, although R of divalent anions usually tends to be higher than R of monovalent anions.

CONCLUSIONS

The performances of membranes prepared from DMF, DMA, and NMP solution were similar, while membranes prepared from DMSO behaved quite differently, displaying a very low R of NaCl with a large difference in R between NaCl and $CoCl_2$. This is attributable to the low affinity of DMSO to PS polymer compared with the other three aprotic solvents, which probably leads to a membrane containing a number of small pores as observed by SEM. The $CoCl_2$-complexed membrane was found to be converted into a very hydrophilic one, and water permeated preferentially when an organic solute-containing feed was supplied. The separation factor strongly depended on the molecular size of the solute and, to some degree, on the viscosity. Complexation with $CoCl_2$ gave more stable and more hydrophilic membranes which showed a higher flux and rejection than with $CoSO_4$.

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REFERENCES

1. S. Harada, *Kobunshi Kako*, *33*, 493 (1984).
2. Nitto Boseki Co., European Patent Application EP 143,328 (1985); 207,495 (1987).
3. S. Kobayashi, M. Kokunoh, T. Saegusa, and F. Mashio, *Macromolecules*, *18*, 2357 (1985).
4. E. Oikawa and K. Yahata, *Polym. Bull.*, *17*, 315 (1987).
5. E. Oikawa and H. Makino, *Sep. Sci. Technol.*, *24*, 659 (1989).
6. E. Oikawa, K. Katoh, and K. Yahata, *Ibid.*, *25*, 45 (1990).
7. S. Manjikian and C. Allen, *Research and Development Progress Report No. 378*, Office of Saline Water, 1968.
8. R. E. Kesting, *J. Polym. Sci.*, *Polym. Lett. Ed.*, *27*, 187 (1989).
9. H. Burrell and B. Immergut, in *Polymer Handbook* (J. Brandrup and E. Immergut, eds.), Wiley-Interscience, New York, 1967, p. IV–341.
10. G. B. Tanny, *J. Appl. Polym. Sci.*, *18*, 2149 (1974).
11. K. Darcovich and O. Kutowy, *Ibid.*, *35*, 1769 (1988).
12. E. Oikawa, Y. Honda, and Y. Sawada, *Polym. Bull.*, *6*, 169 (1981).
13. S. Asakura, N. Tokura, M. Okawara, J. Kumanodani, and M. Senoh (eds.), *Yohzai Handobukku* (*Solvent Handbook*), Kohdansha, Japan, 1976.
14. A. Mochizuki, Y. Sato, H. Ogawara, and S. Yamashita, *J. Appl. Polym. Sci.*, *37*, 3357 (1989).

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