Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Oikawa, Eizo , Katoh, Kazunori and Yahata, Ken(1990) 'Reverse Osmotic Separation of Sodium Chloride and Cobalt (II) Chloride through Membranes Prepared from Schiff Bases of Polyallylamine', Separation Science and Technology, 25: 1, 45 — 62

To link to this Article: DOI: 10.1080/01496399008050320

URL: http://dx.doi.org/10.1080/01496399008050320

SEPARATION SCIENCE AND TECHNOLOGY, 25(1 & 2), pp. 45–62, 1990

Reverse Osmotic Separation of Sodium Chloride and Cobalt(II) Chloride through Membranes Prepared from Schiff Bases of Polyallylamine

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Abstract

Crosslinked membranes from Schiff base derivatives of polyallylamine were prepared with 2-pyridinecarboxaldehyde (P) and with P followed by salicylaldehyde, and used for the reverse osmotic separation between sodium chloride (NaCl) and cobalt(II) chloride ($CoCl_2$). The membranes whose rejection (*R*) was high against $CoCl_2$ and low against NaCl at each single feed supply showed a reduced difference in *R* in the case of a mixed solute feed due to Donnan exclusion by fixed charges in the $CoCl_2$-complexed membrane. An approximate calculation of the complexed $CoCl_2$ revealed that a very small portion of Schiff base groups took part in the complexation. Composite membranes on a cellulosic sheet solved the problem of an extreme reduction of the membrane strength after complexation, enabling continuous and repeated use. Some transport parameters were determined. Since they indicated a semipermeable character for $CoCl_2$, multistage runs of a single membrane or low pressure runs of a more porous composite membrane were suggested for the effective separation of NaCl and $CoCl_2$.

INTRODUCTION

In the course of our studies on the preparation of membrane materials and the properties of their membranes for reverse osmosis, we have dealt with several 4-vinylpyridine (4VP) copolymers (*1*) because the poly4VP (P4VP) membrane was found to have a high salt rejection while retaining a fair water permeability (*2*). In particular, membranes from 4VP co-polymer with 2,4-diamino-6-vinyl-*s*-triazine (DAVT), when complexed with cobalt or other transition metal salts, considerably improved rejection (*R*) without flux decrease (*3*). Since then the following other 4VP copolymers containing functional groups capable of complexation were prepared and their membrane properties were examined: poly(4VP-*co*-methyl vinyl ketone (MVK)) (*1*) and poly(4VP-*co*-methacrolein (ML)) (*4*) crosslinked with malonyl dihydrazide (MD) or 2-phenyl-4,6-dihydrazino-*s*-triazine to form functional groups $-C{=}NNHC({=}O)-$, the oxime of poly(4VP-*co*-MVK) containing $-C{=}N{-}OH$ groups (*5*), polyhydrazone from 2,5-pyridinedicarboxylic acid chloride and MD (*6*), and the amidoxime of poly(4VP-*co*-acrylonitrile (AN)) containing $-C(NH_2){=}N{-}OH$ groups (*7*). The reverse osmosis membranes prepared from those copolymers commonly showed a high rejection of $CoCl_2$ due to complexation. However, some membranes which had a low rejection of NaCl resulted in a large difference in *R* between the two salts. The difference amounted, for example, to about 60% for poly(4VP-*co*-ML) (*4*), 39% for the oxime of poly(4VP-*co*-MVK) (*5*), 56–76% for the polyhydrazone membranes fabricated with an inorganic additive such as lithium chloride, lithium nitrate, and magnesium perchlorate (*6*), and 46% for the amidoxime of poly(4VP-*co*-AN) (*7*). Those membranes showed potential capability to separate each other from a mixture of NaCl and $CoCl_2$.

We recently prepared Schiff base derivatives of polyallylamine (PAAm) with 2-pyridinecarboxaldehyde (P) and/or salicylaldehyde (S) and investigated their reverse osmotic behavior (*8*). Some P derivatives crosslinked with diacetyl showed about 80% difference, and the other membranes derived from both P and S crosslinked with ethylene glycol diglycidyl ether (EGE) showed about 90% difference. Those Schiff base membranes especially have a potential for practical use for the separation of transition metal and alkali metal salts. The present study, therefore focuses on the actual behavior of those membranes in the reverse osmotic separation of mixed feeds, the improvement of membrane performance, and some transport properties of the Schiff base membranes.

EXPERIMENTAL

Preparation of Schiff Bases

The free PAAm was prepared from a PAAm · HCl salt (MW = 50,000–65,000), supplied by Nitto Boseki Co. (Japan), by anion exchanger treatment and used for the preparation of P and PS Schiff base polymers by reaction with P, and P followed by S, respectively [as in a previous report (*8*)]. P polymers: a 10% methanol solution of P was added to a 10% methanol solution of PAAm and the mixture was stirred at 40°C for 2 h. The product was precipitated in diethyl ether. PS polymers: the solvent for P was DMF and the reaction was conducted at 40°C for 3 h. After the removal of methanol under reduced pressure, a 10% DMF solution of S was added and the mixture was stirred at 40°C for 3 h. The product (Table 1) was precipitated in dilute ammonia (PS3) or diethyl ether (PS11–13).

The composition was determined by NMR in CD_3OD solution for the pyridine ring content of the P derivatives and in DMSO-d_6 solution for the benzene ring content of the PS derivatives. The difference was assumed to be unreacted amino groups.

Reaction of Diacetyl (DAc) with Butylamine

A 10% ethanol solution of 1.723 g (20 mmol) DAc and 2.96 g (40 mmol) butylamine was refluxed with stirring for 2 h. After the removal of ethanol,

TABLE 1
Preparation of Schiff Bases of Polyallylamine[a]

Polymer code	PAAm (g)	P (g)	S (g)	Yield, g (%)	Composition,[b] $[NH_2]/[P]/[S]$	$[\eta]$[c]
P7	3.89	5.47	—	8.36 (99.1)	26.2/73.8	
P8	2.70	3.80	—	5.70 (97.3)	27.6/72.4	
PS3	2.30	2.42	1.12	5.04 (∼100)	18.6/59.0/22.4	
PS11[d]	3.75	3.94	1.88	1.91 (22.6)[e]	20.0/59.4/20.6	0.490
PS12	5.60	5.89	2.82	4.31 (41.1)[e]	16.4/61.6/22.0	0.334
PS13	5.00	5.25	2.52	5.03 (44.4)[e]	20.1/58.3/21.6	0.325

[a] For P polymers, 75 mol% of P based on PAAm monomer unit was added, and for PS polymers, 56 mol% of P and then 24 mol% of S were added.

[b] Molar ratio determined by NMR.

[c] In DMF solution at 25°C.

[d] MW = 50,000–83,000, from which about one-fourth of the higher molecular weight fraction was removed by fractional precipitation with actone.

[e] The uncollected polymer fraction remained in a turbid suspension.

the residue was distilled at 6 mmHg. An oily yellow liquid [1.501 g (61%)] was collected at 81-82°C; NMR shift from TMS in CCl_4: δ3.37 (2H, triplet, $-CH_2-N=C-$), δ1.93 (3H, singlet, $CH_3-C=N$), δ1.2-1.6 (4H, multiplet, $-CH_2CH_2-$), δ0.95 (3H, triplet, end CH_3).

Membrane Preparation

The general procedure is the same as before (*1*, *8*). On a glass plate coated with polyacrylamide, a 10% benzyl alcohol (BzOH) solution of P polymer (10% DMSO solution of PS polymer) containing the required amount of crosslinking agent was cast and dried at 80°C for a given time.

In the preparation of composite membranes crosslinked with 50 mol% DAc or EGE based on NH_2 groups, a membrane filter (denoted as M in the code) of Toyo Roshi Inc. (regenerated cellulose TM-300P, 3.0 μm pore size) was coated with 10% BzOH solution of P7, P8, or P11, and a sheet of quantitative No. 7 filter paper (denoted as F) of Toyo Roshi Inc. was coated three times with a 10% DMSO solution of PS12 or 13, each time dried for 2, 1.5, and 1.5 h at 80°C. Those membranes were immersed in water overnight before use. Membrane thickness was measured with an electomagnetic meter.

Reverse Osmosis (RO)

A batch-type apparatus of 300 mL capacity and a circulating-type apparatus manufactured by Atsuryoku Kiki Engineering Co. were used. NaCl feed (0.06 *M*) was supplied first, the membrane was washed with water under pressure overnight, and then 0.06 *M* $CoCl_2$ feed was supplied. The initial product of 5 mL NaCl and 15 mL $CoCl_2$ was discarded and the succeeding 10 mL product was collected. A nitrogen pressure of 80 kg/cm^2 (7.85 MPa) was usually applied at 25°C. When the pressure was changed, the starting high pressure of 80 kg/cm^2 was successively lowered. The product concentration was determined by electric conductance measurement. In the case of a mixed feed of NaCl and $CoCl_2$, chelate-forming titration was used for the Co^{2+} ion and the Mohr method for the total Cl^- ion. Salt rejection R and hydraulic permeability K_1 were obtained from the following equations, respectively:

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

$$J_1 = K_1(\Delta P - \Delta\pi)/\Delta x \qquad (2)$$

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.

RESULTS AND DISCUSSION

Preparation of Schiff Bases and Their Membrane Performance for the Mixed Feed of NaCl and $CoCl_2$

The results of the Schiff base preparation are presented in Table 1. P readily reacted in nearly quantitative yield, as is seen in the results of P7 and P8. S, on the other hand, was prone to show relatively lower reactivity in view of the composition. The slightly higher compostion of P than the ratio added is not understood at present, but possible reasons include a slight excessive addition of P because of incomplete drying of the aqueous-free P solution in the determination of its concentration, and a change in the NMR area of free amino groups, probably due to oxidation of the amino groups or to deuterium exchange. Lower yields in PS11–13 can be attributed to preferential precipitation of a higher molecular weight fraction, thereby leaving a lower molecular weight fraction in the turbid ether suspension. Recovery of the suspended fraction was not carried out because a higher molecular weight is considered to be advantageous in membrane performance. The close resemblance in the composition of PS11–13 and PS3, in which the product was almost completely recovered, indicates the homogeneity of the Schiff base formation.

It has been reported that most of those Schiff base membranes effectively rejected $CoCl_2$ and some of them exhibited a large difference in R between the NaCl and $CoCl_2$ feeds (*8*). Remarkable examples are shown in Table 2. That DAc reacts with 2 mol of amino groups was proved (described in a model reaction in the Experimental Section), and the crosslinking reaction of EGE has already been confirmed (*8*). The difference, ΔR in Table 2, was obtained in a separate run for each salt. Hence, ΔR for the case of a mixed feed of both salts was examined. The results for P8 membranes are illustrated in Fig. 1, and those of corresponding separate runs appear in Fig. 2. At 35 mol% addition of DAc in Fig. 2, R's of NaCl and $CoCl_2$ are 7.0 and 88.1%, respectively, the difference

TABLE 2
The Difference in Rejection (ΔR) between NaCl and $CoCl_2$ Feed

Polymer code	Crosslinking agent added (mol%)[c]	Drying time (h)	$K_1 \times 10^9$ ($cm^2/s \cdot atm$) NaCl	$K_1 \times 10^9$ ($cm^2/s \cdot atm$) $CoCl_2$	R (%) NaCl	R (%) $CoCl_2$	ΔR (%)
P7[a]	DAc	25.5[d]	2	1.4	7.1	7.9	89.4
81.5			35.1	2	1.8	7.0	14.2
96.0	81.8			50.2	2	0.3	6.3
89.2	98.3	9.1					
PS3[b]	EGE	50	1.25	6.0	4.7	0.8	66.0
65.2			50	1.5	0.9	3.3	1.7
96.8	95.1			50	2	0.4	2.9
8.6	99.8	91.2					

[a] Cast from 10% benzyl alcohol solution.

[b] Cast from 10% DMSO solution.

[c] Based on NH_2 groups.

[d] Water content: 52.1%. Tensile strength relative to that of cellulose acetate: 0.09 before RO test.

being 81.7%. R's in Fig. 1, in contrast, are 52.5 and 90.5%, respectively, the difference being reduced to 38.0% This phenomenon may be explained principally in terms of Donnan exclusion by a $CoCl_2$-complexed charged membrane. The assumption, illustrated in Fig. 3, allows calculation of the approximate concentration of fixed $CoCl_2$ in the membrane for the case in which NaCl in the membrane is in equilibrium with the high pressure phase. At equilibrium the concentration of each ion is denoted as shown in Fig. 3, neglecting the boundary effect for stirring around the membrane surface at the high pressure side. The average concentration of NaCl is

$$(c + c')/2 = \{c + c(1 - R)\}/2 = c(2 - R)/2 = 0.03(2 - 0.525)/2 = 0.0221$$

In the Donnan equilibrium between the membrane and the high pressure phase, the following equation holds for NaCl, assuming c is constant because of an excessive amount of feed and $c_l = 0.0221$:

$$(2x + c_l)c_l = 3c^2$$

$$\therefore x = (3c^2 - c_l^2)/2c_l = 0.050$$

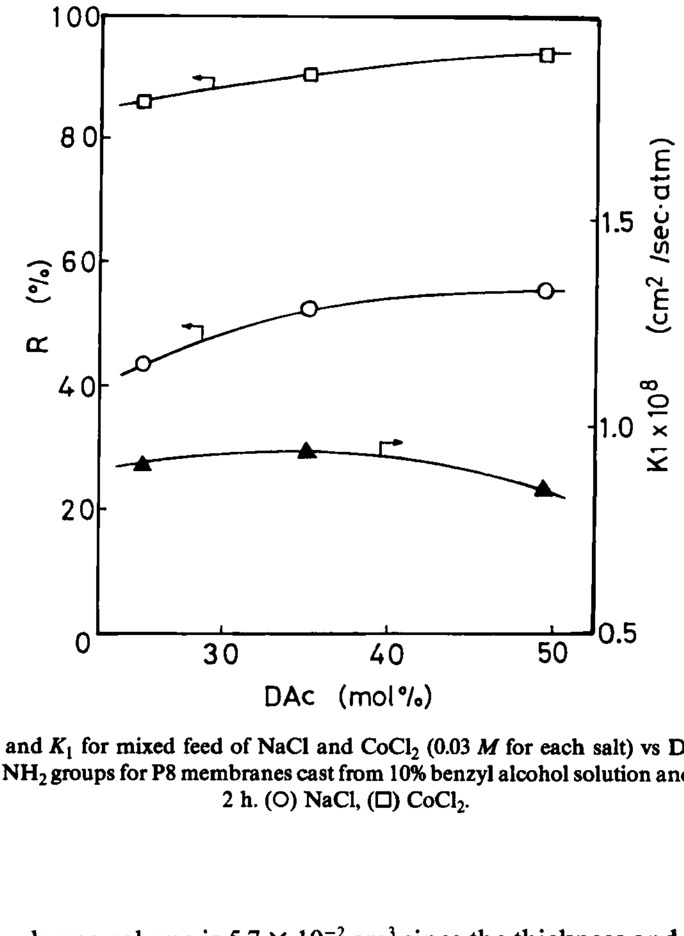

FIG. 1. R and K_1 for mixed feed of NaCl and $CoCl_2$ (0.03 M for each salt) vs DAc added based on NH_2 groups for P8 membranes cast from 10% benzyl alcohol solution and dried for 2 h. (○) NaCl, (□) $CoCl_2$.

The membrane volume is 5.7×10^{-2} cm^3 since the thickness and effective area were 31.5 μm = 3.15×10^{-3} cm and 18.1 cm^2, respectively. Thus, the volume contains $(0.050 \times 5.7 \times 10^{-2})/1000 = 2.85 \times 10^{-6}$ equivalent of Co^{2+}. This volume involves 4.69×10^{-4} mol of the structural unit as calculated from the average molecular weight (121.4) of P8 which is derived from the composition, supposing that the density of the membrane is close to unity. Since the water content of the membrane is ~50%, the same volume involves 2.35×10^{-4} mol of the polymer. Therefore, only $(2.85 \times 10^{-6} \times 100)/(2.35 \times 10^{-4}) = 1.2\%$ of the structural unit, or 2.4% in a 1:2 complex of Co^{2+} to the unit, participated in the complexation. These small values are only doubled even through the density is reduced to 0.5. This estimation indicates that the complexation takes place mainly at the

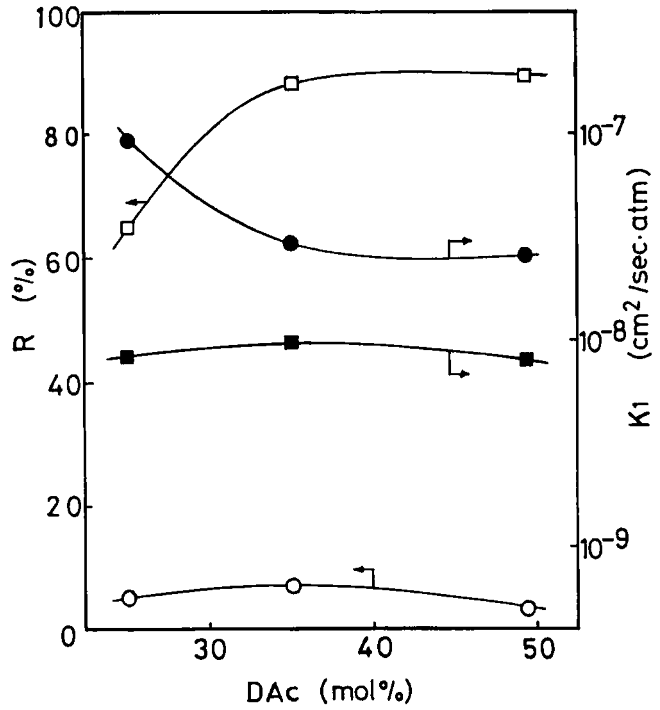

FIG. 2. R and K_1 for separate feed of NaCl followed by $CoCl_2$ feed (0.06 M each) vs DAc added for the same P8 membranes as in Fig. 1. (○, ●) NaCl, (□, ■) $CoCl_2$.

membrane surface and around the path of $CoCl_2$. Coexisting $CoCl_2$ in the feed may have an influence on the Donnan equilibrium of NaCl, but the influence is not considered to be appreciable because of the high rejection of $CoCl_2$. If R for 0.03 M NaCl feed in the absence of $CoCl_2$ ($x = 0$) is close to 7.0%, which is probable for a neutral membrane, the average concentration of NaCl would be $c(2 - R)/2 = 0.03(2 - 0.07)/2 = 0.02895$. Hence, the average concentration of NaCl in the membrane decreases by about $(0.02895 - 0.0221) \times 100/0.02895 = 24\%$ owing to the coexistence of the same concentration of $CoCl_2$ in the feed.

Although ΔR was reduced to 38.0% from 81.7% (~53% reduction) by Donnan exclusion, two- or three-step operation of RO seems to attain complete separation of NaCl and $CoCl_2$. Drawbacks of the P membranes are a low mechanical strength (see footnote d in Table 2) and the in-

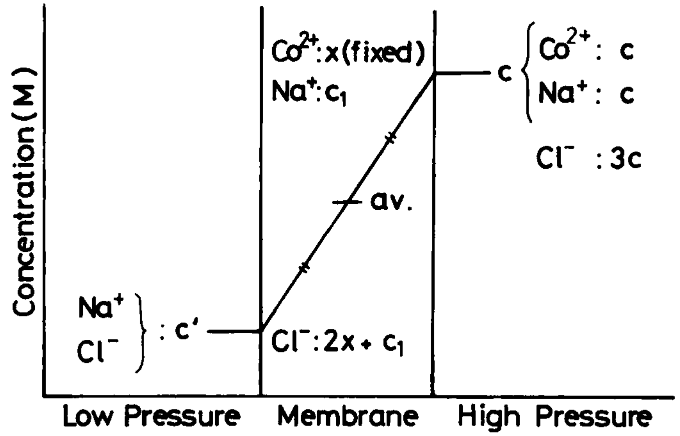

FIG. 3. Illustration of concentration profile at stationary (equilibrium) state ($c = 0.03$).

capability of repeated use because of swelling of the complexed membrane into a gelled state. PS membranes gave larger values of ΔR as shown in Table 2 and were stronger than P membranes, but their strength decreased to a great extent once $CoCl_2$ feed was supplied (*8*). Some difficulty always accompanied PS membrane fabrication because DMSO is not a good solvent for PS polymers.

Improvement of the Performance of PS Polymer Membrane–Composite Membrane

The problem of strength reduction was solved by using a membrane support which was porous, mechanically strong, and invulnerable to solvent. Filter papers and membrane filters made of cellulose and regenerated cellulose, respectively, satisfy the requirements. A three times coating of 10% DMSO solution on a sheet of filter paper was necessary in order to prepare an entirely defect-free membrane, while one time was enough for a membrane filter which had a smoother surface. A great advantage of the composite membrane over the single membrane is that the former can endure repeated use. The composite membrane did not show any apparent change even after a RO test of $CoCl_2$ except for coloring. Experimental results for repeated use are shown in Figs. 4 and 5. One cycle consists of RO of NaCl feed, water washing, RO of $CoCl_2$ feed, and water

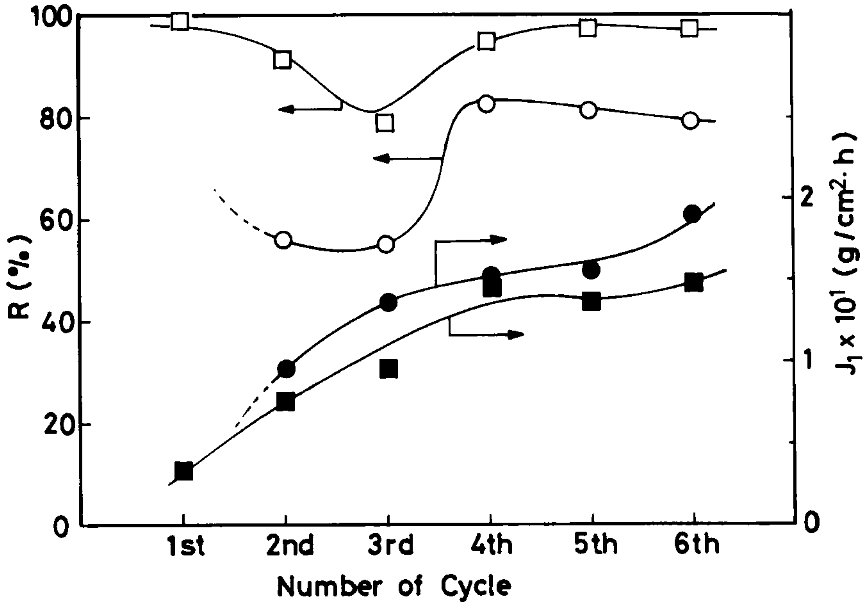

FIG. 4. R and J_1 vs number of feed cycle for PS12-EGE50F composite membrane cast from 10% DMSO solution on filter paper (Δx of coated polymer = 117 μm). (○, ●) NaCl, (□, ■) $CoCl_2$.

washing. The absence of R and J_1 for NaCl in the first cycle in Fig. 4 was because of a too small flux of the membrane containing a thick layer of coated polymer. However, $CoCl_2$ feed made it possible for water to readily penetrate due to swelling of the complexed polymer. After that, NaCl feed could give a product in a reasonable time. For another composite membrane shown in Fig. 5, NaCl feed gave a large flux and low rejection, presumably because the membrane had thin areas. High rejection of $CoCl_2$ and NaCl in the 2nd cycle and thereafter indicates that swelling after contact with $CoCl_2$ restored the membrane function. A gradual increase in fluxes and high rejections against $CoCl_2$ are commonly observed both in Figs. 4 and 5. It took more than 5 weeks to finish the 7th cycle. The high rejection of $CoCl_2$ for a long time period verifies the stability of the composite membrane. Figure 6 depicts the dependence of R and J_1 on the initial period in continuous RO test for $CoCl_2$ feed. The initial increase in both R and J_1 is attributable to swelling of the polymer phase due to complexation with $CoCl_2$, and the membrane stability to reinforcement by the support matrix.

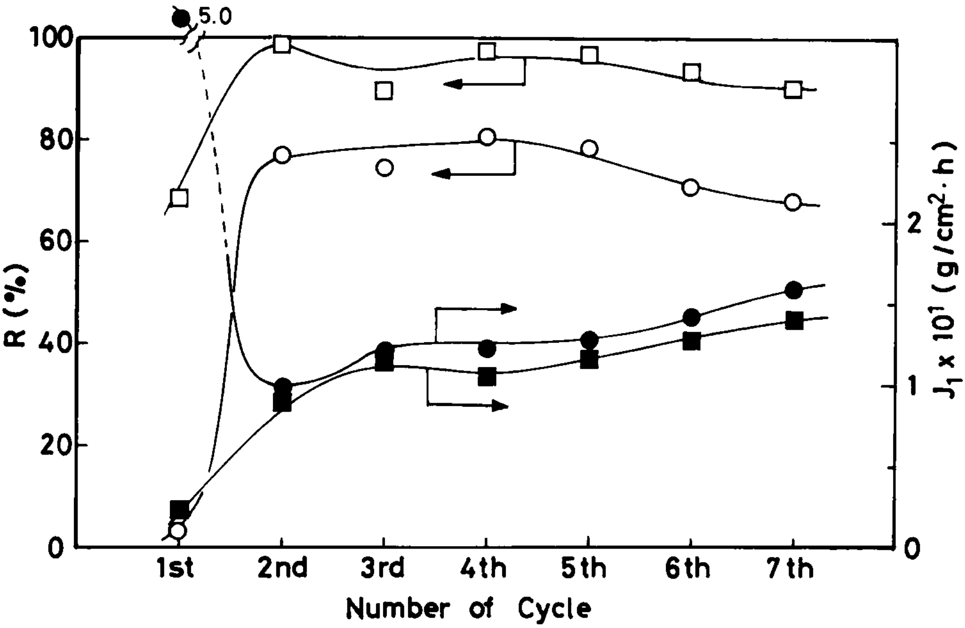

FIG. 5. R and J_1 vs number of feed cycle for PS13-EGE50F-2 composite membrane cast from 10% DMSO solution on filter paper (Δx of coated polymer = 81 μm). (○, ●) NaCl, (□, ■) $CoCl_2$.

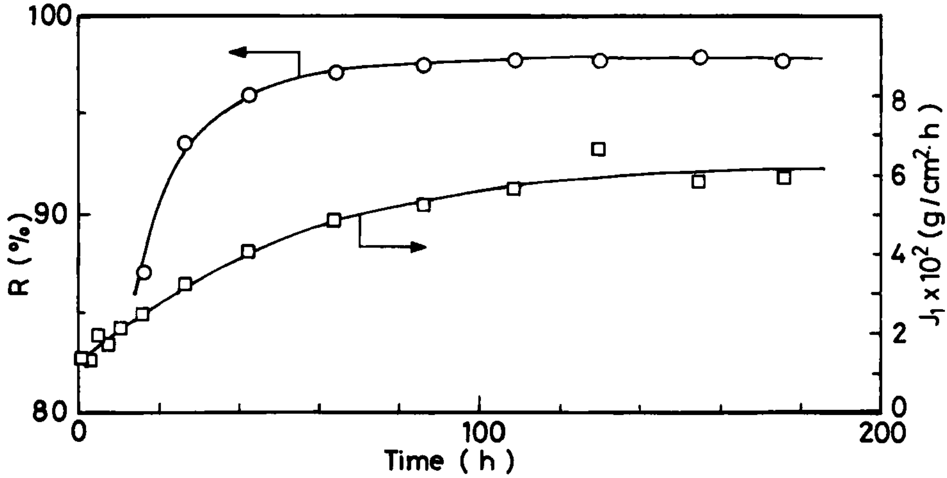

FIG. 6. R and J_1 in a continuous run for PS13-EGE50F-3 (Δx of coated polymer = 96 μm); $CoCl_2$ feed.

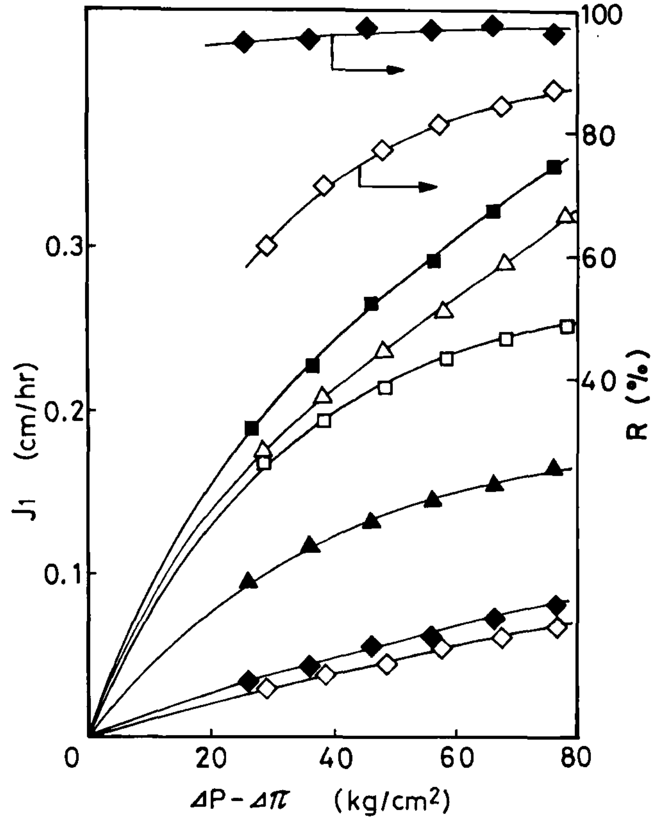

FIG. 7. R and J_1 vs effective pressure ($\Delta P - \Delta\pi$) for P membranes. The following circled numbers denote the order of feed supply. (□ ①) NaCl, (■ ②) $CoCl_2$: P7-DA50M. (▲ ①) $CoCl_2$, (Δ ②) NaCl: P8-DA50M. (◇ ①) NaCl, (◆ ②) $CoCl_2$: PS11-EGE50M (Δx of coated polymer = 69 μm).

The dependence of J_1 and R on the effective pressure is shown in Fig. 7 for membrane filter-based composite membranes. A change in the order of feed supply reversed the magnitude of J_l. This can also be explained in terms of membrane swelling. An initial supply of $CoCl_2$ leads to swelling of the membrane, resulting in a larger flux for the NaCl feed, which is consistent with the results in Figs. 4 and 5. On the other hand, an initial supply of NaCl feed before membrane swelling yields smaller fluxes. The curvature is attributed to membrane compaction. The same tendency was observed for a single membrane with a larger flux. A PS11-EGE50M membrane with a large thickness gives straight lines, indicating increased resistance against pressure. Outstanding and interesting is ΔR between $CoCl_2$ and NaCl for separate RO tests for each salt. The lower the effective pressure, the larger is the difference. This suggests the possibility of practical application. Figure 8 shows the results for PS12-EGE50F at 10, 20, and 30 kg/cm^2 for the mixed feed. A lower pressure gives a larger difference, at some cost of flux. Although ΔR at 30 kg/cm^2 is similar to that in Fig. 1, the composite membrane is advantageous over a single one in that the former can be used continuously for a long period. These results indicate the

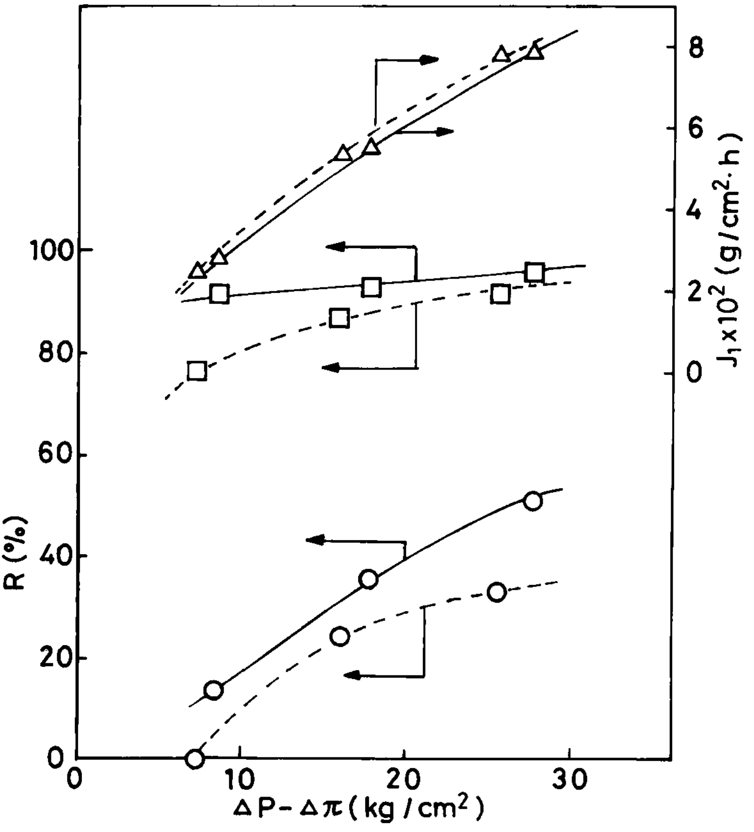

FIG. 8. R and J_1 for mixed feed of NaCl and $CoCl_2$ vs low effective pressure for PS12-EGE50F, the same as used in Fig. 4. (○) NaCl, (□) $CoCl_2$. (——) 0.03 M for each salt, (- -) 0.06 M for each salt.

usefulness of a separation system like ultrafiltration at a lower pressure using more porous membranes. Such a separation method will be investigated.

Transport Properties

In order to study further the characteristics of the Schiff base membranes, some transport parameters were determined. Reflection coefficient σ is given in the following equations introduced by Spiegler and Kedem (*9*):

$$R = \sigma(1 - F)/(1 - \sigma F) \tag{3}$$

$$F = \exp\{-J_1(1 - \sigma)/P\} \tag{4}$$

where P is the transport coefficient of solute. If $J_1 \rightarrow \infty$, then $R \rightarrow \sigma$. Since an infinite increase in J_1 is attained at an infinite increase in ΔP, σ can be obtained by extrapolation of R at $\Delta P \rightarrow \infty$, i.e., $1/\Delta P \rightarrow 0$. Figure 9 illustrates the results for single membranes of P7 crosslinked with DAc and composite membranes of DAc-crosslinked P7 and P8 coated on a membrane filter. Most of the points form straight lines. Values of σ close to unity for $CoCl_2$ and lower values of σ for NaCl indicate that the P membranes are highly semipermeable to $CoCl_2$ but not to NaCl. This difference is useful for the separation of the two salts, as shown in Fig. 1.

The thick composite membrane PS11-EGE50M shown in Fig. 7 gave $\sigma = 1$ for both NaCl and $CoCl_2$.

Yasuda, on the other hand, proposed another parameter, ω, on the basis of the free volume theory (*10*):

$$1/R = \omega + P_2R'T/P_1v_1(\omega P - \Delta\pi) \tag{5}$$

where P_1 and P_2 are diffusive permeability of water and solute, respectively, v_1 is the molar volume of water, and R' is the gas constant. A plot of $1/R$ against $1/(\Delta P - \Delta\pi)$ for the above membranes is shown in Fig. 10. The intercept gives ω, which is a little over unity for $CoCl_2$ and appreciably over unity for NaCl, indicating that the membranes are of the diffusion type for $CoCl_2$ and of the flow type for NaCl. The parameters thus obtained are tabulated in Table 3.

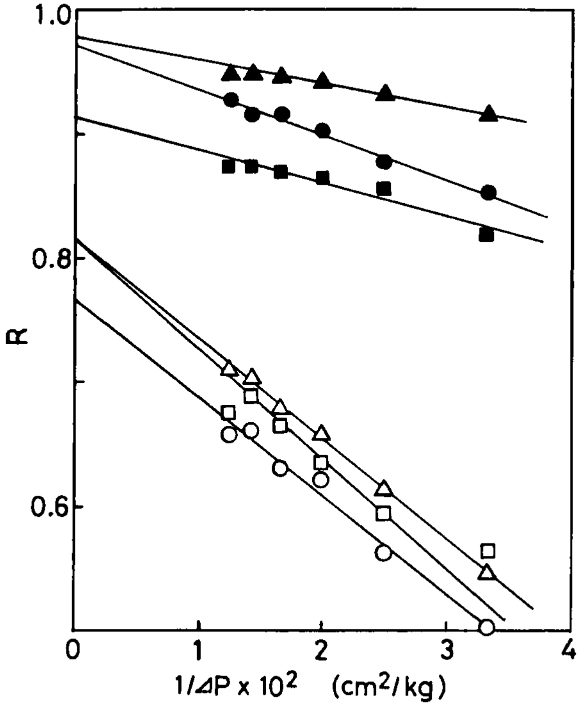

FIG. 9. R and $1/\Delta P$ for P membranes. (○, □, △) NaCl, (●, ■, ▲) $CoCl_2$ feed. (○) P7-DA50-11, (●) P7-DA50-10, (□, ■) P7-DA50M, (△,▲) P8-DA50M.

A very similar relationship was proposed by Pusch from irreversible thermodynamics (*11*):

$$1/R = 1/R_{\max} + A(1/J_1) \tag{6}$$

where $R_{\max}$ is intrinsic rejection and A is a constant containing $R_{\max}$ and other coefficients. If plots of J_1 against $\Delta P - \Delta\pi$, as illustrated in Fig. 7, give straight lines, then comparison of Eqs. (5) and (6) shows that $1/R_{\max}$ can be replaced by ω. This was the case for the membranes of poly(4VP-*co*-DAVT) (*12*) and the oxime of poly(4VP-*co*-MVK) (*5*). Since Fig. 7

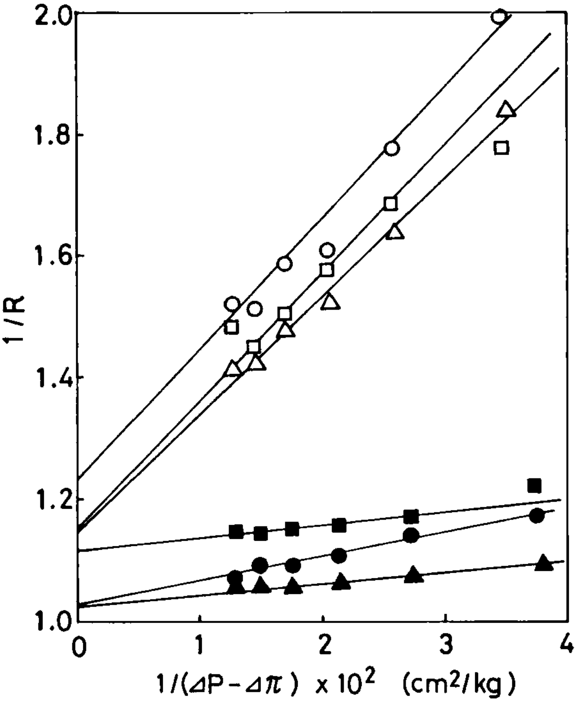

FIG. 10. $1/R$ vs $1/(\Delta P - \Delta\pi)$ for P membranes. Symbols are the same as in Fig. 9.

TABLE 3
Transport Parameters

Membrane[a]	Total thickness (μm)	σ NaCl	σ $CoCl_2$	ω NaCl	ω $CoCl_2$
P7-DA50-11	37	0.766	—	1.229	—
P7-DA50-10	32	—	0.973	—	1.027
P7-DA50M-5	104[b]	0.813	0.910	1.152	1.114
P8-DA50M-1	171[c]	0.813	0.979	1.143	1.024

[a] Crosslinked with 50 mol% DAc based on NH_2 groups. M denotes a membrane filter-based composite membrane.

[b] Including a membrane filter of 89 μm thickness.

[c] Including a membrane filter of 88 μm thicknes.

shows the actual relationship to have considerable curvature, R_{max} did not coincide with $1/\omega$ but exceeded it in the present case.

These parameters indicate that Schiff base membranes are semipermeable to $CoCl_2$ principally due to complexation despite their change into swelled membranes. The resulting considerable difference in semipermeability between NaCl and $CoCl_2$ allows the separation of the two salts.

CONCLUSIONS

The large difference in *R* between NaCl and $CoCl_2$ in a separate run with P and PS membranes decreased when a mixed solute feed solution was supplied. This was accounted for by Donnan exclusion of the $CoCl_2$-complexed membrane. This exclusion was effected by participation of only a small fraction of Schiff base groups in the complexation. As for separation of the two salts, those membranes may still be useful when multistage runs are conducted even if the *R* difference is reduced. Another effective separation was demonstrated by lowering the applied pressure with a decrease in *R* for NaCl accompanied with an increasing *R* difference. This fact suggests the usefulness of a porous Schiff base membrane at low pressure.

Although the complexed P and PS membrane swelled considerably to form a gel-like membrane and their mechanical strength greatly decreased, the performance was considerably improved by forming a composite membrane with a piece of membrane filter or filter paper as a support. The composite membrane permitted continuous and repeated RO operations for a long period.

The transport parameters of these membranes indicated that the membranes were semipermeable to $CoCl_2$ but not to NaCl. Consequently, RO with a composite membrane at low pressure is useful in the practical separation of NaCl and $CoCl_2$.

Acknowledgment

The authors wish to express their thanks to Nitto Boseki Co. for supplying polyallylamine hydrochloride.

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Received by editor February 6, 1989