

Solute Separation by the Amidoxime of Poly(4-Vinylpyridine-co-Acrylonitrile)

EIZO OIKAWA and SHIGERU TSURUMAKI, *Faculty of Engineering, Niigata University, Ikarashi, Niigata 950-21 Japan*

Synopsis

The quantitatively amidoximated poly(4-vinylpyridine-co-acrylonitrile) (4VNX) could be cast with divinyl sulfone as a crosslinking agent to form membranes for reverse osmosis. They were stronger than a cellulose acetate membrane when dried for more than 45 min at 80°C, most balanced in their performance when 4VNX was composed of about 60 mol % acrylonitrile amidoxime, and highly rejected NaCl, CoCl₂, NiCl₂, and phenol as well at pH 12. They were superior in the performance to the membranes prepared from the amidoximes of poly(2,4-diamino-6-vinyl-s-triazine-co-acrylonitrile) and polyacrylonitrile. 4VNX membranes prepared by drying for about 30 min were capable of separating NaCl and transition metals under lower pressures because of great differences in rejections between NaCl and those metals. Potential use of 4VNX membranes in ultrafiltration was demonstrated, particularly to the effect that flux was enhanced while the rejection differences were hardly changed. It was also demonstrated that the isolation of transition metals of considerably different uptake from their mixture could be achieved by breakthrough of the column packed with divinylbenzene-crosslinked 4VNX resin.

INTRODUCTION

Since the advent of asymmetric cellulose acetate membrane for desalination of saline water, membrane technology has attained its development and found wide applications in many fields of industry. Recovery of valuable metals and other solutes by concentration of their dilute solutions is an important application as well as water supply for drinking and industrial use. A familiar method for the recovery and separation of those metals includes the use of various types of ion exchange resins which contain functional groups capable of coordinating or forming chelates with metal ions. As another type of the identical materials, ion exchange membranes have been employed industrially, but those commercially available are not suitable for pressure-driven separation such as reverse osmosis and ultrafiltration. We have prepared several functional polymer materials containing pyridine moieties by copolymerization of readily available monomers¹⁻⁶ and investigated the membrane performance in reverse osmosis. The results were that the copolymer membranes which contained functional moieties like pyridine rings could effectively reject heavy metal ions by forming complexes^{3,4} and that the oxime of poly(4-vinylpyridine-co-methyl vinyl ketone) (4VK) which contained two different functional groups showed the potential for isolation of transition metal ions from alkali metal ions.⁶ In the present study we prepared the amidoxime of poly(4-vinylpyridine-co-acrylonitrile) (4VN) of several monomer compositions as a copolymer containing another functional group, and investigated the separation of metal salts and organic solutes by using the membranes com-

posed of the amidoxime, and also by the column breakthrough with divinylbenzene-crosslinked amidoxime of 4VN.

EXPERIMENTAL

Solution Copolymerization

A definite amount of distilled 4-vinylpyridine (4VP) and acrylonitrile (AN) with 0.5 mol % (based on the monomers) azobisisobutyronitrile (AIBN) and dimethylformamide (DMF) (30 wt % monomer) was copolymerized in an ampoule under nitrogen atmosphere at 70°C for 5 h. The content was poured into 0.3% dilute ammonia solution. The precipitated copolymer was filtered, reprecipitated, and dried at 50°C under reduced pressure.

Similarly was carried out the copolymerization of AN with 2,4-diamino-6-vinyl-*s*-triazine (DAVT) which was prepared from dicyandiamide and β -dimethylaminopropionitrile.⁷ In this case 20 or 25 wt % dimethylsulfoxide (DMSO) solution was heated in an ampoule at 60 or 70°C for 0.5 h. The precipitant was methanol.

Polyacrylonitrile (PAN) was prepared as a control polymer by heating 20 wt % DMF solution with 0.5 mol % AIBN at 70°C for 5 h and precipitating in methanol.

Preparation of Crosslinked Resin (4VNC)

In a three-necked flask equipped with mechanical stirrer, thermometer, and reflux condenser were placed distilled 4VP and AN in molar ratio of 3:7, distilled 55% divinylbenzene solution (10 wt % based on monomers; percentages in the following parentheses are denoted similarly), benzoyl peroxide initiator (0.27 mol %), poly(vinyl alcohol) (1 wt %), calcium carbonate (6 wt %), anhydrous sodium sulfate (ca. 27 wt %), toluene (100 vol %), and deionized water (600 vol %).⁸ The flask was heated with stirring for 3 h. The precipitated resin was washed with a large amount of water and 1*N* hydrochloric acid, and then filtered by suction. The resin on the filter was washed with 0.01*N* aqueous ammonia until the filtrate became neutral, with deionized water, and finally with methanol. Yield was 89.6%

Amidoximation

The amidoximation was carried out at 75°C in 15 wt % DMF solution of 4VP-AN copolymer (4VN) for 8-12 h, in 10 wt % solution of PAN for 8-12 h, and in 10-15 wt % DMSO solution of DAVT-AN copolymer (TN) for 8 h. Hydroxylamine hydrochloride was used 1.5-3 times as calculated amount, and anhydrous sodium carbonate in an amount equivalent to the hydrochloride. After the reaction, the content was filtered and the filtrate was added to methanol to precipitate the produce (4VNX and TNX). Water was used as a precipitant for 4VN composed of more than 50 mol % 4VP. The crosslinked resin was amidoximated (4VNCX) at 60°C for 6 h according to the procedure of Egawa and Harada⁹ with hydroxylamine freed from hydrochloride with sodium metal.

Desalination

The procedure for membrane preparation was similar as in a previous publication.³ The membranes of 4VNX were prepared by drying at 80°C from 20 wt % DMSO solution, and those of TNX from 13 wt % solution, with 30 mol % divinyl sulfone (DVS) based on the amidoxime as a crosslinking agent. The thickness of the membranes was in the range from 50 to 70 μm , and about 100 μm at a short drying time (about 30 min).

The apparatus for reverse osmosis and experimental procedures were similar as described in previous papers.^{1,3} Nitrogen pressure of 80 kg/cm^2 was applied at 25°C. Ultrafiltration was conducted by using UHP-43 filter manufactured by Toyo Kagaku Sangyo Co., Ltd. (effective area of 11.5 cm^2 and a capacity of 70 mL) under nitrogen pressure of 5 kg/cm^2 . The salt concentration of feed solutions was 0.06M. The product concentration was determined by electric conductivity measurement for inorganic feeds, except for NiCl_2 , which was determined by chelate-forming titration with EDTA using murexide (ammonium purpurate) as an indicator.¹⁰ The concentration of phenol and urea was determined with an Atago Differential Refractometer Model DD-5 for pure solution and by colorimetric method^{11,12} with Hitachi Spectrophotometer Model 100-10 for acidic and basic solutions. pH was controlled by hydrochloric acid and sodium hydroxide.

Rejection R and hydraulic water permeability K_1 were obtained from the following equations, respectively:

$$R = 100(c - c')/c \quad (1)$$

$$J_v = K_1(\Delta P - \Delta\pi)/\Delta x \quad (2)$$

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

Determination of Uptake Capacity for Metal Ions

The capacity was determined by the batch technique. A 100 mg of dry pulverized (100–200 mesh) resin was added to 10 mL of metal ion solution (0.2M) buffered with sodium acetate and hydrochloric acid [acetic acid for Hg(II)]. After equilibration for 24 h with stirring the resin was filtered off and washed with the buffer solution of the same pH. The resin was then stirred with 20 mL of 1N hydrochloric acid [nitric acid for Hg(II)] for 3 h, filtered again with the same filter, and washed with 10 mL of 1N hydrochloric acid [nitric acid for Hg(II)]. The combined filtrate containing the stripped metal ion was subjected to the chelate-forming titration.¹⁰

Column-Breakthrough Experiments

A 1.8 g of the resin (100–200 mesh) soaked in water was poured into a glass tube (9.8 mm ϕ). The height of the packed resin was 22.7 cm. The pH-adjusted 1:1 mixture solution of two metal ions (about 5 mM for each original metal

solution) was passed through the column at a rate of 1 mL/min. The effluent was fractionated into 5 mL portions, and the concentration of metal ion was determined by atomic absorption spectrometry with Hitachi Atomic Absorption Spectrophotometer Model 180-50. Before elution the column was washed with a buffer solution of the same pH to remove free metal ions. The pH of the buffered eluent employed first was chosen so as to elute only one metal ion leaving the other, in consideration of the results of the capacity at various pH (Fig. 7), and then 1*N* hydrochloric acid was used to liberate the whole remaining ions. The pH of the feed mixture solution was 5.2 for (i) CuCl₂-CoCl₂ mixture, 2.3 for (ii) CuCl₂-ZnCl₂ mixture, and 5.0 for (iii) ZnCl₂-CoCl₂ mixture. The pH and volume (mL) of the eluent, and volume (mL) of 1*N* HCl were 3.0 (115), 1.5 (100), 1*N* HCl (85) for (i), 6.0 (120), 1*N* HCl (80) for (ii), and 2.3 (118), 1*N* HCl (82) for (iii), respectively. The fractionation of the effluent and determination of the concentration were the same as described above.

Measurements

The measurements of water content, relative tensile strength which is defined as tensile strength of the copolymer membranes divided by that of cellulose acetate (CA) membrane prepared by Manjikian's method¹³ and NMR for the determination of monomer composition of copolymers were conducted in the same manner as described previously.¹

RESULTS AND DISCUSSION

Preparation of Copolymers and Their Amidoximes

The copolymerization of AN with 4VP have previously been carried out in bulk.¹ In the present study DMF was used as a solvent, and results are

TABLE I
Results of Copolymerization^a of Acrylonitrile and Amidoximation^b of the Copolymers

Code ^c	AN in monomer mix. (mol %)	Yield of copolymer (%)	AN in copolymer (mol %) ^d	[η] ^e	Amidoximation time (h)	Yield of amidoxime ^f (%)
4VN9X	30	74.4	31.0	0.44	8	90.0
4VN6X	50	87.5	43.2	—	10	88.5
4VN4X	70	79.3	64.5	0.58	8	62.6
4VN5X	70	85.6	67.0	0.51	12	76.4
4VN10X	80	86.5	79.0	0.49	10	94.7
PANX	100	70.6	100	0.48	3	89.2
TN1X	70	84.6	67.0	1.09	8	91.1
TN2X	70	74.8	64.9	2.00	8	92.5

^aAIBN: 0.5 mol % based on total monomers. 70°C, 5 h with 20–30 wt % DMF soln (70°C, 0.5 h with 25 wt % DMSO soln for TN1X and 60°C, 0.5 h with 20 wt % DMSO soln for TN2X).

^b([NH₂OH]/[CN]) = 3 (1.5 for PAN2X), 15 wt % DMF soln (15 wt % DMSO soln for TN1X and 10 wt % DMSO soln for TN2X), 75°C.

^cComonomer; 4VN = 4-vinylpyridine, TN = DAVT.

^dBy NMR.

^eAt 25°C in DMF soln (DMSO soln for TN).

^fEstimated assuming that CN was completely converted to amidoxime.

summarized in Table I. The difference in AN composition between monomer mixture and the copolymers implies that 4VP is more reactive than AN, which is in accordance with the previous results of bulk copolymerization.¹ The viscosity shows that molecular weight of the copolymers is similar to each other irrespective of the compositions. The molecular weight of PANX amounts to 1.0×10^4 when calculated on the intrinsic viscosity 0.48 from the Mark-Houwink-Sakurada equation.¹⁴

In the copolymerization of AN with DAVT, AN was again less reactive in view of smaller AN contents in the copolymers than those in monomer mixtures. The lower reactivity of AN was confirmed by calculation of monomer reactivity ratio of both monomers, $r_1(\text{DAVT}) = 3.43$, $r_2(\text{AN}) = 0.213$ from $Q_1 = 5.52$, $e_1 = 1.76$, $Q_2 = 0.6$, and $e_2 = 1.2$.¹⁴

The amidoximation of PAN at 75°C required only 3 h until C≡N stretching vibration in an IR spectrum completely disappeared. However, a longer time of more than 8 h was necessary for the completion of the reaction in AN copolymers, probably due to steric disturbance of comonomer rings.

Effect of Drying Time on Membrane Performance

The oxime of 4VK was effectively crosslinked with DVS by hydrogen transfer, giving one of the membranes of a maximum performance when crosslinked with 30 mol % DVS based on amidoxime group.⁶ A similar crosslinking reaction was possible in the amidoxime. The actual occurrence of the crosslinking is apparent from the fact that a strong membrane was readily obtained from the amidoxime in the presence of DVS, whereas a brittle and weak membrane was formed in the absence of DVS.

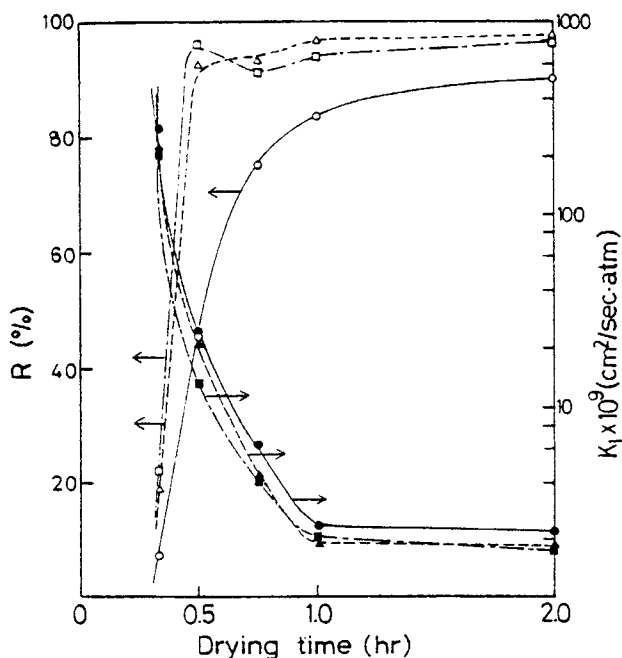


Fig. 1. R and K_1 vs. drying time for 4VN₄X membranes. Feed: (○, ●) NaCl; (△, ▲) CoCl₂; (□, ■) NiCl₂.

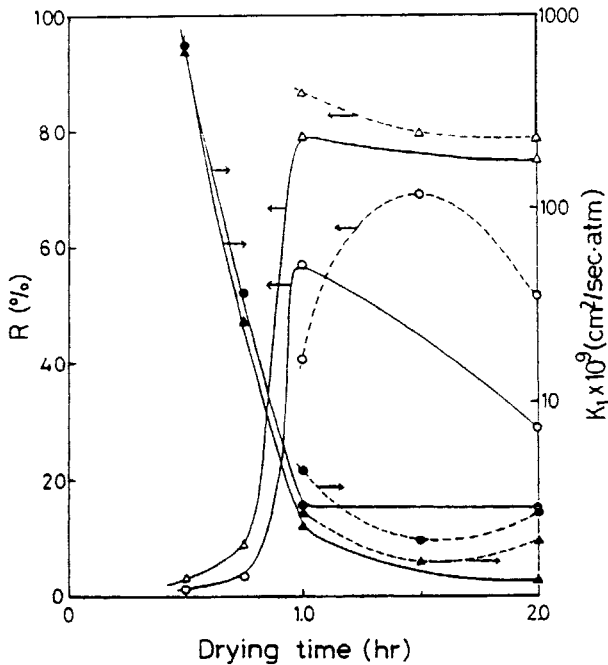


Fig. 2. R and K_1 vs. drying time for TN1X and TN2X membranes: (---) TN1X; (—) TN2X. Feed: (○, ●) NaCl; (△, ▲) CoCl_2 .

The effect of drying time on R and K_1 of the copolymer membranes of nearly the same composition is shown in Figures 1 and 2. It is seen from those figures that a less porous membrane can be formed by drying at 80°C for more than 1 h and highly rejects transition metal salts in 4VN4X. An empirical parameter A^2/B proposed by Lonsdale,¹⁵ which includes both coefficients A and B related to flux and salt rejection, respectively, in the following equations:

$$J_1 = A(\Delta P - \Delta\pi) \quad (3)$$

$$J_2 = B\Delta c_2 \quad (4)$$

where J_1 is water flux, J_2 salt flux, and Δc_2 difference in external salt concentration across the membrane, was calculated for 4VN4X and TN2X, and is listed in Table II, assuming $J_1 = J_2$. A higher value, namely a higher performance, of 4VN4X is due to a much higher R of 4VN4X than R of TNX as shown in Figures 1 and 2. However, TNX membranes showed a higher K_1 , particularly at less than 1 h; i.e., TNX membranes are more permeable to water than 4VN4X. This originates from the fact that DAVT is more hydrophilic than 4VP.^{4,16} Therefore, the incorporation of DAVT and 4VP is effective to the enhancement of K_1 and R , respectively. The values in Table II also indicate that 2 h drying is preferable for the performance of 4VN4X, while 1 h for that of TN2X. Unusually high values at 0.5 h can be attributed to a large contribution of flux.

The tensile strength relative to that of CA membrane and water content are shown in Figure 3. 4VNX forms a stronger membrane than CA at a drying

TABLE II
Parameter $A^2/B \times 10^8$ (cm/s atm²) of 4VN4X and TN2X

Code	Feed	Drying time (h)				
		0.33	0.5	0.75	1.0	2.0
4VN4X	NaCl	2.05	3.00	2.96	2.26	3.73
	CoCl ₂	3.46	38.4	9.96	11.2	14.8
TN2X	NaCl	—	0.62	0.20	0.82	0.23
	CoCl ₂	—	2.03	0.41	1.89	0.75

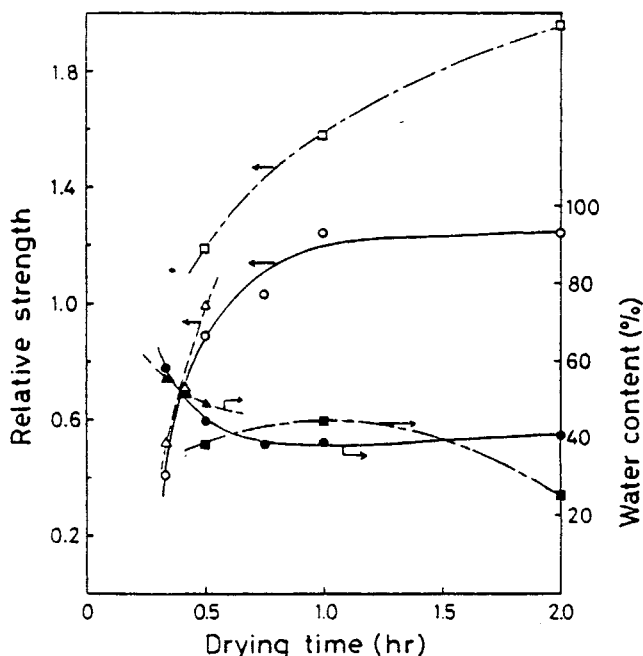


Fig. 3. Relative strength and water content vs. drying time: (○, ●) 4VN4X 80 kg/cm²; (△, ▲) 4VN4X 40 kg/cm²; (□, ■) PAN2X 80 kg/cm².

time longer than 45 min, which also proves effective crosslinking with DVS. The strength of membranes dried for 1 and 2 h did not differ substantially, indicating that the crosslinked reaction almost completes in 1 h. A higher strength of PAN2X results from a higher crosslinking density because more DVS was added at a constant addition ratio of 30 mol %.

The 4VNX membranes had a water content of about 40% which was greater than that of 4VKX membranes (about 30%⁶). This indicates that 4VNX membranes are more hydrophilic and porous than 4VKX membranes.

Dependence of Copolymer Composition

It was demonstrated in 4VKX membranes that about 1 : 1 composition gave the most balanced membrane performance.⁶ The dependence of the performance of 4VNX membranes on the composition is shown in Figures 4 and 5. R of CoCl₂ hardly changed from 30 to 60 mol % of AN, but R of NaCl had a

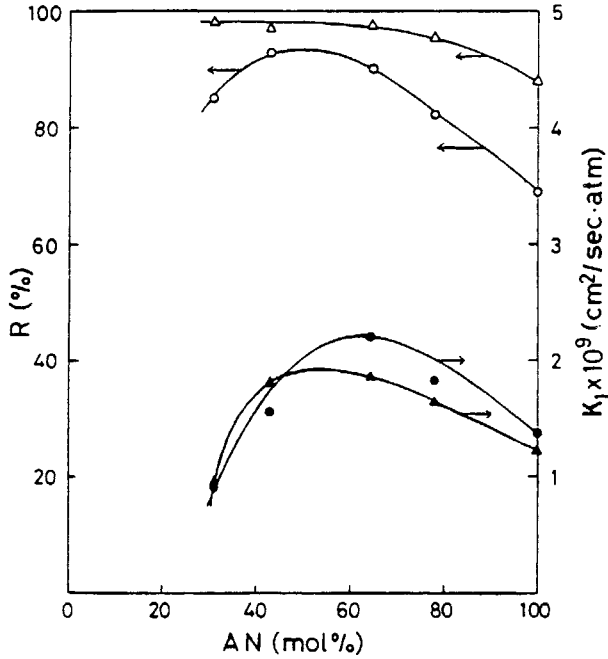


Fig. 4. R and K_1 of 4VNX vs. copolymer composition. The composition denotes AN content of the precursor copolymer 4VN. Membranes were dried for 2 h. Feed: (O, ●) NaCl; (Δ, ▲) CoCl_2 .

maximum at about 50 mol %. K_1 of both feeds showed a similar trend, reaching a maximum at 60 mol % AN. This behavior of K_1 is parallel to that of water content in Figure 5. The presence of a maximum in both R and K_1 may be closely related to the monomer rearrangement of alternating tendency, which would favor a dense packing of the copolymer chains⁵ and a

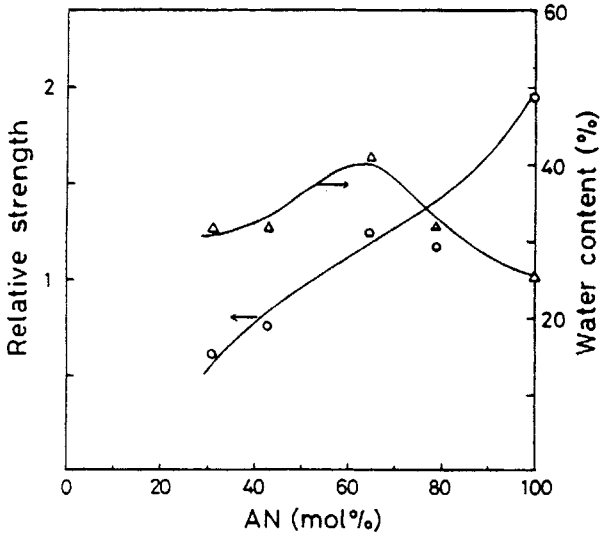


Fig. 5. Relative strength and water content vs. copolymer composition. The composition was the same as in Figure 4.

maximum amount of hydrogen-bonded water molecules in the membrane structure.

The relative strength increases with increasing content of AN, because of increasing crosslinking density, exceeding unity at more than about 50 mol %.

From the above results it can be summarized that about 60 mol % AN amidoxime content can give the most balanced performance under the conditions employed.

Separation of Metal Salts At Lower Pressures

In Figure 1 the curve of R for NaCl feed reveals that a drying time shorter than 1 h gives a membrane of a higher porosity. At 0.5 h of drying, however, transition metals were highly rejected while R of NaCl was low. The difference leads to about 50%, which strikingly exceeds the difference in R (ca. 7% at 2 h in Fig. 1) caused by the difference in valence of the metal ion. This can be attributed to the capture of transition metal ions by complexing with functional amidoxime groups as previously suggested.^{3,6} Hence, the membrane prepared by drying 0.5 h is favorable for separation of transition metal salts and NaCl. Since porous membranes readily undergo compaction and reduce flux under high pressure, separation behaviors of the membranes prepared at about 0.5 h were investigated under a lower pressure of 40 kg/cm². The results are illustrated in Figure 6. It can be seen that the difference in R reaches a maximum at 25 min [$R(\text{Ni}) = 82\%$, $R(\text{Co}) = 62\%$, and $R(\text{Na}) = 17\%$], and NiCl_2 is separated from NaCl to a larger degree than CoCl_2 . The strength of these membranes has been shown in Figure 3. The

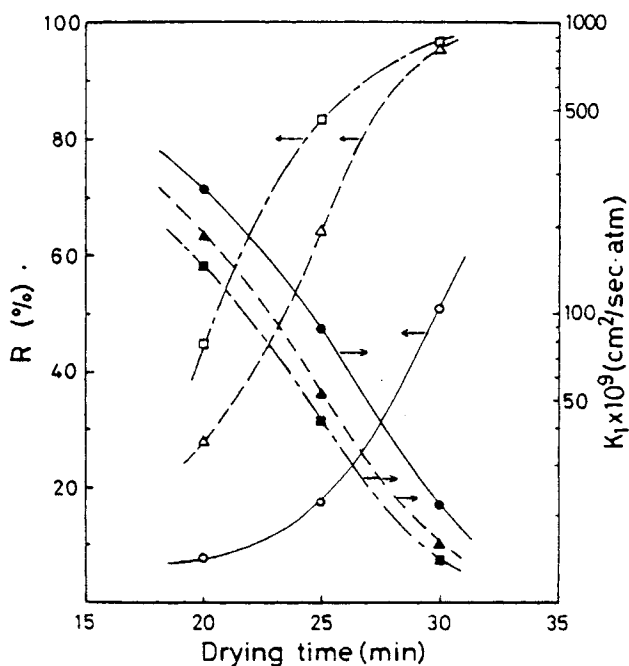


Fig. 6. R and K_1 vs. drying time for 4VN4X membranes; 40 kg/cm², 25°C. Feed: (○, ●) NaCl; (△, ▲) CoCl_2 ; (□, ■) NiCl_2 .

membrane of 25 min drying has a fair strength, though it is a little weaker than CA.

Consequently, under a lower pressure of 40 kg/cm² the membrane prepared by drying for 25 min is very useful for separation between transition metal salts and NaCl with a higher flux, and much energy can be saved by this technique.

Solvent-resistant membranes of the amidoxime of poly(AN-co-vinyl acetate) has been prepared,¹⁷ but no such separation as above has been attempted.

More porous membranes under lower pressure than 40 kg/cm² may work for the same purpose. Thus, the membranes of 20 min drying were applied to ultrafiltration under a pressure of 5 kg/cm². Three membranes were obtained by cutting off from a single membrane and put in the apparatus one upon another. If the feed concentration c_0 changes to c_1 of the product after passing through the first membrane, c_1 is also the concentration of the feed for the second membrane, and similarly c_1 changes to c_2 , and c_2 to c_3 , concentration of the final product. Let R' be rejection for a single membrane, then apparent and experimentally obtainable rejection R'' after passing through three membranes is derived as follows:

$$\begin{aligned} R' &= (c_0 - c_1)/c_0 = (c_1 - c_2)/c_1 = (c_2 - c_3)/c_2 \\ &= 1 - c_1/c_0 = 1 - c_2/c_1 = c_3/c_2 \\ 1 - R' &= c_1/c_0 = c_2/c_1 = c_3/c_2, \quad \therefore (1 - R')^3 = c_3/c_0 \\ R'' &= (c_0 - c_3)/c_0 = 1 - c_3/c_0 = 1 - (1 - R')^3 \end{aligned} \tag{5}$$

Since R' was 37.1% for CoCl₂, calculation according to eq. (5) gives an R'' value of 75.1%. Actually R'' was 82.3%. The difference may stem from inhomogeneous porosity, different degree of compaction among three membranes, even though they were derived from a single membrane, and capture by complexation. R' for NaCl feed was 13.7% and then R'' can be calculated to be 35.7%. The difference of 39.4% (= 75.1 - 35.7) for 20 min-dried membrane is comparable to that for 25 min-dried membrane (62 - 17 = 45%). Simultaneous use of more membranes than three would increase rejection at the expense of flux. The flux in the above three membranes experiment was 0.0366 cm/h and K_1 2.13×10^{-7} cm²/s atm which is about four times as the case of 40 kg/cm².

In summary, for a small quantity of feed, use of multiple porous membranes in ultrafiltration is an energy saving and effective means for increasing flux to a great extent and for separating transition metal salts and NaCl to a degree similar to the case of 40 kg/cm².

Separation of Metal Salts Through Column

An attempt to conduct the separation under further low pressure will result in column technique which make use of gravitational flow of feed at the atmospheric pressure. The transition metal salts may be readily separated from sodium salt by this method because polyacrylamidoxime could adsorb

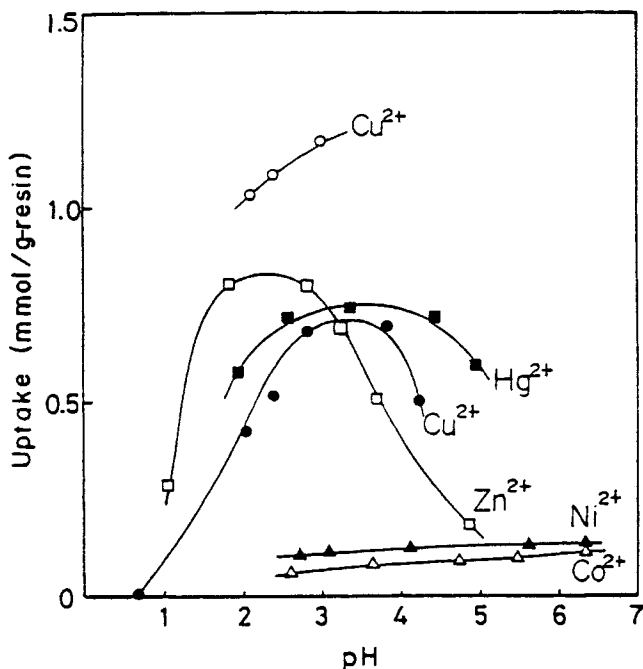


Fig. 7. Metal uptake at various pH with 4VNCX resin: (○) CuCl_2 ; (●) $\text{Cu}(\text{NO}_3)_2$; (△) CoCl_2 ; (▲) NiCl_2 ; (□) ZnCl_2 ; (■) $\text{Hg}(\text{O}_2\text{CCH}_3)_2$.

heavy metals but not alkali metals.¹⁸ It has been known as well that amidoxime-containing polymers can take up uranium from sea water.^{19,20} 4VNCX here showed a capacity of 0.012 mmol/g for $\text{UO}_2(\text{II})$ as determined by the Arsenazo III method.²¹ Since the present study deals with familiar transition metals, we confined them to Co(II), Ni(II), Cu(II), Zn(II), and Hg(II). Thus, the capacity of 4VNCX was measured for those metals at various pH, as shown in Figure 7. The results suggest the possibility of the separation from a mixture of two metal ions at an appropriate pH. Therefore, three pairs of metal salts were chosen— CuCl_2 and CoCl_2 , CuCl_2 and ZnCl_2 , and ZnCl_2 and CoCl_2 —and an attempt was made to separate from each other. Examples are given with the mixture of CuCl_2 and CoCl_2 in Figure 8 for adsorption and in Figure 9 for elution. The results clearly show the predominant and nearly exclusive adsorption of CuCl_2 . When calculated from the area in Figure 9, the total effluent contained 99.3 mol % Cu. Colella et al. reported that DVB-cross-linked polyacrylamidoxime resin adsorbed 95.5 mol % Cu and 4.5 mol % Co.¹⁸ These results indicate that 4VNCX resin is more selective to Cu than the polyacrylamidoxime. Almost the same is the case for the mixture of CuCl_2 and ZnCl_2 though ZnCl_2 was completely eluted out with eluent of pH 6. The Cu content was 94.5 mol %. Colella's case was 91.8 mol % Cu,¹⁸ and again 4VNCX showed a more selective character to Cu. For a mixture of ZnCl_2 and CoCl_2 , the initial effluent of pH 2.3 contained about 8 mol % of CoCl_2 , and the total effluent 87.5 mol % Zn and 12.5 mol % Co. Colella's results were 26.7 mol % Zn and 73.3 mol % Co.¹⁸ This great discrepancy seems to be attributed to a higher affinity of 4VP to Zn. Repeated runs appear to be able to isolate each other.

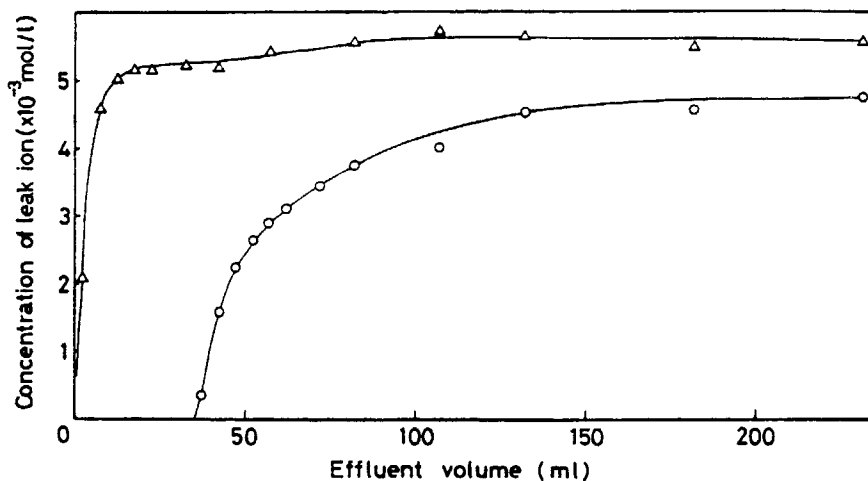
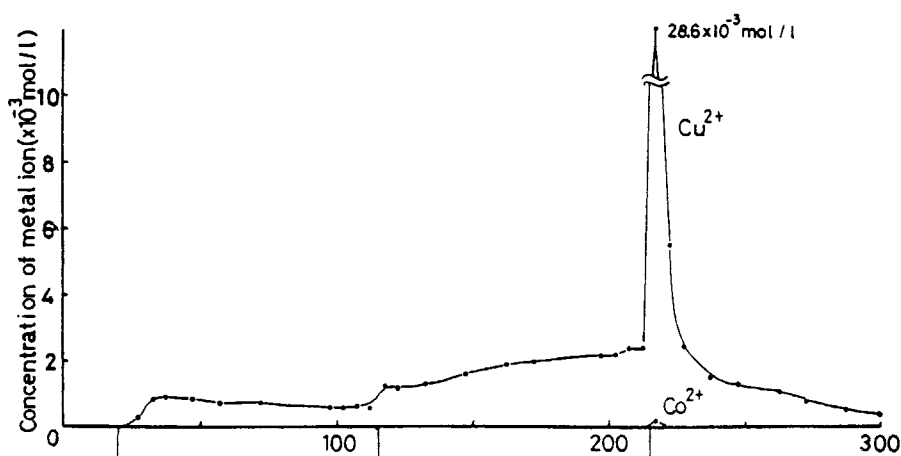


Fig. 8. Breakthrough profile of the mixture of CuCl_2 and CoCl_2 solution with the column of 4VNCX resin at pH 5.2: (O) Cu^{2+} ; (Δ) Co^{2+} .

The equilibrium uptake test of Hg and Zn at about pH 5 in their acetate mixture showed a preferential adsorption of Hg.

Consequently, the selectivity for adsorption results in the order at about pH 6, $\text{Cu} \gg \text{Hg} > \text{Zn} > \text{Ni} > \text{Co}$, though some extent of difference in capacity was observed depending on anions.

The difference in the uptake of the metals shown in Figure 7 cannot directly relate to the difference in R among them in reverse osmosis, because the complexation of the membrane with one of those metal ions rejects not only the same kind but also the other kinds of metal ions,⁶ incapable of separating each other, whereas the column method can separate them chromatographically as is described above, which is an advantage over the membrane technique. The column method, on the other hand, always requires reactiva-



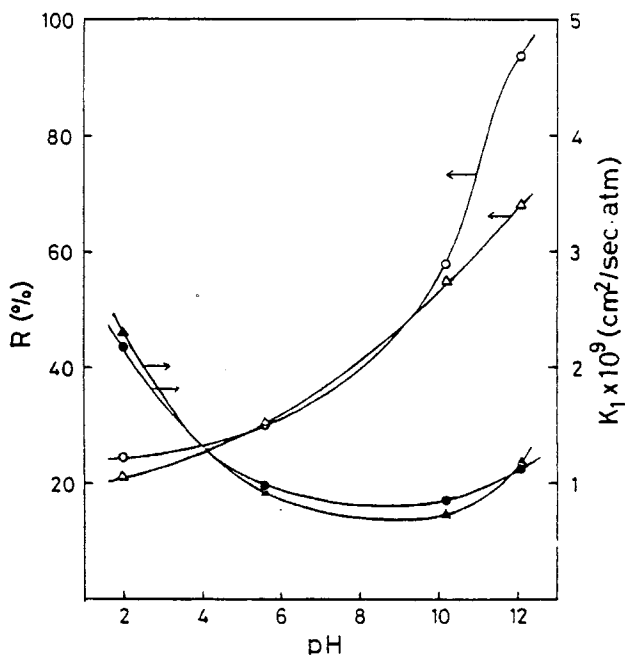


Fig. 10. R and K_1 vs. pH of aqueous phenol solution for 4VN10X membranes: (O, ●) dried for 2 h; (Δ, ▲) dried for 3 h.

tion of the metal-saturated column by stripping the ions, while the membrane technique does not.

Separation of Phenol or Urea

It is a well-known fact that a CA membrane exhibits negative rejection for phenol. At a higher pH, however, rejection has increased to 92%.²² Thus, the pH dependence of rejection was investigated for 4VN10X membrane, and the results are given in Figure 10. R increased with increasing pH, reaching 93% at pH 12. Phenol forms sodium salt at a higher pH and dissociates in the solution just like an inorganic solute. The enhancement of R seems to be caused by electrostatic repulsion between phenolate ion and membrane material of weakly basic character. The tendency of K_1 to augment slightly at pH 12 may due to the formation of $C=N-ONa$ from $C=N-OH$ group with a concurrent increase in polarity and hydrophilicity.

From the same point of view, rejection of urea of basic character is expected to increase at a lower pH. However, the change was not marked at all, R staying to 30% at most at pH 4. This may be ascribed to the observed swelling of membrane at a lower pH.

CONCLUSIONS

The less porous membranes of 4VNX prepared by drying for 2 h and by crosslinking with DVS showed a higher strength than a CA membrane and a maximum reverse osmosis performance at the monomer composition of about 60 mol % AN, rejecting 90% of NaCl, 98% of $CoCl_2$, 97% of $NiCl_2$, and 93% of

phenol as well at pH 12. Porous membranes prepared by drying for a much shorter time exhibited their usefulness in an effective separation between NaCl and transition metal salts under lower pressure because of a remarkable difference in their rejections, along with a flux increase. Application of ultrafiltration to the porous membranes was found to be more advantageous in a considerable enhancement of flux with the rejection difference almost unchanged. Membrane compaction and durability under low pressure are still open to investigation. Since DVB-crosslinked resin showed a highly selective affinity to Cu(II), the separation of Cu(II) from other transition metals as well as NaCl from those metals could be readily conducted by column-breakthrough technique, which is the separation method under the least pressure.

References

1. E. Oikawa and T. Ohsaki, *Desalination*, **25**, 187 (1978).
2. E. Oikawa, K. Arai, and R. Tachibana, *Maku (Membrane)*, **5**, 323 (1980).
3. E. Oikawa, Y. Honda, and Y. Sawada, *Polym. Bull.*, **6**, 169 (1981).
4. E. Oikawa and Y. Honda, *Kobunshi Ronbunshu*, **39**, 571 (1982).
5. E. Oikawa and Y. Igarashi, *J. Appl. Polym. Sci.*, **29**, 1723 (1984).
6. E. Oikawa, Y. Igarashi, and S. Tsurumaki, *J. Appl. Polym. Sci.*, **30**, 1511 (1985).
7. Farbweker Hoechst Akt, Fr. 1,563,255 (1969).
8. K. Itagaki, Y. Umezawa, and H. Ohuchi, Jpn. Kokai Tokkyo Koho 83 59204 (1983).
9. H. Egawa and H. Harada, *Nippon Kagaku Kaishi*, **1980**, 1767.
10. G. Schwarzenbach and H. Flaschka, *Die Komplextometrische Titration*, 2nd ed., Ferdinand Enke, Stuttgart, 1965.
11. T. Takeuchi, M. Furusawa, and Y. Takayama, *Jpn. Analyst*, **4**, 568 (1955).
12. H. H. Brown, *Anal. Chem.*, **31**, 1844 (1959).
13. S. Manjikian and C. Allen, Office of Saline Water, Res. and Dev. Rep. No. 378 (1968).
14. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Wiley-Interscience, New York, 1967.
15. H. K. Lonsdale, *Desalination*, **13**, 317 (1973).
16. E. Oikawa, O. Suzuki, and M. Fukushima, *Maku (Membrane)*, **7**, 35 (1982).
17. C. Linder, G. Aviv, M. Perry, and R. Kotraro, Eur. Pat. Appl. EP 61,610 (1982).
18. M. B. Colella, S. Siggia, and R. M. Barnes, *Anal. Chem.*, **52**, 967 (1980).
19. L. Astheimer, H. J. Schenk, E. G. Witte, and K. Schwochau, *Sep. Sci. Technol.*, **18**, 307 (1983) and references cited therein.
20. H. Omichi and A. Katakai, T. Sugo, and J. Okamoto, *Sep. Sci. Technol.*, **20**, 163 (1985).
21. H. Ohnishi and Y. Toida, *Jpn. Analyst*, **14**, 1141 (1965).
22. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, **16**, 2531 (1972).

Received July 29, 1986

Accepted November 18, 1986