

Characterization of Reverse Osmosis Membranes Prepared from the Oxime of Poly(4-Vinylpyridine-Co-Methyl Vinyl Ketone)

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Synopsis

The copolymer (4VK) of 4-vinylpyridine (4VP) and methyl vinyl ketone (MVK) was nearly quantitatively converted into an oxime (4VKX) which could be complexed with various metal salts. 4VKX was compared with 4VK in their membrane performance. When crosslinked with divinyl sulfone (DVS), the 4VKX membrane showed a higher strength than cellulose acetate (CA) membrane and a higher performance than 4VK membrane crosslinked with dihydrazine derivatives. The most adequate DVS content and copolymer composition were found to be 25 mol % based on MVK oxime and 1:1, respectively. A metal salt taken up by the membrane in a much larger amount tended to be highly rejected. The crosslinking quaternization of 4VKX with diisobutane (DIB) very effectively improved water permeability, as did 4VK, and gave a membrane performance superior to that of 4VK. The most appropriate charge ratio of DIB was 15–20 mol % based on 4VP. Some transport characteristics and compaction in a long-term operation were investigated and discussed.

INTRODUCTION

In a series of the studies on the properties of reverse osmosis membranes prepared from copolymers comprised of monomers in common use, we have dealt with 4-vinylpyridine copolymer membranes, demonstrating that those complexed with a transition metal salt enhanced salt rejection (R) without substantial flux decrease.^{1,2} The preceding paper focused on the properties of poly(4-vinylpyridine-co-methyl vinyl ketone) (4VK) which contains functional carbonyl groups.³ It was found in the preceding paper that water permeability (K_1) of the 4VK membranes was improved to a considerable extent by crosslinking quaternization with DIB and by chemical modification of 4VK to an oxime and that the quaternization with DIB reduced membrane strength even when the membrane was crosslinked, while the oximation did not. In addition to the strength retention the oxime membrane is of great interest because usually an oxime readily forms a complex with various transition metal cations, thereby possibly increasing rejection of those and other cations in reverse osmosis. The purpose of the present study is to characterize reverse osmosis membranes prepared from 4VK oxime (4VKX) and to compare their performance with that of 4VK membranes. Moreover, attempts were made to improve water permeability by modification with DIB, to investigate transport characteristics, and to operate for a long period.

EXPERIMENTAL

The 4VK copolymers, their oxime and crosslinking agents [malonyl dihydrazide (MD) and 2-phenyl-4,6-dihydrazino-*s*-triazine (PDT)], solvents, and metal salts were the same as those used in the preceding paper.³ DVS was purchased and distilled under reduced pressure before use.

Membranes were prepared from 25 wt % DMF solution by casting it and drying at 80°C for a required period, similarly as before.²

The reverse osmosis was carried out under the nitrogen pressure of 80 kg/cm² at 25°C using a 300-mL batch cell. The salt concentration of all the feed solutions was 0.06*M*. The product concentration was determined by Mohr's method for sodium chloride and by electric conductance measurements for CoCl₂ and NiCl₂. Salt rejection 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.

For the determination of transport parameters and for a long term operation a reverse osmosis apparatus (membrane transport area of 18.1 cm²), manufactured by Atsuryoku Kiki Engineering Co., Ltd., was used.

Water content was estimated as weight fraction of water from the weight difference between dry and wet membrane which was leached in water at 25°C for 48 h and blotted with filter paper. The relative strength is defined as tensile strength of the copolymer membrane divided by that of CA membrane prepared by Manjikian's method,⁴ and was obtained in the same way as already described.³

Adsorption of metal ions was carried out as follows: A given amount (0.1 g) of 200-mesh powdered polymer was gently stirred in 20 mL of 2 mM metal salt solution (30 mL of 0.04 mM for uranyl acetate) and allowed to stand at room temperature for 24 h. The metal uptake per unit weight of the polymer was determined from the concentration of the filtrate. The concentration was measured by chelate titration or by atomic absorption spectrometry with Hitachi Atomic Absorption Spectrophotometer Model 180-50. Uranium was determined spectrophotometrically by forming a complex with Arsenazo III in the presence of perchloric acid.⁵

RESULTS AND DISCUSSION

Oximation Reaction and Performance of the Oxime Membrane. 4VK copolymers were successfully oximated as tabulated in Table I. Although the conversion into the oxime was calculated to be less than 100% from the results of elemental analysis, the conversion may be considered almost quantitative because the absorption due to carbonyl group at 1700 cm⁻¹ in 4VKX was hardly detected.

It was anticipated that the hydroxyimino group in the oxime is more

TABLE I
Oximation of 4VK Copolymers

Code	Oximation yield (%)	Composition of 4VKX (mol %) ^a			Conversion ^b (%)
		[4VP] : [MVK] : [MVK-oxime]			
4VK7X	93.1	33.2	0.2	66.6	99.7
4VK9X	94.3	40.5	2.4	57.1	96.0
4VK10X	80.9	46.5	3.2	50.3	94.0
4VK8X	79.7	47.1	0.6	52.3	98.7
4VK6X	79.2	64.6	6.6	28.8	81.4

^a Determined by elemental analysis.

^b 100 [MVK-oxime]/([MVK] + [MVK-oxime]).

hydrophilic than carbonyl group and thereby increases water permeability of the membrane. Therefore, the performance of the partially oximated polyMVK (MVKX) membrane was compared with that of polyMVK (PMVK) and a copolymer 4VK8. The results were summarized in Table II. Apparently, K_1 of MVKX for NaCl feed considerably increased compared with K_1 of PMVK despite of a larger thickness of MVKX. In addition, water content and relative strength increased. When PMVK is compared with 4VK8, it is evident that the incorporation of 4VP into the polymer enhanced rejection to a great extent and also contributed to increase water permeability.

Preparation of 4VKX Membranes. 4VKX itself gave such a brittle membrane that it was readily broken when used in the reverse osmosis apparatus. Some trials to reinforce membranes by crosslinking with a reagent such as pyromellitic dianhydride and a diisocyanate failed because the former did not improve the performance at all and the latter formed a gel so quickly as to be incapable of casting. However, a hydrogen transfer crosslinking with DVS was successful, giving a tough membrane. The performance under the same operating conditions as described in the experimental section was checked for 4VK6X membranes which were cast from 25 wt % DMF solution charged with 10 mol % DVS based on MVK oxime and dried at 80°C for 0.5–3 h. R was maintained between 96% and 99% at

TABLE II
Performance of PMVK, Partially Oximated PMVK (MVKX), and 4VK Membranes^a

Membrane	MVKX ^b	PMVK	4VK8 ^c
Membrane thickness after RO test (μm)	100	82	53
NaCl feed R (%)	48.2	33.5	85.4
NaCl feed $K_1 \times 10^{10}$ ($\text{cm}^2/\text{s} \cdot \text{atm}$)	9.01	1.42	2.77
CoCl ₂ feed R (%)	64.4	— ^d	87.4
CoCl ₂ feed $K_1 \times 10^{10}$ ($\text{cm}^2/\text{s} \cdot \text{atm}$)	6.89	— ^d	2.56
Relative strength	1.03	0.47	0.45
Water content (%)	28.7	14.7	18.0

^a Cast from 25 wt % DMSO solution with 5 mol % (based on MVK) of MD as a crosslinking agent and dried at 80°C for 2 h. Operating conditions in RO; 80 kg/cm² at 25°C, 0.06M feed.

^b Contained 58.1 mol % oxime.

^c 47.1 mol % 4VP, 52.9 mol % MVK, $[\eta] = 0.33$.

^d Broken.

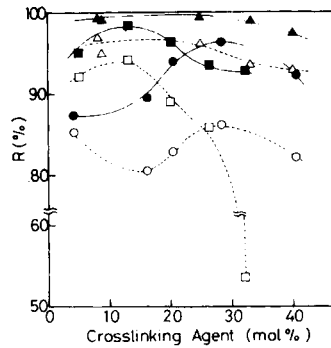


Fig. 1. R vs. crosslinking agent charged based on MVK of 4VK membranes: (○, □, △) NaCl feed; (●, ■, ▲) CoCl_2 feed; (△, ▲) 4VK8X cast from DMF solution with DVS and dried for 1 h; (○, ●) 4VK8 cast from DMSO solution with MD and dried for 2 h; (□, ■) 4VK10 cast from DMSO solution with PDT and dried for 2 h. Operating conditions for this and following figures of R and K_1 : 80 kg/cm² at 25°C, 0.06M feed. See Experimental for details.

0.5 and 1 h drying but decreased at 2 and 3 h drying. Hence the membranes were prepared thereafter from 25 wt % DMF solution by drying at 80°C for 1 h.

Effect of Crosslinking Agent. Since DVS has hydrophilic SO_2 groups an increase in DVS content may give rise to enhancement of K_1 . The effect of DVS, therefore, on the performance was investigated. The results were illustrated in Figures 1–3 together with those of 4VK membranes.³ Although the crosslinking agent was different from each other, R of 4VK8X crosslinked with DVS was higher than R of 4VK8 and 4VK10 crosslinked with MD and PDT, respectively, and showed a maximum at about 25 mol % DVS, as shown in Figure 1. In Figure 2, K_1 of 4VK8X exceeded K_1 of 4VK's in the range from 10 to about 35 mol %. Figure 3 indicates that the relative strength of 4VK8X lay between those of 4VK8 and 4VK10 in a wide range of larger content of the crosslinking agent and showed a maximum of 1.46

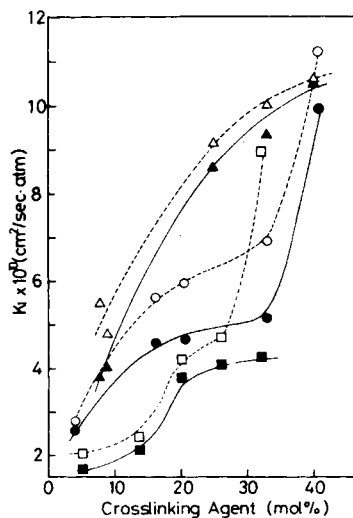


Fig. 2. K_1 vs. crosslinking agent charged; cf. Figure 1 for symbols.

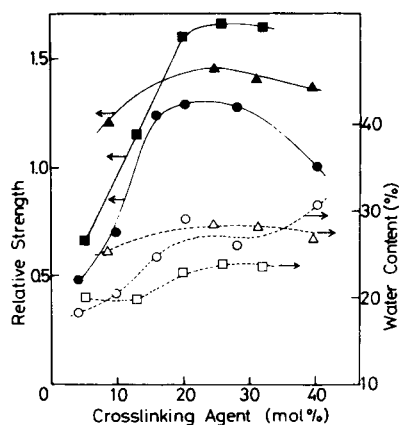


Fig. 3. Relative strength and water content vs. crosslinking agent charged: (△,▲) 4VK8X; (○,●) 4VK8; (□,■) 4VK10.

at about 25 mol %. It is noted that the DVS-crosslinked 4VK8X membranes have a characteristic to be stronger than CA membrane even at a low content of less than 10% crosslinking agent. Water content of 4VK8X was a little greater than 4VK10, probably because of a greater hydrophilicity of DVS than of PDT.

R and relative strength of 4VK8X showed a tendency to decrease at a DVS content over 25 mol %. The membranes with more than 25 mol % DVS seem to include incompletely crosslinked DVS which behaves as a side chain and interrupts a dense fabrication of polymer molecules. Consequently, the most adequate DVS content was 25 mol % based on MVK oxime.

Dependence of Copolymer Composition. It was demonstrated in 4VK copolymer membranes that the copolymer composition which showed a maximum rejection was about 50 mol % 4VP (or MVK)³. The dependence of the performance of 4VKX membranes on copolymer composition was shown in Figures 4 and 5. For CoCl_2 feed, a maximum of R was attained at about 50 mol %, and the increase in K_1 and water content were small beyond 50 mol %. For NaCl feed, on the other hand, R remained substan-

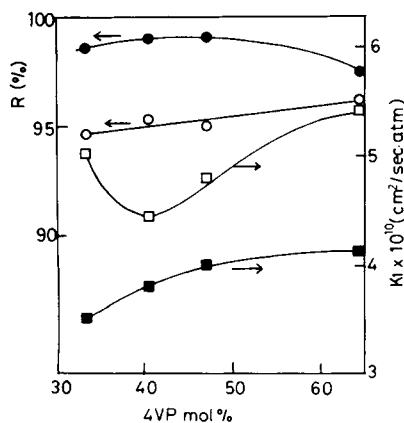


Fig. 4. R and K_1 vs. copolymer composition. Cast from DMF solution charged with 10 mol % DVS based on MVK oxime; (○,□) NaCl feed; (●,■) CoCl_2 feed.

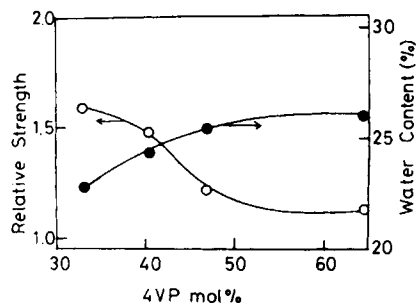


Fig. 5. Relative strength and water content vs. copolymer composition for the same membranes as in Figure 4.

tially constant, and K_1 at 50 mol % was a little lower than that of the two extreme compositions. All the relative strengths in the range of the composition exceeded unity, and the more the hydroxyimino groups, the higher the strength.

In summary, about 50 mol % composition gave the most balanced performance under the conditions used, similarly as in 4VK membranes.³

Rejection of Various Metal Salts. It has been discussed that a metal salt complexed with membrane plays an important role in enhancing rejection of CoCl_2 or other transition metal salts.^{1,2} If there is a large difference among metals in their complex stability or readiness to form a complex, metal separation would be feasible; i.e., a metal salt which readily and preferentially forms a stabler complex with 4VKX would be hard to permeate, resulting in a higher rejection. The readiness can be estimated by adsorption of metal salts onto 4VKX. The adsorption results are tabulated for several metal salts in Table III. The differences in the uptake are not necessarily reflected on reverse osmosis; e.g., zero uptake in Table III does not mean zero rejection in reverse osmosis, as is evident from the fact that NaCl which was not taken up by 4VKX had a fair rejection through 4VKX membranes. However, since the adsorbed amount of mercury and copper salt was remarkably larger than that of nickel and cobalt salt and the selective chelate formation of dimethylglyoxime with nickel ions is well

TABLE III
Uptake of Metal Ions by 4VKX

Metal salt ^a	pH	4VK6X [(mM/g) $\times 10^2$] ^b	4VK7X [(mM/g) $\times 10^2$] ^b
$\text{Hg}(\text{OCOCH}_3)_2$	4.41	(22.3)	(26.0)
CuCl_2	5.79	13.8	10.4
NiCl_2	6.24	0.8	0.8 (1.65)
CoCl_2	6.18	1.1	1.5 (0.15)
CrCl_3	3.90	(0)	(0)
ZnCl_2	7.05	1.03	0
MnCl_2	6.19	0 (0)	0 (0)
MgCl_2	6.12	1.6 (0)	1.2 (0)
$\text{UO}_2(\text{OCOCH}_3)_2$	6.2	0.819 ^c	

^a Concentration of 2 mM except for $\text{UO}_2(\text{OCOCH}_3)_2$ (4×10^{-2} mM).

^b By atomic absorption spectrometry; () by chelate titration.

^c Spectrophotometrically with Arsenazo III complex.

TABLE IV
Influence of Solute on R and K_1

Feed solution ^a	Membrane					
	4VK7X-3		4VK7X-5 ^c		4VK7X-6 ^c	
	R (%)	$K_1 \times 10^{10}$ (cm ² /s · atm)	R (%)	$K_1 \times 10^{10}$ (cm ² /s · atm)	R (%)	$K_1 \times 10^{10}$ (cm ² /s · atm)
NaCl	89.7	5.05	90.6	4.39	90.4	4.27
CoCl ₂	96.8	3.55				
NiCl ₂	95.2	3.84				
CoCl ₂			92.8(Co)		97.6(Co)	
+NiCl ₂ ^b			92.8(Ni)	3.93	98.4(Ni)	3.53
CoCl ₂					95.8(Co)	
+CuCl ₂ ^b					99.98(Cu)	2.06

^a Feed concentration was 0.06M. The same 4VK7X-3 membrane was used for NaCl, CoCl₂, and NiCl₂ in this order. The membrane was washed with water under pressure overnight before a different feed was charged.

^b Mixture of each salt solution. Total concentration was 0.06M. R was determined by atomic absorption spectrometry.

^c The same membrane was used for two or three different feed in the order of NaCl and the mixture feed. The membrane was washed before feed change.

known, an attempt was made to separate cobalt from nickel or copper in reverse osmosis. Table IV summarizes the results. R 's of cobalt, nickel, and copper were close to each other, R of copper being a few percent higher. This practically impossible separation of those three metal ions can be accounted for by clogging the membrane channels with the metal salt that is most readily taken up, its disturbing subsequent permeation of the solute and also Donnan exclusion through the charged membrane, thus giving an analogous R irrespective of the metal sort. It is noteworthy, however, that a highly adsorbable metal salt like CuCl₂ is almost completely rejected. This fact supports our view that the metal ion which easily forms a complex with membrane is prone to be effectively rejected in reverse osmosis. This view is supported also by the fact that for an amidoximated 4VP-acrylonitrile copolymer membranes prepared by heating the DMSO solution with DVS as a crosslinking agent at 80°C for 1 h and 0.5 h, 1 h-heated membrane rejected 97% of CoCl₂ and 94% of NiCl₂ and 0.5 h-heated membrane which was supposed to be more loosely fabricated than the former also retained a high rejection of 92% and 96% of CoCl₂ and NiCl₂, respectively, while the former membrane rejected 84% of NaCl and the latter only 46% of NaCl.⁶ The difference in R (46% for CoCl₂ and 50% for NiCl₂) in the latter membrane is greater than that (39% for CoCl₂) encountered in 4VK10 membrane crosslinked with PDT.³

Improvement of Water Permeability by DIB. Crosslinking quaternization of pyridine moieties with DIB converts the membrane character into ionic one. Such a modification considerably increased water permeability, as was reported earlier.⁷⁻⁹ The improvement of water permeability of 4VK membranes was also demonstrated along with potential application to 4VKX membranes in the preceding paper³. The actual change in the performance of 4VKX membrane is illustrated in Figures 6 and 7 in comparison with that of 4VK membrane. The striking difference between the two mem-

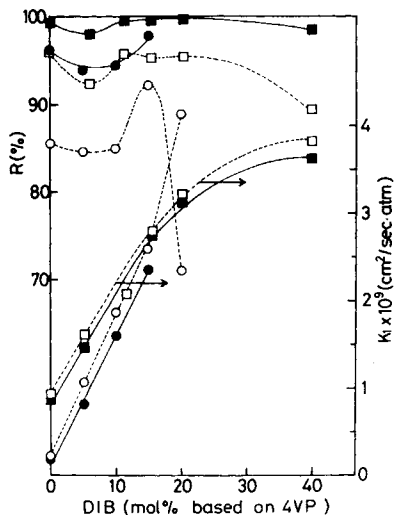


Fig. 6. R and K_1 vs. DIB charged: (○, □) NaCl feed; (●, ■) CoCl_2 feed; (○, ●) 4VK3 charged with 5 mol % PDT based on MVK; (□, ■) 4VK10X charged with 25 mol % DVS based on MVK oxime.

branes is that in DIB content. 4VKX membrane could be charged with up to 40 mol % DIB, whereas 4VK membrane with more than 15 mol % DIB could not endure against the pressure applied. This fact indicates that the former is stronger than the latter at the same DIB charge, which is clearly shown in Figure 7. In the addition of PDT, the relative strength showed a maximum at about 25 mol % charge,³ but the membrane preparation with a charge of 10 and 20 mol % PDT and also 20 mol % MD was not successful in the presence of DIB because of the occurrence of cracks.

Other features are higher R and K_1 in 4VKX than in 4VK membrane as is seen in Figure 6. These superiorities of 4VKX can be attributed to the effect of hydroxyimino groups on the DVS crosslinked membrane system. In view of the decrease in the strength and the behavior of R , 15–20% addition of DIB based on 4VP was the most appropriate. The membrane with 20% DIB was 81.7 μm thick and had a flux of 24 $1/\text{m}^2 \cdot \text{day}$ which was 2.6 times that of the membrane without DIB.

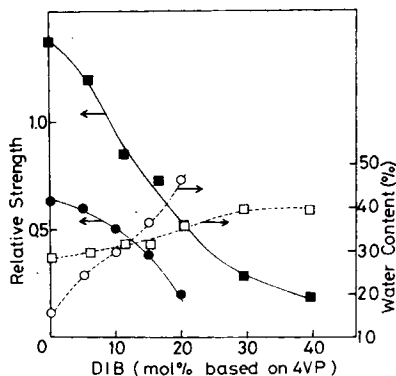


Fig. 7. Relative strength and water content vs. DIB charged; cf. Figure 6 for symbols of membrane.

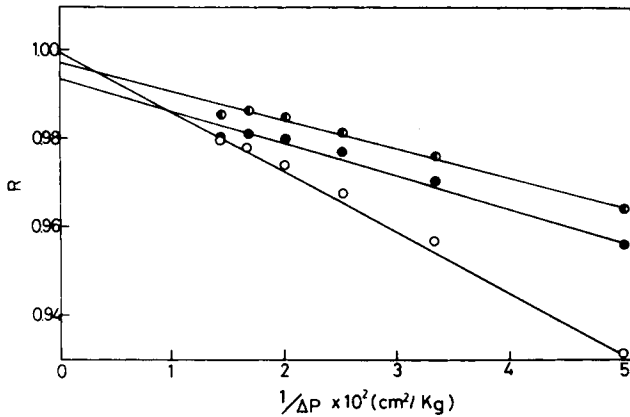


Fig. 8. R vs. reciprocal of pressure; NaCl feed; (○) 4VK10Xa (thickness $\Delta x = 68.7 \mu\text{m}$); (●) 4VK10Xb ($\Delta x = 76.3 \mu\text{m}$); (○) 4VK10X-D ($\Delta x = 85.8 \mu\text{m}$). Cf. Footnote in Table V.

Transport Properties. In order to acquire further knowledge about 4VKX membranes, some transport parameters were estimated. In the first place reflection coefficient σ was obtained from the following equations introduced by Spiegler and Kedem¹⁰:

$$R = \sigma(1 - F)/(1 - \sigma F) \quad (3)$$

$$F = \exp[-J_v(1 - \sigma)/P] \quad (4)$$

where P is the transport coefficient of solute and J_v is volumetric flux. If $J_v \rightarrow \infty$, then $F \rightarrow 0$, and, therefore, $R = \sigma$. When $\Delta P \rightarrow \infty$, i.e., $1/\Delta P \rightarrow 0$ instead of $J_v \rightarrow \infty$, σ can be obtained by extrapolation. Figure 8 depicts the results for membranes with (4VK10X-D) or without (4VK10Xa and 4VK10Xb) DIB. The latter two membranes were prepared by cutting the same membrane and used for the sake of reproducibility. All the three membrane had σ very close to unity, indicating that they are highly semi-permeable.

Yasuda, on the other hand, proposed the following equation on the basis of free volume theory¹¹:

$$1/R = \omega + P_2 R' T / P_1 v_1 (\Delta P - \Delta \pi) \quad (5)$$

where P_1 and P_2 are diffusive permeability of water and solute, respectively, v_1 molar volume of water, R' gas constant, and $\Delta P - \Delta \pi$ effective pressure. The plot of $1/R$ against $1/(\Delta P - \Delta \pi)$ for the above three membranes is shown in Figure 9. The intercept gives the parameter ω , which is slightly over unity. This indicates that the membranes are of diffusion type.¹¹

A very similar relationship was proposed by Pusch from the standpoint of irreversible thermodynamics as follows¹²:

$$1/R = 1/R_{\max} + A(1/J_v) \quad (6)$$

where R_{\max} is intrinsic rejection and A is a constant which contains R_{\max} and other coefficients. R_{\max} ought to be obtained from the intercept in the

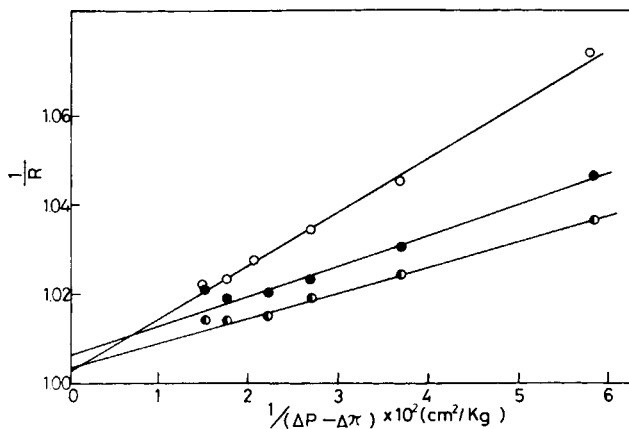


Fig. 9. Reciprocal of salt rejection vs. reciprocal of effective pressure $\Delta P - \Delta \pi$; cf. Figure 8 for symbols.

plot of $1/R$ against $1/J_v$. Since J_v against $\Delta P - \Delta \pi$ forms a straight line through the origin as is shown in Figure 10, the reciprocal of the intercept in Figure 9 should correspond to R_{\max} . The parameters thus obtained by the least squares method are tabulated in Table V. As all of σ , ω , and R_{\max} are very close to unity, the membrane transport is classified as diffusion type. The membranes seem to be dense and tight in view of their transparency as well as the values of those parameters.

Pusch has further obtained hydrodynamic permeability l_p of CA and ion-exchange membranes from the following equation¹³:

$$J_v = l_p(\Delta P - \sigma \Delta \pi) \quad (7)$$

The values of l_p obtained when applied to our case is shown in the last column of Table V. The modification by DIB nearly doubled l_p , indicating that DIB is considerably effective for the improvement of water permeability. The l_p of 4VR10X-D is very close to the value 0.25 obtained by Pusch

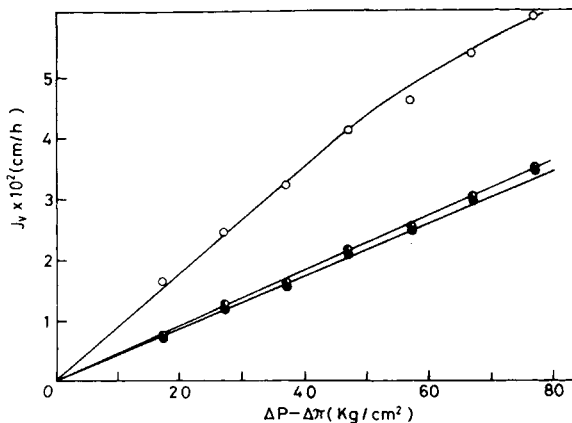


Fig. 10. Flux J_v vs. effective pressure $\Delta P - \Delta \pi$; cf. Figure 8 for symbols.

TABLE V
Parameters of 4VK10X and 4VK10X-D Membranes^a

Membrane	σ	ω	$1/\omega$ (= R_{max})	$l_p \times 10^6$ (cm/s · atm)
4VK10Xa ^b	0.997	1.005	0.995	0.128
4VK10Xb ^b	0.993	1.008	0.995	0.128
4VK10X-D ^c	1.000	1.002	0.998	0.258

^a NaCl feed.

^b Prepared by cutting the same membrane crosslinked with 25 mol % DVS (based on the oxime).

^c Charged with 12.2 mol % DIB (based on 4VP).

for a strong cation-exchange membrane,¹³ and also to the value 0.253 for 4VP-2,4-diamino-6-vinyl-s-triazine copolymer membrane complexed with CoCl_2^2 .

Finally, 4VKX membranes were subjected to a long term reverse osmosis. Figure 11 shows the results. The initial increase in R and decrease in J_v are explained in terms of membrane compaction. The initial flux decline is usually expressed by the following exponential equation:

$$(J_v/J_0) = (t/t_0)^{-m} \quad (8)$$

where J_v and J_0 are the flux at time t and t_0 , respectively, and m is a measure for the compaction resistance of membrane. In the present study $t_0 = 1$ h. The plot of $-\log(J_v/J_0)$ against $\log(t/t_0)$ gave nearly straight lines in the range of 130 h. The values of m obtained from the slope were 0.0373 for 4VK10Xa, 0.0352 for 4VK10Xb and 0.0235 for 4VK10K-D. The values cannot be compared with reference data in a simple manner because m depends on the initial flux,¹⁴ but it is noted that the flux of 4VK10X-D is fairly stable after about 50 h.

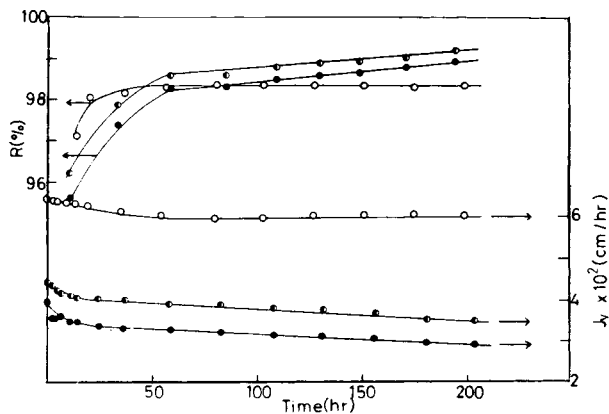


Fig. 11. R and J_v in a long-term test; NaCl feed; cf. Figure 8 for symbols.

CONCLUSIONS

The oximation of 4VK gave membranes of higher performance than 4VK and tougher membranes than CA when crosslinked with DVS at 80°C for 1 h. The most adequate DVS content and copolymer composition which present the most balanced performance under the fabrication conditions were 25 mol % based on MVK oxime and 1:1, respectively. It was difficult for 4VKX membranes to separate a particular metal ion from mixture feed of metal salts, but there was a tendency for a highly adsorbable metal salt to be almost completely rejected.

The modification of 4VKX membranes with DIB by crosslinking quaternization was very effective for the improvement of water permeability and the most appropriate charge ratio was 15–20 mol % based on 4VP. The 4VKX and its DIB modified membrane were considered to be of diffusion type judging from reflection coefficient very close to unity and other parameters, and had potential to be used for a long period.

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APPENDIX:

CA cellulose acetate
 DIB diiodobutane
 DMF *N,N*-dimethylformamide
 DMSO dimethyl sulfoxide
 DVS divinyl sulfone
 MD malonyl dihydrazide
 MVKX partially (58.1 mol %) oximated poly(methyl vinyl ketone)
 MVK methyl vinyl ketone
 PDT 2-phenyl-4,6-dihydrazino-*s*-triazine
 PMVK poly(methyl vinyl ketone)
 4VK copolymer of 4-vinylpyridine and methyl vinyl ketone
 4VKX oxime of 4VK; e.g., 4VK8X stands for the oxime of 4VK8
 4VK10X-D 4VK10X membrane charged with 12.2 mol % DIB based on 4VP
 4VP 4-vinylpyridine

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