

Novel Ion-Containing Reverse Osmosis Membranes.

II. Reverse Osmosis Properties

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Synopsis

The reverse osmosis properties of ion-containing membranes prepared by ^{60}Co mutual irradiation grafting of 2-vinylpyridine to poly(3,3-bis(chloromethyl)oxetane) (polyoxetane, Penton) followed by quaternization with methyl bromide are presented. In general, the volumetric fluxes varied linearly with pressures up to 55 atm. Katchalsky's treatment of membrane permeability was used to analyze the data. Membrane constants and diffusion coefficients of water and sodium chloride were determined with membranes containing different volume fractions of water. The diffusion coefficients of water in the membranes were of the same order of magnitude as the self-diffusion coefficient of water ($\sim 3 \times 10^{-5} \text{ cm}^2/\text{s}$). The diffusion coefficients of sodium chloride in the membrane were of the order of $10^{-7} \text{ cm}^2/\text{s}$. The diffusion coefficients increased with hydration, and the salt rejections were markedly affected by the external salt concentrations. The apparent energies of activation for the volumetric flux were calculated in distilled water and in 0.5% sodium chloride solution.

INTRODUCTION

Details of the preparation and the water sorption properties of the membranes were presented in part I of this series, together with some relevant mechanical properties.¹ Briefly, 1.5-mil films were grafted by direct irradiation under nitrogen or vacuum in 20–30–50 2-vinylpyridine–methanol–dimethylformamide solution. The films were then washed with methanol to constant weight and quaternized with methyl bromide at 60°C and washed with water to constant weight. Strong stable films with close to 100% quaternization were obtained. The different percent grafting yields were obtained by changing the total radiation dose. In this report, the reverse osmosis behavior of these membranes is described and discussed.

EXPERIMENTAL

Distilled water was used throughout; reagent-grade sodium chloride furnished by Fisher Scientific was used without further purification.

The reverse osmosis apparatus used in this work, described elsewhere,² permits the control of pressure and temperature and utilizes circular cells designed to avoid the interference of concentration polarization. The salt concentration was measured conductimetrically.

Equilibrium constants for salt in the membranes (K_s) were measured by neutron activation analysis of sodium absorbed by the membranes in equilibrium with sodium chloride solutions. After exposing the membranes to the solutions, they were blotted with filter paper to remove excess solution. It should be

pointed out that measuring only the cation concentration is only an approximate estimate of the salt concentration in a charged membrane, but is the best data available in this work.

TREATMENT OF THE DATA

The salt rejections R_s measured in reverse osmosis experiments can be related to the volumetric fluxes J_v by eq. (1) developed from the theory of irreversible thermodynamics³⁻⁵:

$$R_s = R_\infty \frac{[\exp(BJ_v) - 1]}{[\exp(BJ_v) - R_\infty]} \quad (1)$$

where B is the membrane constant and R_∞ is the asymptotic solute rejection at infinitely large volume flux, corresponding to an infinite transmembrane pressure drop, and is essentially equal to the reflection coefficient.³⁻⁶ This equation was used to calculate the values of R_∞ from the experimental results. A trial-and-error computer examination of the data from all the membranes studied except the 30.5% graft, which was closer to 0.95, showed clearly that a value close to unity, >0.99 , gave the best fit. A simplified equation was therefore used for the volumetric flux:

$$J_v = L_p(\Delta P - \Delta \pi) \quad (2)$$

where L_p is the permeability coefficient and $\Delta \pi$ the osmotic pressure difference which is equal to $2RT \Delta C$, where ΔC is the difference in the salt concentrations, R is the gas constant, and T is the absolute temperature. With distilled water, $J_v = L_p \Delta p$; in this case, we also have

$$L_p = \frac{\phi_w \bar{V}_w}{f_{wm} \Delta x} \quad (3)$$

where ϕ_w is the volume fraction of water in the membrane, \bar{V}_w is the molar volume of water, Δx is the membrane thickness, and f_{wm} is the frictional coefficient between the water and the membrane. A diffusion coefficient of water, D_{wm} , in the membrane can also be calculated using the relationship^{3,4}

$$D_{wm} = \frac{RT}{f_{wm}} \quad (4)$$

The molar flux of salt, J_s , is given by³

$$J_s = \bar{C}_s(1 - R_\infty)J_v + \omega \Delta \pi \quad (5)$$

where \bar{C}_s is the logarithm average salt concentration and ω is the coefficient of solute permeability. When $R_\infty \sim 1$, as found with the present membranes, this equation simplifies to

$$J_s \simeq \omega \Delta \pi \quad (6)$$

In the case of membranes with high fixed charge concentrations relative to the external salt concentration, ω is given^{3,4}

$$\omega = \frac{K_s}{f_{2W} + f_{2m}} \quad (7)$$

where K_s is the average partition coefficient of salt between the membrane and

the water and f_{2W} and f_{2m} represent the friction coefficient between sodium and the water and sodium and the membrane, respectively.

With membranes where the salt rejection is high, it can be assumed that $f_{2m} \gg f_{2W}$. Using $\Delta\pi = 2RT \Delta C$, we obtain with eq. (6) the expression for the salt flux:

$$J_s = -2K_s D_{2m} \frac{\Delta C}{\Delta X} \quad (8)$$

corresponding to the solution-diffusion model relationship. It should be pointed out that K_s , in the case of ion-containing membranes, depends on the external salt concentration. Using the definition of salt rejection combined with eqs. (2) and (8), eq. (9) is obtained, when $R_\infty \sim 1$:

$$\frac{1}{R_s} - 1 = \frac{2K_2 D_{2m}}{L_p} \cdot \frac{1}{(p - R_\infty \Delta\pi)} \quad (9)$$

With values of L_p , R_∞ , and K_s obtained independently, eq. (9) can be used to determine the value of D_{2m} , which is the diffusion coefficient of sodium in the membrane. In the present work, $R_\infty \sim 1$ and eq. (9) can be used in a correspondingly simplified form. D_{2m} is obtained by a curve-fitting procedure where the data points are values of R_s measured at different ΔP values. The methods used actually measured the sodium in the membrane, which is close, but not exactly equivalent to, the salt concentration itself.

The quantitative approach used in this work was based on the language of irreversible thermodynamics: more especially, using the physical interpretation of the phenomenological coefficients developed by Kedem and Katchalsky⁴ for membrane permeability. This treatment can be applied to the transport of nonelectrolytes and electrolytes through ionic and nonionic membranes and leads, as pointed out by Kedem and Katchalsky, to a simple interpretation of such remarkable phenomena as anomalous osmosis. It should be pointed out that R_∞ , the reflection coefficient, is generally omitted in quantitative treatments found in the reverse osmosis literature. However, the omission of R_∞ , a parameter obtained from the use of the concepts of irreversible thermodynamics to study membrane permeability, will result in limiting the validity of many studies to membranes which approach the behavior of ideally semipermeable membranes. In any case, the data should be explored, as in this article, to show that R_∞ does indeed approach unity.

Pusch, in two very interesting articles,^{7,8} gives an excellent account of the methods of determination of the transport parameters in hyperfiltration experiments. He also derived a linear relationship between $1/R$ and $1/J_v$ with the phenomenological relationships and compared this with the relationship of the solution-diffusion, fine-pore, and the Kedem-Spiegler models and presented experimental support with cellulose acetate and strong ion exchange membranes.

RESULTS AND DISCUSSION

The volumetric fluxes of the quaternized membranes are shown in Figures 1 and 2 for membranes tested in distilled water and 0.5% salt solution, respectively. There was no observed tendency for the slope of the curves to decrease with increasing pressure due to compaction.

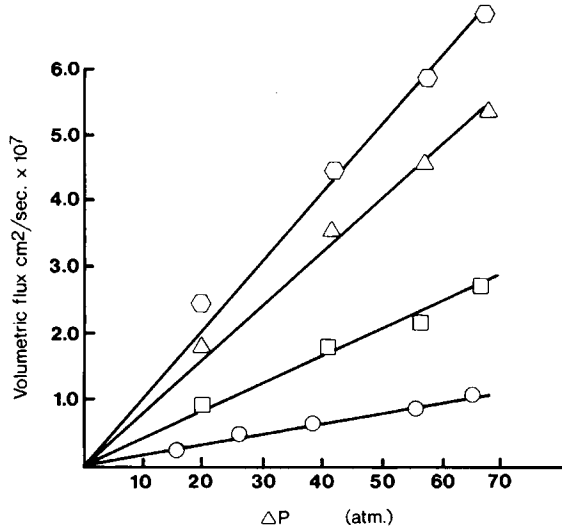


Fig. 1. Volumetric fluxes normalized to 1 cm thickness of Penton films grafted with 2-vinylpyridine and quaternized with methyl bromide. % Grafting: (O) 30.5%; (□) 49.4%; (Δ) 63.5%; (◇) 91.3%. Temperature 28°C, distilled water.

Volumetric fluxes and salt rejection data were used to calculate membrane constants. Typical salt rejection and volumetric flux curves are shown in Figure 3. In general, similar curves were obtained with all the membranes tested.

Table I presents values of L'_p (equal to $L_p \Delta x$) of the membranes tested in distilled water and in 0.5% sodium chloride solution. The values of L'_p were found to be higher in distilled water than in 0.5% salt solution, although no measurable differences in the water sorption was observed.

The values of L_p were determined using eq. (2). Values of D_{wm} calculated using eq. (4) and (5) are included in Table I. Using the data of Wang,⁹ the

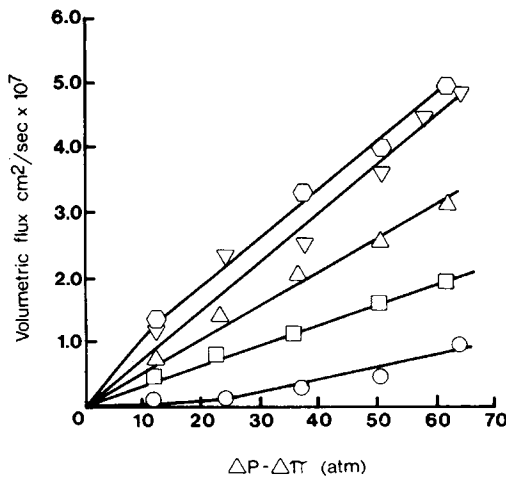


Fig. 2. Volumetric fluxes normalized to 1 cm thickness of Penton films grafted with 2-vinylpyridine and quaternized with methyl bromide. % Graftings: (O) 30.5%; (□) 49.4%; (Δ) 63.5%; (▽) 80.0%; (◇) 91.3%. Temperature 28°C; salt concentration 0.5%.

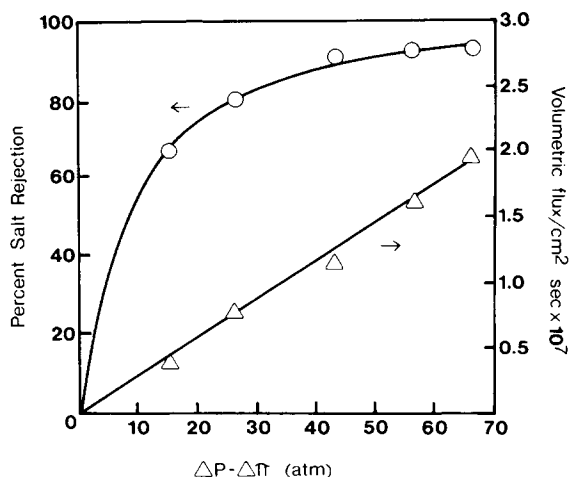


Fig. 3. Percent salt rejection and volumetric fluxes of Penton films grafted with 2-vinylpyridine and quaternized with methyl bromide. Temperature 28°C, salt concentration 0.5%, % grafting 49.4.

self-diffusion constant of water at 28°C is calculated to be $2.63 \times 10^{-5} \text{ cm}^2/\text{s}$. In general, the D_{wm} values were somewhat higher than this value. Higher values have been reported for a wide range of membranes with differing hydrations (see Yasuda,¹⁰ for example, who studied the diffusion and permeation of water in a number of nonionic hydrophilic membranes). It is interesting, although not explicitly relevant, that recently D_{wm} and D_{wm}^* values have been reported for cellulose acetate membranes of different acetyl content⁶:

$$D_{wm}^* = D_{wm} (1 - b)^2$$

where b is the water content of the membrane. Here, D_{wm}^* is essentially equal

TABLE I
Membrane Constants of Grafted Penton Films at 28°C

% Grafting	$L'_p, (\text{cm}^2/\text{s atm}) \times 10^9$		$L_p, (\text{cm}/\text{s atm}) \times 10^6$		ϕ_w	$D_{wm}, (\text{cm}^2/\text{s}) \times 10^5$
	Distilled water	0.5% NaCl solution	Distilled water	0.5% NaCl solution		
30.5	2.0	2.4	0.38	0.45	0.12	2.3
49.4	4.3	3.2	0.74	0.55	0.20	2.9
63.5	8.6	5.2	1.41	0.85	0.21	5.6
80.0	—	7.9	—	1.2	0.24	—
91.3	10.0	8.3	1.41	1.2	0.25	5.5

TABLE II
Values of the Diffusion Coefficient of Salt in Penton Membranes Grafted with 2-VP at 28°C and with 0.5% NaCl Solution

% Grafting	ϕ_w	K_s	$D_{sm}, (\text{cm}^2/\text{s}) \times 10^7$
49.4	0.20	0.059	3.1
63.5	0.21	0.062	5.9
80.0	0.24	0.071	8.6
91.3	0.25	0.074	8.7

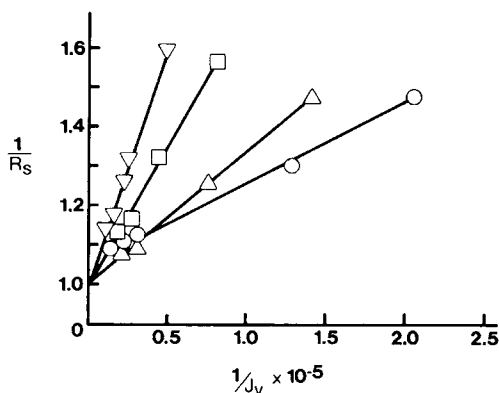


Fig. 4. Relationships between $1/R_s$ and $1/J_v$ for the grafted membranes, see Pusch.^{7,8} (∇) 80% grafting; (\square) 63.5%; (Δ) 49.4%; (\bullet) 30.5%. (J_v values divided by 5 for the 30.5% graft.)

to the diffusion coefficient with respect to the center of mass fixed reference system.

The diffusion constants of salt in the membranes, D_{sm} , were calculated from eq. (8), which is similar to the equation for the molar flux of salt obtained via the solution diffusion model if one assumes that $D_{sm} = 2D_{2m}$ to be calculated from eq. (9). The K_s values were determined independently using neutron activation analysis, and L_p values were obtained as described above. The data points used were the values of R_s found at different ΔP_s . The values of D_{sm} obtained are presented in Table II and are of the same order of magnitude as the ones found by Yasuda et al.¹¹ with nonionic hydrophilic membranes of comparable hydration in a direct study of salt diffusion.

A linear relationship between the reciprocals of the volumetric flux and the rejection was predicted by the derivations of Pusch.^{7,8} The present data have also been plotted in this way, and the results are shown in Figure 4. Good linear plots approaching an $1/R_s$ value of unity at infinite flux were obtained in agreement with the predictions of Pusch. The effect of salt concentration on the reverse osmosis properties was studied with two membranes of different percent grafting and hydration and the results are presented in Figures 5 and 6. A strong dependence of the salt rejection on the salt concentration is indicated, which is a well-known characteristic of charged membranes.¹² The effect of increasing the salt concentration will be to increase ω and also decrease R_∞ , resulting in a higher salt flux and in an increasing contribution of the term $\bar{C}_s(1 - R_\infty)J_v$ to the molar flux of salt, eq. (5); ω increases as K_s increases with the

TABLE III
Effect of Salt Concentration on the Salt Rejection of Penton Membranes Grafted with 2-Vinylpyridine and Quaternized with Methyl Bromide^a

% Grafting	% Salt rejection R_s			$K_l = L'_p$, ($\text{cm}^2/\text{s atm}$) $\times 10^9$
	0.5% ^b	3.5%	5.0%	
30.5	90.0	45.0	37.0	2.4
80.0	86.0	58.0	45.0	7.9

^a Temperature: 28°C.

^b Percent salt in solution.

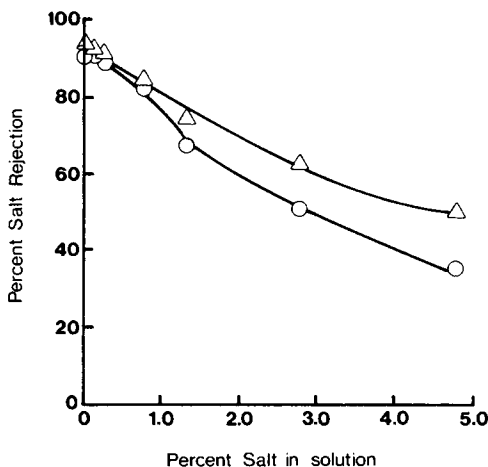


Fig. 5. Effect of the external salt concentration on the salt rejection of Penton films grafted with 2-VP and quaternized with methyl bromide. Measured at 28°C, 80 psi; (O) 30.5% grafting; (Δ) 80.0% grafting.

external salt concentration. Therefore, R decreases as indicated by the equation below,¹ which relates L_p and ω :

$$R_{\infty} = 1 - \omega \left(\frac{\bar{V}_s}{L_p} - \frac{f_{sw} \Delta x}{\phi_w} \right) \tag{10}$$

where f_{sw} is the friction coefficient between salt and water. Negative values for R_{∞} are possible.⁶ However, the equation shown here relating R_{∞} and ω is valid only for membranes with a high concentration of fixed charges compared to the external salt concentration. In the present work, however, $R_{\infty} \sim 1$ with all the membranes studied. The behavior of membranes with lower charge density is

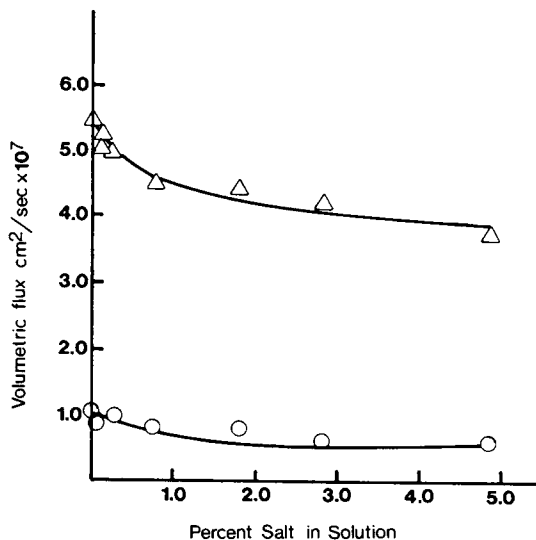


Fig. 6. Effect of the external salt concentration on volumetric flux of Penton films grafted with 2-vinylpyridine and quaternized with methyl bromide. Temperature 28°C; pressure 54.4 atm; percent grafting: (O) 30.5%, (Δ) 80.0%. Fluxes normalized to 1 cm thickness.

included in the study of Kedem and Katchalsky,⁴ and more complex relationships involving frictional coefficients are obtained. The salt rejections obtained with the membranes tested in 0.5% sodium chloride at 54.4 atm and 28°C were higher than those found by Yasuda et al.¹³ for ionic membranes of comparable permeability. Their testing conditions were, however, different: 3.5% sodium chloride, 25°C, and 100 atm. At 54.4 atm, the membranes tested in this work were very close to the asymptotic values for salt rejection as Δp is increased (Fig. 3). The salt rejection varied little with temperature, and the effect of this temperature difference (3°C) can be shown to be insignificant with respect to volumetric flux. Therefore, the results obtained here can be compared with the ones obtained by Yasuda bearing in mind the differences in salt concentrations. The relationship shown below was found by Yasuda et al.¹⁰:

$$L'_p = A \exp(-BR_s) \quad (12)$$

relating the permeability constant L'_p to the salt rejection, where A and B are membrane constants.

In the range of permeabilities of the membranes tested in this work (2.0×10^{-9} to 10.0×10^{-9} cm²/s · atm), the salt rejections were higher (90.0 to 86%) than the salt rejections found by Yasuda¹³ (70 to 55% approximately) with a number of their ionic membranes.

As illustrated by Table III (see also Fig. 5), the salt rejections decrease markedly with increasing concentration of salt in the external solution, and the values for R_s at 3.5% salt are quite close to the ones found by Yasuda et al.¹³ The membrane with 30.5% grafting has a salt rejection well below what is predicted by Yasuda et al.'s relationship for its permeability. Although the range of permeability tested in this work was relatively small, they indicate that the external

TABLE IV
Apparent Activation Energies for Permeation of Grafted Penton 800 PSI

% Grafting	ϕ_w	Activation energy, (kcal/mol)	
		Distilled water	0.5% Salt
30.5	0.12	3.33	8.67
49.4	0.20	5.57	4.38
63.5	0.21	5.77	5.20
91.3	0.25	4.33	4.91

TABLE V
Percent Salt Rejection of Penton Films with Different Percent Graftings Measured in 0.5% Sodium Chloride, 800 PSI, at Different Temperatures

$1/T^{10^3}$ K ⁻¹	% Salt rejection R_s			
	30.5% ^a	49.4%	63.0%	91.3%
3.340	90.5	—	—	—
3.322	90.5	92.9	89.1	87.7
3.294	—	92.7	88.9	87.5
3.260	89.0	—	—	—
3.246	—	92.3	88.3	86.5
3.213	89.0	92.3	88.4	86.5
3.160	87.0	—	—	—
3.060	—	85.3	83.2	—

^a Percent grafting.

salt solution, as can be expected in the case of ionic membranes, has to be considered in addition to the concentration of fixed ions in the membrane. Since the external salt concentration is lower compared to the fixed ion concentration than the one used by Yasuda et al.,¹³ higher values for R_s are obtained in the permeability range studied in this work. If the external salt concentration is increased well above the concentration of fixed ionic sites in the membrane, the behavior should be closer to the behavior of nonionic membranes; i.e., a marked drop in the salt rejection as the permeability is increased. As shown by Kedem and Katchalsky⁴ for high external salt concentration with respect to the fixed ion concentration, the equations for the fluxes reduce to the ones for nonelectrolytes.

The effect of temperature on the reverse osmosis properties of the membranes was studied, and the results are summarized in Table V.

In general, the values for the apparent activation energies of volumetric fluxes calculated in distilled water and in 0.5% salt solution were very close, with the exception of the membrane with the lowest grafting. Values for the apparent energy of activation for permeability of water in various membranes can be found in Barrer¹⁴ and vary between 3 and 8 kcal/mol. Values for activation energies for permeation of water in cellulose acetate membranes measured by Reid and Kuppers¹⁵ varied between 4.9 and 7.7 kcal/mol.

The salt rejection, as illustrated in Table V, decreased with increasing temperature. Comparatively, the volumetric flux is considerably more sensitive to temperature than the salt rejection.

CONCLUSIONS

The ionic membranes prepared in this work have shown comparatively high salt rejection combined with high permeabilities. In general, as shown for example by Yasuda et al.,¹³ above a certain value of permeability the salt rejection of nonionic membranes decreases markedly. Therefore, ionic membranes may have a better performance in a certain range of permeability with respect to salt rejection. However, the salt concentration affects the salt rejection of ionic membranes; and, depending on its value, for a certain value of permeability the salt rejection can be above or below the ones predicted by Yasuda. Furthermore, increasing the temperature increases significantly the volumetric flux with comparatively less significant changes in salt rejection.

Studies of ionic and nonionic membranes with a wide range of reverse osmosis properties utilizing the treatment presented by Kedem and Katchalsky,⁴ as used in this report, should be quite rewarding. Finally, it should be pointed out that heterogeneous grafting to films, however well swollen, is diffusion controlled.¹⁶ This implies that such films are by nature asymmetric. By the judicious choice of the grafting conditions, membranes combining high flux and good salt rejections should be able to be prepared. It is hoped that such studies will be conducted in these laboratories in the near future.

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