Selective Permeability of PVA Membranes. II. Heat-Treated Membranes

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Synopsis

The water and salt transport properties of untreated and heat-treated poly(vinyl alcohol) (PVA) membranes were investigated. Water and salt permeabilities decreased abruptly as a result of heat treatment. The effect of heat treatment on the water and salt transport in PVA is expressed mainly by changes in the activation energies of the corresponding permeability coefficients. Due to the fact that the decrease in the salt permeability with heat treatment was considerably greater than the decrease in the water permeability, a pronounced improvement in the salt rejection of PVA membranes was found as a result of heat treatment.

INTRODUCTION

The transport properties of radiation crosslinked PVA reverse osmosis (RO) membranes were investigated and reported in Part I of this study.[1] It was found that radiation-crosslinked PVA membranes do not constitute a significant improvement over untreated PVA with regard to the selective transport of water and salt. Apparently the poor reverse osmosis performance of these membranes was due to their strong water affinity. As pointed out earlier,[2,3] the degree of swelling of hydrogel membranes has a strong influence on their permeability. The water content of the swollen radiation-crosslinked PVA membranes investigated[1] was over 100% of the dry material, thus creating an open structure highly permeable to water and salt and, therefore, it has low salt rejection.

Heat treatment of PVA is known to have a pronounced influence on its solubility in water.[4] Heat treatment is applied to PVA fibers by the textile industry,[5] where insolubility in hot water is required. The heat treatment of PVA fibers also improves their mechanical properties and dimensional stability. One of the principal effects of heat treatment on PVA at moderate temperatures (below 160°C) is an increase in the crystalline fraction of the polymer.[6] Extensive heat treatment at higher temperatures induces chemical changes such as unsaturation, chain scission, and crosslinking.[6,7] As a result of the changes induced by heat treatment, the affinity of PVA to water is also reduced considerably, resulting in a lower water content of the swollen material.[8] Therefore, heat treatment of PVA membranes is expected to be a method for improving their salt rejection or selectivity. Data reported by Chapurlat et al.[9] regarding the permeability to salt and water of heat-treated PVA membranes support this conclusion.

The objective of this study was to further investigate the transport properties of heat treated PVA membranes and, in particular, the water and salt permeabilities of these membranes and the various factors affecting the permeabilities.

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PERMEABILITY TESTING

The procedures and equipment employed for water and salt permeability measurements were identical with those described in Part I of this study.[1] The heat treatment conditions employed in this study are listed in Table I. In order to provide a basis of comparison, the transport properties of the corresponding untreated PVA membranes were also determined and reported in this study.

TABLE I
Heat Treatment Conditions of the Investigated PVA Membranes

Treatment	Temperature (°C)	Duration (min)
0	untreated	
1	120	80
2	160	70
3	175	30
4	175	70

EXPERIMENTAL

Materials and Film Casting

The materials and the film casting procedure were identical with those employed in Part I of this study.[1] Two grades of PVA supplied by Aldrich Chemical Co. were tested: (a) 100% hydrolized, 86,000 MW (molecular weight), and (b) 100% hydrolized, 115,000 MW. Samples made of 86,000 MW material were designated by the prefix 80 while samples made of the other material were designated by the prefix 90.

Heat Treatment

The heat treated samples were 5.08 cm in diameter and 4–10-μm-thick PVA discs. The heat treatments were performed for various times and at various temperatures in a forced air convection thermostated oven supplied by Ransco Industries. During the heat treatment the samples were placed between two 5-mm-thick flat aluminum plates.

RESULTS

The solution diffusion model, developed by Lonsdale,[10] was employed in the analysis of the water and salt transport through the homogeneous heat-treated PVA membranes, which was also the approach adopted in Part I of this study. According to this model, the water flux (F_w), the salt flux (F_s), and the salt rejection (R_s) of a membrane are given by the following equations:

$$F_w = - \frac{D_{wm} C_{wm} \overline{V}_w}{RT} \frac{(\Delta P - \Delta \pi)}{\lambda} = - \frac{P_w \overline{V}_w}{RT} \frac{(\Delta P - \Delta \pi)}{\lambda} \tag{1}$$

$$F_s = - D_{sm} K \frac{\Delta C_s}{\lambda} = - \frac{P_s \Delta C_s}{\lambda} \tag{2}$$

$$R_s = \frac{\Delta C_s}{C'_w} = \left(1 + \frac{P_s}{P_w} \frac{RT C''_w}{\overline{V}_w (\Delta P - \Delta \pi)} \right)^{-1} \tag{3}$$

where

D_{wm}	= water diffusion coefficient (cm^2/s)
C_{wm}	= equilibrium water content of the swollen membrane (g/cm^3)
$\overline{V}_w$	= partial molar volume of water in the membrane (cm^3/mol)
R	= gas constant
T	= absolute temperature (°K)
ΔP	= hydrostatic pressure drop across the membrane (psi)
$\Delta\pi$	= osmotic pressure drop across the membrane (psi)
λ	= effective membrane thickness (cm)
P_w	= $D_{wm}C_{wm}$ = water permeability coefficient (cm^2/s)
D_{sm}	= salt diffusion coefficient (cm^2/s)
K	= molar distribution coefficient [(g salt/cm^3 membrane)/(g salt/cm^3 solution)]
ΔC_s	= bulk solution concentration difference across the membrane (g/cm^3)
P_s	= $D_{sm}K$ = salt permeability coefficient (cm^2/s)
C_w', C_w''	= water concentration on the high and low pressure sides of the membrane, respectively (g/cm^3)

The temperature dependence of water and salt permeabilities of untreated and heat-treated PVA membranes are given in Figures 1(a)–(e). The reported data were obtained from RO experiments performed at 1000 psi applied pressure. The results of heat treatment no. 4, on PVA membranes at various feed concentrations, is shown in Figure 1(e). The water permeability coefficients fall on a single line, regardless of the feed concentration, while the salt permeabilities were explicitly concentration-dependent. Arrhenius-type dependence on temperature was observed in all cases. This dependence may be expressed by the following equation:

$$P = P_\infty e^{-E_a/RT} \qquad (4)$$

where P and P_∞ are the permeability coefficient values in cm^2/s at temperatures T(°K) and infinity, respectively (P_∞ is usually referred to as the "pre-exponential factor"), E_a is the activation energy in kcal/mol and R is the gas constant. Arrhenius-type temperature dependence is uniquely defined by its pre-exponential factor P_∞ and activation energy E_a the so-called "activation parameters." The activation parameters of the salt- and water-permeability coefficients were derived from the corresponding Arrhenius plots by linear regression analysis and are listed in Table II.

The pressure dependence of water flux at various temperatures through heat treated PVA membranes is shown in Figure 2.

The salt rejections of the untreated and heat-treated PVA membranes were determined at 30°C, at an applied pressure of 1000 psi and at various feed concentrations, as shown in Figure 3.

DISCUSSION

Inspection of the temperature dependence of the permeabilities, at various feed concentrations, given in Figure 1(e), indicates that, within the studied range of feed concentrations, the water permeability coefficients appeared to be in-
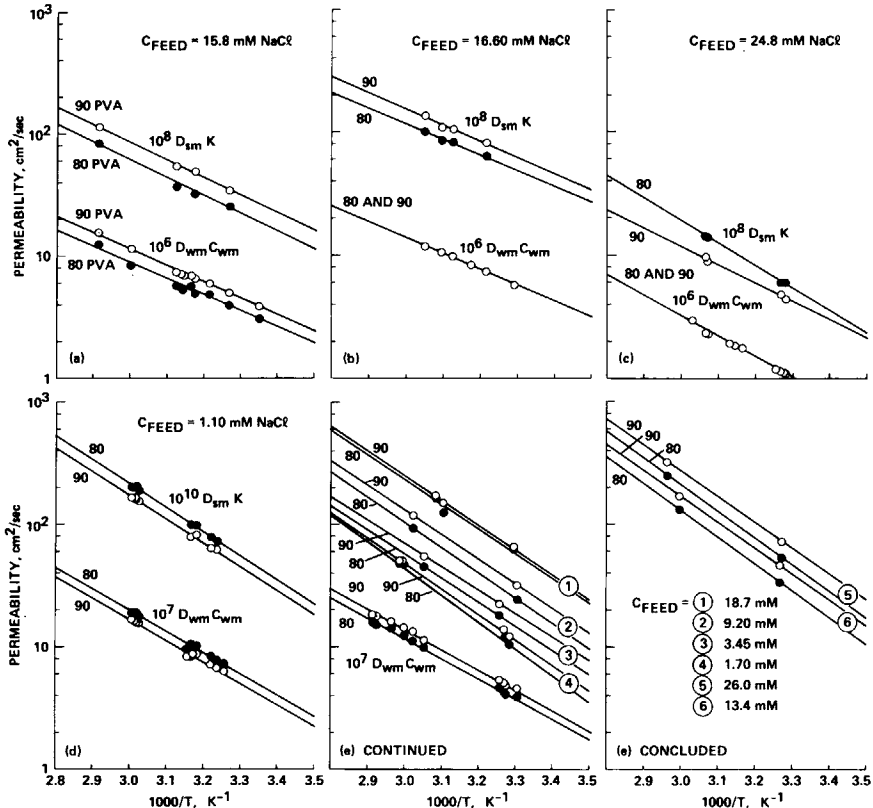
Fig. 1. Temperature dependence of water and salt permeabilities of untreated and heat-treated PVA membranes (the lines are the best fit to the data points evaluated by linear regression analysis). (a) Untreated PVA; (b) heat treatment 1; (c) heat treatment 2; (d) heat treatment 3; (e) heat treatment 4.

dependent of changes in the feed concentration, while the salt permeability coefficients were found to increase systematically with the feed concentration. The activation energies of the salt permeability through the subject membranes, given in Table II, however, were not found to be influenced by the feed concentration. Even though some spread was found among the activation energy values obtained at various salt concentrations, no systematic trend in the activation energy with feed concentration was observed. The effect of feed salt concentration on the salt permeability coefficients was expressed only in the pre-exponential factors, showing a trend toward higher values with increasing feed concentration. Therefore, with the remaining studied membranes, the temperature dependence of the salt and water permeabilities was investigated only at a single, arbitrarily chosen, feed concentration.

The activation energies of the permeability coefficients listed in Table II indicate a pronounced dependence on the intensity (duration and temperature) of the heat treatment. While the activation energies of water and salt permeabilities of untreated PVA and PVA membranes treated at 120°C (treatment 1) were comparable to those found for radiation-crosslinked PVA membranes[1]; the activation energies obtained for the membranes treated at 160°C and 175°C were significantly higher. It was also evident that the increase of the salt per-

TABLE II
Activation Parameters of Water and Salt Permeabilities of Untreated, Heat-Treated, and
Radiation-Crosslinked PVA Membranes (Determined by RO Experiments Performed at 1000 psi
Applied Pressure)

| Heat treatment conditions | | Activation parameters | | | | NaCl feed concentration | PVA type |
| Temperature (°C) | Duration (min) | Water | | Salt | | | |
		E_a (kcal/mol)	P_∞ (cm²/s)	E_a (kcal/mol)	P_∞ (cm²/s)	(mM)	
Untreated		6.39 ± 0.16	0.18 ± 0.04	6.63 ± 0.21	19 ± 6	15.8	90
		6.21 ± 0.31	0.11 ± 0.05	6.85 ± 0.49	19 ± 10		80
120	80	6.12 ± 0.23	0.14 ± 0.04	6.00 ± 0.61	14 ± 9	16.6	90
		6.20 ± 0.19	0.17 ± 0.04	5.67 ± 0.24	6 ± 2		80
160	70	7.54 ± 0.26	0.27 ± 0.10	6.79 ± 0.39	3 ± 3	25.0	90
		7.39 ± 0.21	0.22 ± 0.07	8.31 ± 0.33	53 ± 23		80
175	30	7.86 ± 0.27	0.24 ± 0.08	8.87 ± 0.28	11 ± 4	1.10	90
		7.86 ± 0.32	0.27 ± 0.11	8.94 ± 0.18	15 ± 4		80
175	70	7.54 ± 0.14	0.13 ± 0.03	9.59 ± 0.20	9 ± 4	1.70	90
		7.57 ± 0.11	0.11 ± 0.02	9.95 ± 0.34	15 ± 5		80
175	70	7.54 ± 0.14	0.13 ± 0.03	9.27 ± 0.20	16 ± 6	9.20	90
		7.57 ± 0.11	0.11 ± 0.02	9.59 ± 0.34	21 ± 13		80
175	70	7.54 ± 0.14	0.13 ± 0.03	9.69 ± 0.20	38 ± 15	13.4	90
		7.57 ± 0.11	0.11 ± 0.02	10.11 ± 0.34	53 ± 30		80
175	70	7.54 ± 0.14	0.13 ± 0.03	9.34 ± 0.20	34 ± 12	18.7[a]	90
		7.57 ± 0.11	0.11 ± 0.02	9.28 ± 0.34	29 ± 16		80
175	70	7.54 ± 0.14	0.13 ± 0.03	9.70 ± 0.20	62 ± 20	26.0	90
		7.57 ± 0.11	0.11 ± 0.02	10.0 ± 0.34	74 ± 40		80
Radiation crosslinked[1]		6.03 ± 0.07	0.10 ± 0.01	6.03 ± 0.07	3 ± 2	2.0	90
		6.03 ± 0.07	0.10 ± 0.01	6.03 ± 0.07	14 ± 3	20.0	90

[a] At this feed concentration the RO experiment was performed at ∼560 psi applied pressure.

meation activation energy with heat treatment was about two to three times as fast as the increase of the water permeation activation energy. Thus, the activation energies of salt and water permeability of the PVA membranes treated at 175°C for 70 min (treatment 4) were in the range of 9.52 ± 0.20 and 7.54 ± 0.14 kcal/mol, respectively, while those of untreated PVA were 6.6 ± 0.2 and 6.4 ± 0.2 kcal/mol, respectively. At the same time, the pre-exponential factors of the salt and water permeabilities did not change systematically as a result of the heat treatments, but were confined to a narrow range of values, which suggests that the heat-treatment effect on the water and salt permeabilities of the PVA membranes can be expressed mainly in changes of the activation energies. To determine if this conclusion can be applied to radiation-crosslinked PVA membranes, the pre-exponential factors of the water and salt permeabilities of these membranes were calculated from the data published in Part I of this study[1] and are also listed in Table II. These values are in good agreement with the corresponding data obtained from the heat-treated and the untreated PVA membranes at comparable salt concentrations.

An important corollary of the different activation energies for water and salt permeabilities is that the transport of these permeants through heat-treated PVA membranes was taking place independently of each other, thus providing support to the applicability of the solution–diffusion model to this case.

The water and salt permeability data shown in Figures 1(a)–(e) also indicate
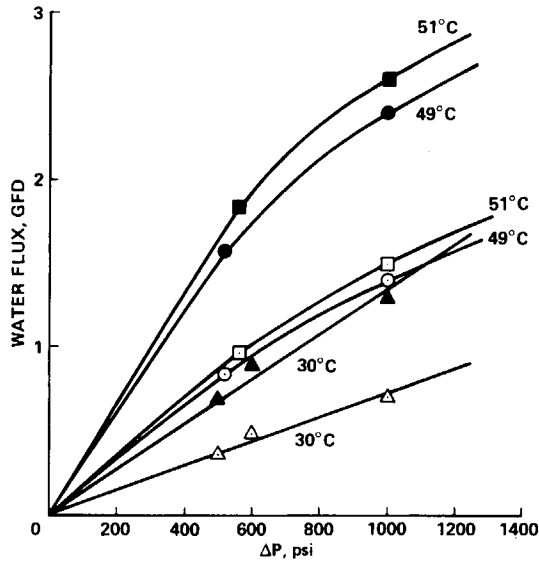
Fig. 2. Pressure dependence of water flux through heat treated PVA membranes (heat treatment 4; see Table I). (■,●,▲) 80 PVA, (□,⊙,△) 90 PVA.

a considerable decrease of the permeabilities of the PVA membranes with the intensity of the heat treatment. This is demonstrated more clearly in Figure 4, where the salt and water permeabilities at 30°C of PVA membranes heat-treated at 175°C for various times is presented as a function of the heat-treatment duration. The data in this figure indicate that the decrease in salt permeability
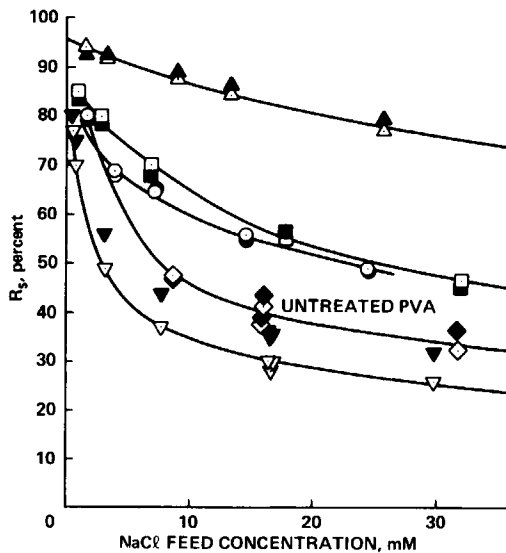
Fig. 3. Feed concentration dependence of the salt rejection of untreated and heat treated PVA membranes tested at $\Delta P = 1000$ psi and 30°C. (◊) Untreated (90 PVA), (♦) untreated (80 PVA), (▽) treatment 1 (90 PVA), (▼) treatment 1 (80 PVA), (○) treatment 2 (90 PVA), (●) treatment 2 (80 PVA), (□) treatment 3 (90 PVA), (■) treatment 3 (80 PVA), (△) treatment 4 (90 PVA), (▲) treatment 4 (80 PVA).
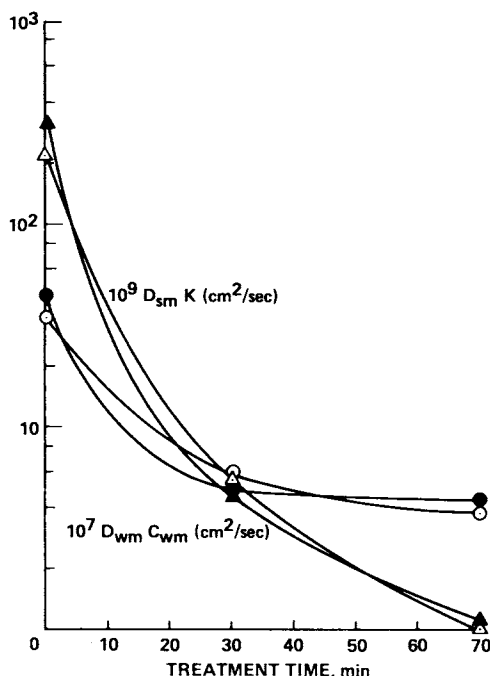
Fig. 4. Effect of the duration of heat treatment at 175° on salt and water permeabilities of PVA at 30°C and ΔP = 1000 psi. (●,▲) 80 PVA; (○,△) 90 PVA.

of the heat-treated PVA membranes was much steeper than the decrease in the water permeability with duration of heat treatment. This decrease also explains the general improvement in selectivity (except for treatment 1) of the heat-treated membranes as indicated by Figure 3. As shown in Figure 2, near room temperature the water flux through the heat-treated PVA membranes was found to be proportional to the pressure differential across the membrane, as expected from eq. (1). At higher temperatures (49–50°C), however, curvature appears, which is probably due to some deterioration of the mechanical properties of the membranes which led to compaction. In this respect, the behavior of the heat-treated PVA membranes was different from that of the radiation-crosslinked membranes, where at all temperature (24–25°C) a clear dependence of the water and salt permeability coefficients on pressure differential was observed.

The effect of pressure on the salt rejection of heat-treated PVA membranes was not investigated as extensively here as in the case of the radiation crosslinked membranes. Nevertheless, the salt rejection of heat treated membranes (heat treatment 4) was determined in the pressure range of 520–600 psi with a feed concentration of 18.5 mM NaCl at 30°, 49°, and 51°C. The corresponding salt rejections at an applied pressure of 1000 psi were evaluated from the available experimental data and the results are presented in Figure 5. It is evident that even though each line in this figure is based on the minimal two points, in all cases the lines intercept the R_s^{-1} axis very close to the value 1.0, as expected from eq. (3) for a solution–diffusion membrane.

The salt rejections of the heat-treated PVA membranes, as well as those of the untreated PVA membranes, were found to be strongly dependent on the feed salt concentration, as shown in Figure 3. This concentration dependence of the
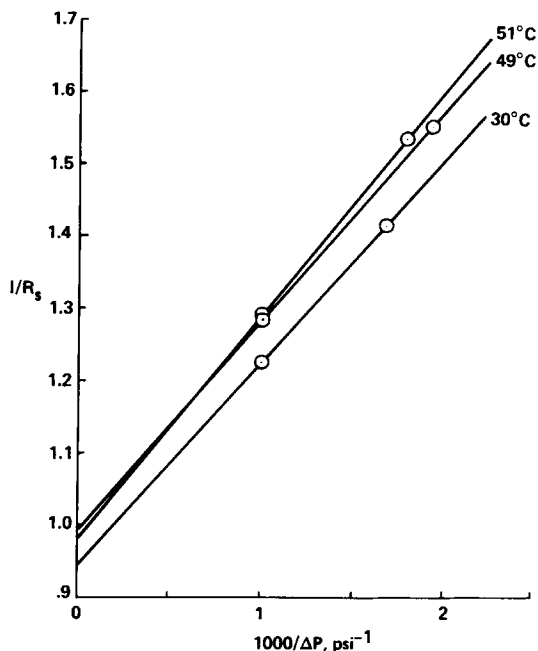
Fig. 5. Pressure dependence of the salt rejection of PVA membranes heat-treated for 70 min at 175°C (treatment 4).

salt rejection was also observed with the radiation-crosslinked PVA membranes. Regarding the possibility mentioned earlier[1] that this phenomenon may be due to Donnan type, ion-exclusion mechanism, it should be noted that heat-treated PVA has been shown to contain charged groups,[7] and, therefore, the salt concentration dependence of the rejection of heat-treated PVA membranes may be rationalized in these terms. No similar evidence exists, however, for untreated and radiation-crosslinked PVA.

A comparison of the transport properties of radiation crosslinked PVA membranes[1] with those of untreated PVA membranes indicated, rather unexpectedly, that the water and salt permeabilities of the radiation crosslinked membranes were somewhat higher. The mechanical and structural stabilization of the polymer network resulting from the radiation crosslinking may account for the higher water and salt permeabilities of the radiation-crosslinked membranes. The crosslinked network may have been more stable dimensionally than the untreated PVA, and this prevents the structure from collapsing under pressure during the RO process. Consequently, a relatively high free volume was available for the transport of the permeants, which led to a high water and salt permeability for radiation crosslinked PVA membranes.

A similar comparison also held for the PVA membranes heat treated at 120°C (treatment 1). Unlike the membranes treated at higher temperatures, the water and salt permeabilities of these membranes were higher than those of untreated PVA membranes (again in contradiction with the general trend), but they compared very closely with those of radiation-crosslinked PVA membranes.[1] This similarity of the transport properties of these two different types of PVA membranes suggests that the radiation crosslinking and the heat treatment at 120°C of the PVA membranes yielded structures of similar characteristics. Such

an interpretation is consistent with earlier statements[8] which consider the crystal micelles formed as a result of the heat treatment acting as multifunctional crosslinks. These crystal nodules stabilize the structure of the polymer network and restrict the free motion of its charges in a similar fashion to the crosslinks induced by treatment with ionizing radiation.

CONCLUSION

The most noticeable effect of heat treatment on PVA membranes relative to untreated membranes was the pronounced improvement of their selectivity with regard to salt. As expected, the lower water content of the heat treated membranes reduced both the water and the salt permeabilities of these membranes. However, as shown in Figure 4, the salt permeability decreased much faster with the duration of heat treatment than the water permeability. The trends indicated in this figure suggest that by increasing the duration of the heat treatment beyond 70 min, membranes with even better rejections should be expected. The various results obtained in this study further substantiate the conclusion suggested earlier[1] that the salt and water transport through PVA membranes is uncoupled and probably follows a solution-diffusion mechanism.

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