

A Zeolite / Polymer Membrane for Separation of Ethanol-Water Azeotrope

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Synopsis

A novel membrane effective in the separation of ethanol-water mixtures by pervaporation was made by combining zeolite NaA and poly(vinyl chloride) modified by 2-(2'-butoxyethoxy)ethyl thiolate. Under ambient conditions, a separation factor ($\alpha_{\text{H}_2\text{O}}$) of 29 and pervaporability ($P_{\text{H}_2\text{O}}$) of $4 \times 10^{-4} \text{ g m}^{-1} \text{ h}^{-1}$ were obtained for the azeotropic mixture whereas, in the absence of zeolite, the respective values were 7 and 7×10^{-5} . A mechanism was proposed relating the preferential water transport at $\approx 50\%$ zeolite content to an interfacial "phase" between the zeolite and the modified polymer.

INTRODUCTION

Pervaporation is a liquid-phase separation technique having commercial potential especially in cases for which ordinary distillation is inapplicable, such as azeotropic mixtures, mixtures of heat-sensitive compounds, or mixtures of compounds having close boiling points.¹ The method has been recently used for separating alcohol-water solutions.²⁻⁹ The employed membranes were made of either rubbery or glassy polymers. In the former case, high pervaporation rates and good separation were obtained at relatively low alcohol concentration while, in the latter case, very high selectivities could be achieved even at high alcohol concentrations, but pervaporate fluxes were extremely small. Achieving high transport rates with satisfactory selectivity is in particular difficult with ethanol-water solutions because of the close similarity in physical properties between these two compounds (boiling point, polarity), and especially at or near the azeotropic point. Thus, designing a membrane for the commercially important separation of ethanol-water azeotrope requires careful choice of materials to enhance the solubility and diffusivity of water, thereby allowing better water than ethanol transport through the membrane. One direction is modifying a polymer by grafting onto it suitable hydrophilic side chains. In addition, beside grafting we have added to polymers a zeolite molecular sieve to further enhance preferential water transport. Previously, a zeolite A/silicone rubber membrane was employed for gas sorption.¹⁰ Here we present preliminary results of our study showing the effect of the zeolite on ethanol-water separation. A plausible model is proposed to explain the observed behavior.

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EXPERIMENTAL

Membrane Preparation

Poly(vinyl chloride) (PVC) was received from Frutarom Electrochemical Co., Israel (MW = 60,000). The polymer was modified by us using the procedure developed by Marian and Levin.¹¹ According to the above procedure, a measured amount of suspension of PVC (grade 43, Frutarom, Electrochemical Industries Co., Haifa, Israel) in water (~ 35% solid content) was continuously stirred in the presence of an equivalent amount of 2-(2'-butoxyethoxy) ethane thiol $[(C_4H_9-(CH_2-CH_2O)_2-\bar{S})]$. A solvent (equal weight to the solid content of the slurry) such as DMF or cyclohexanone was added to the slurry. Addition of the solvent was found to be essential for nucleophilic substitution to occur. After the reaction was completed, the suspension was separated, and the polymer washed several times with distilled water, methanol, and ether. The resulting grafted polymer was dissolved in THF or chloroform and precipitated in methanol or petroleum ether. This procedure was repeated three times. Finally, the polymer was dried in a vacuum oven for 24 h. The sulfur and chlorine content of each polymer was determined. The zeolite component, unless otherwise mentioned, was a Linde-A type synthesized by us according to a literature procedure.¹² The average size of the zeolite was found to be $5 \pm 1 \mu\text{m}$.

A typical procedure for membrane preparation included dissolution of the polymer in dry THF, casting the obtained solution on a glass plate, allowing the solvent to evaporate under ambient conditions for 16 h, and finally vacuum-drying the remaining film at 28°C for ≈ 16 h. In the case of zeolite-containing membranes, the zeolite was added as fine powder to the polymer solution, and the homogenized slurry obtained underwent similar casting and drying steps.

Membrane thickness and swelling measurements were done according to the ordinary procedures. XRD analysis of zeolites and membranes was performed on a Philips PW-1011/02 diffractometer operating with $\text{CuK}\alpha_1$ radiation. DSC analysis was performed using the Mettler System TA3000. Scanning electron micrographs were obtained over a Philips 505 instrument.

Pervaporation Runs

A standard pervaporation apparatus¹ was employed. The upper compartment of the stainless-steel cell had a capacity of 75 cm³, and the effective membrane area was 13.6 cm². The feed solution introduced into the thermostated upper compartment was monotonically stirred throughout the experiment. The temperature was $25 \pm 0.5^\circ\text{C}$, and the vacuum at the lower compartment was 1.33 Pa (10^{-2} torr). The pervaporate was collected in cold traps containing 2-propanol as solvent. Analysis was done by gas chromatography (Tracor Model 570) over a Porapak QS column. Except when otherwise mentioned, the upstream pressure was 0.101 MPa (1 atm).

RESULTS AND DISCUSSION

Selected results of the separation of ethanol-water azeotrope by pervaporation using different membranes are presented in Table I. As seen,

TABLE I
Separation of Ethanol-Water Azeotrope by Pervaporation

Membrane	Membrane thickness (μm)	Run time (h)	Pervaporate		α^a	$10^5 \times P^b$ ($\text{g m}^{-1} \text{h}^{-1}$)
			Water (g)	Ethanol (g)		
1 PVC	73	45	0.029	0.0626	250	3.4
2 modified PVC ^c	50	17	0.033	0.099	7	7.1
3 59% NaA/PVC	260	45	0.117	1.06	2.4	49.7
4 59% NaA/modified PVC	115	18.5	0.082	0.061	28.8	37.4
5 59% P_1 /modified PVC	250	17	0.015	0.0145	22.4	16.2
6 43.4% NaA/modified PVC	98	18	0.047	0.056	18.5	18.8
7 6 treated with HCl ^d	130	17	0.158	1.147	3.0	88.8
8 6 treated with NaOH ^e	75	19.7	0.039	0.114	7.2	10.9

^a $\alpha = [c'/(1 - c')]/[c/(1 - c)]$, c being the weight fraction of water in the feed and c' , in the pervaporate.

^bPervaporability is defined as $P = J \cdot d$, J being the flux and d , the membrane thickness; P is the amount (g) of pervaporate passing through 1 m of a membrane whose surface area is 1 m², for 1 h. For all ethanol-water mixtures, P and J relate in this paper to the water component (i.e., $P = P_{\text{H}_2\text{O}}$, $J = J_{\text{H}_2\text{O}}$).

^cSee text. Elemental analysis: S, 6.3%; Cl, 29.8%.

^dMembrane **6** immersed in 16% aqueous solution of hydrochloric acid for 2 h, at ambient conditions followed by washing with deionized water and drying under air.

^eMembrane **6** immersed in 10% aqueous solution of sodium hydroxide for 7 days at ambient conditions followed by washing with deionized water and drying under air.

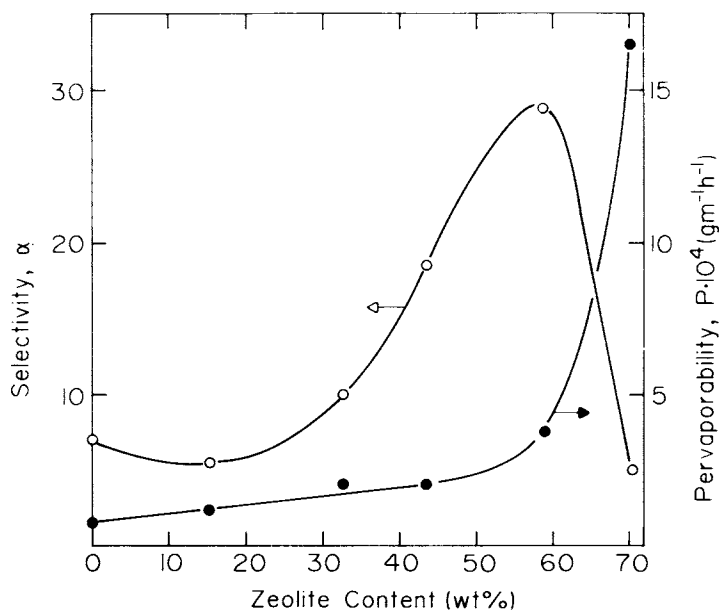


Fig. 1. Effect of zeolite content in modified-PVC membrane on separation factor α and pervaporability P of ethanol-water azeotrope.

membrane 2 prepared from modified PVC—a PVC grafted with $C_4H_9-(CH_2-CH_2-O)_2-S-$ groups¹¹—exhibits drastic reduction in water selectivity (α) compared to membrane 1 obtained from the unmodified PVC, without substantial effect on pervaporability (P). However, when zeolite A is added to the modified PVC, the resulting membrane 4 obtained therefrom shows a remarkable increase in both α and P . The effect of zeolite content on membrane performance is described in Figure 1. As seen, low selectivity is obtained up to $\sim 30\%$ zeolite, but then α increases sharply, passing through a maximum at $\sim 58\%$ and finally declining to a very low value at 70%. In parallel, pervaporability is roughly constant up to the maximum in α and then increases fourfold toward 70%. This behavior can be explained by assuming that in the zeolite/polymer membrane three different transport mechanisms operate, one effective at low (i.e., $< 30\%$), the second at moderate (i.e., 30–60%), and the third at high (i.e., $> 60\%$) zeolite content. When there is insufficient amount of zeolite, the zeolitic crystallites spread in the polymer bulk forming isolated zeolitic “islands” and the membrane behaves essentially as that of pure modified PVC; the rate-determining step in the transport is then diffusion through the “dry” downstream layer of the membrane, which is in equilibrium with the low-pressure region in the pervaporation cell. In

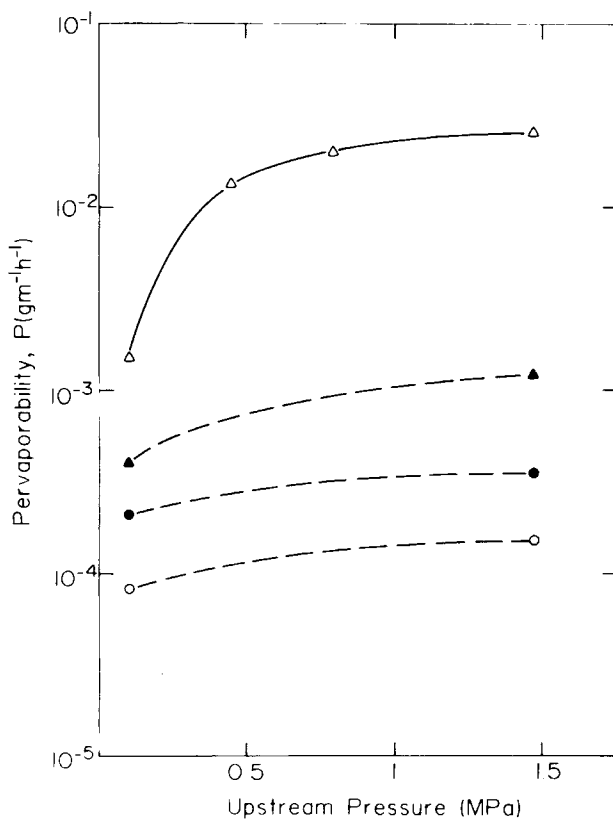


Fig. 2. Effect of upstream pressure on pervaporability of pure water and pure ethanol. Membrane 2: (O) water; (●) ethanol. Membrane 5: (Δ) water; (▲) ethanol.

accord with this mechanism, Figure 2 shows that in the case of membrane 2, pervaporability of both pure water and pure ethanol are almost entirely independent of upstream pressure as measured in the range 0.1–1.5 MPa. When the amount of zeolite in the membrane exceeds a certain critical point, a second mechanism becomes operative, which is characterized by a sharp increase in α but moderate growth in P . We believe that in this case the rate-determining step in the transport is passage through the zeolite/modified polymer interface where the dietheric groups coordinate to external sodium ions, thereby enabling good compatibility between the modified polymer and the zeolite. It is conceivable that the sodium form of the zeolite is suitable for coordination with the polymer's side chain. This kind of interaction was proposed previously by Nkansah and Levin.¹³ In contrast, the aluminosilicate structure may be of less importance. This is suggested by the fact that when zeolite NaA is replaced by a synthetic gismondinelike zeolite (P_t), in its sodium form¹⁴ the effectiveness of the membrane obtained (i.e., 5) remains virtually unchanged (Table I), although these small-pore zeolites which have similar elemental composition are structurally entirely different. However, according to some preliminary results, highly siliceous zeolites appear to be unsuitable for ethanol–water separating membranes, perhaps because of their lower surface sodium content and the consequent diminishing of interaction points with the modified polymer.

A supporting evidence for the special interaction between the zeolite and the modified polymer is the fact that, on mixing the two, a more homoge-

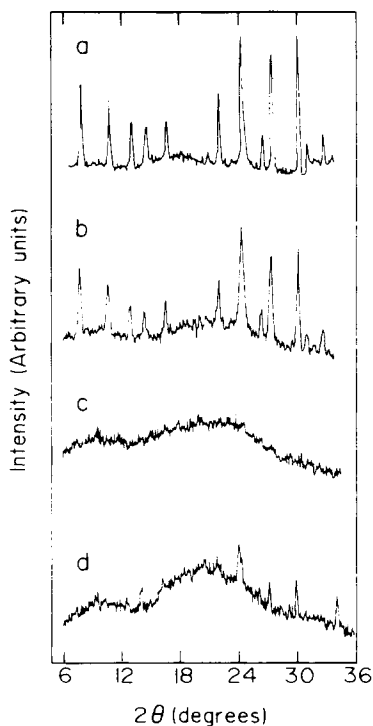
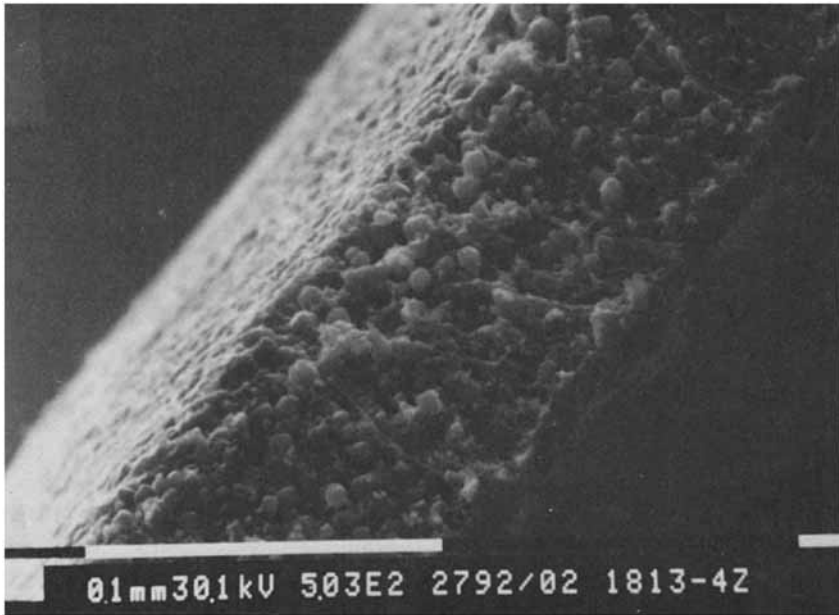
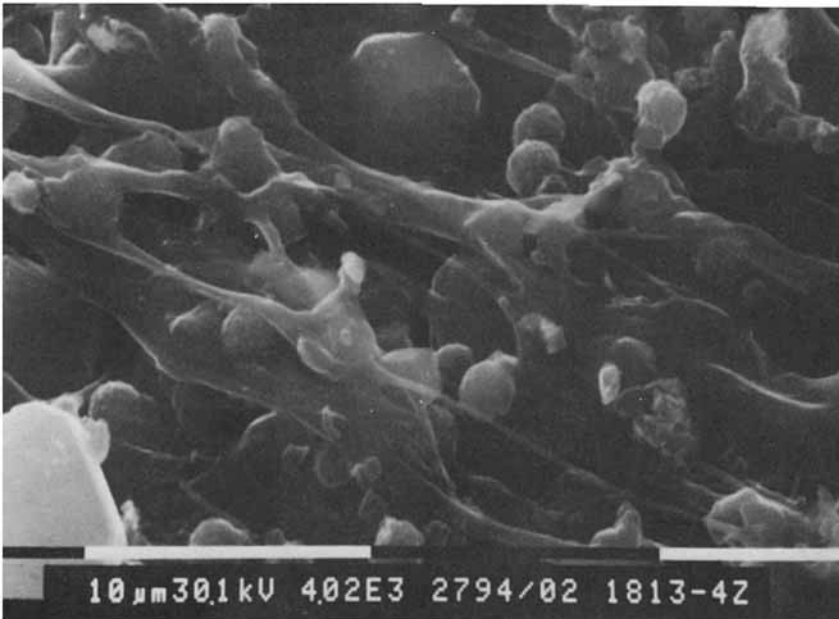


Fig. 3. XRD spectra: (a) NaA; (b) membrane 4; (c) membrane 7; (d) membrane 8.

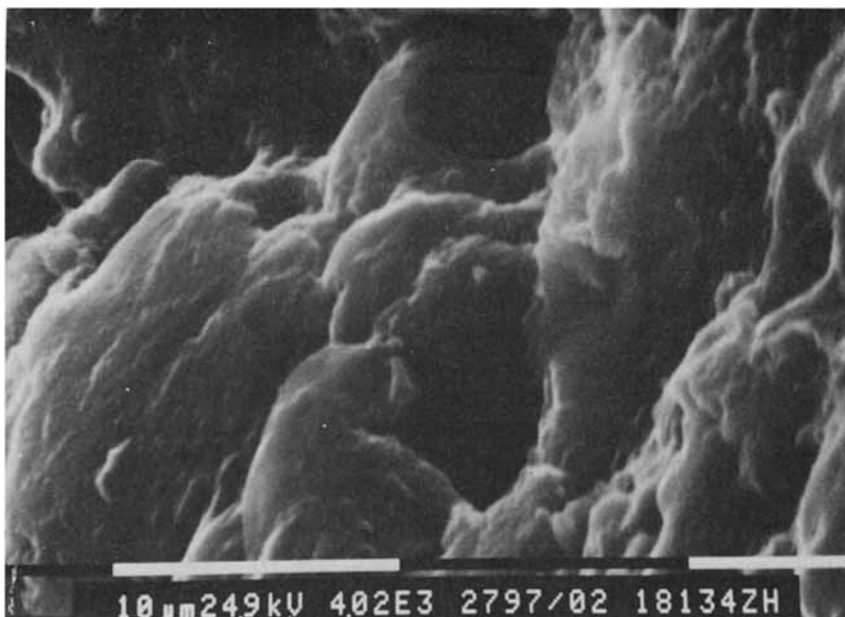


(a)

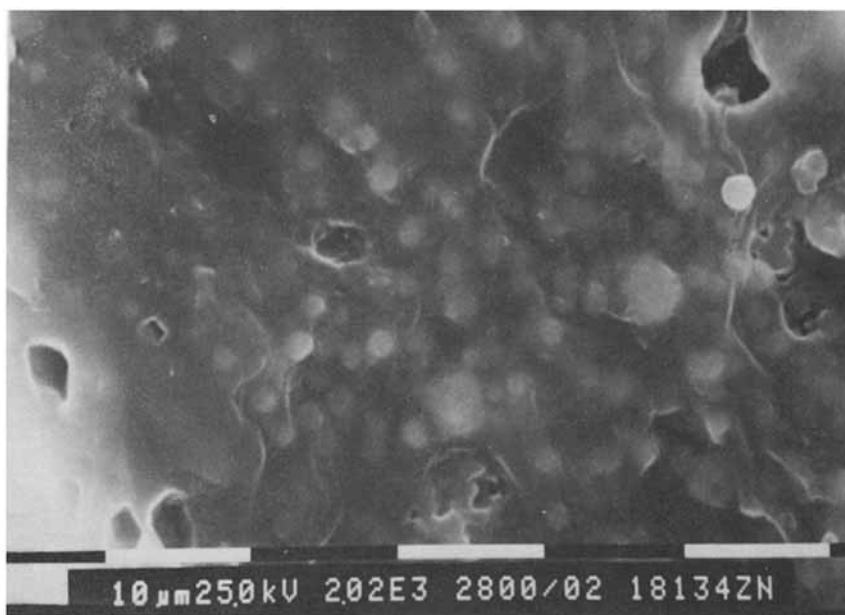


(b)

Fig. 4. Scanning electron micrographs: (A) cross section of membrane 4; (B) surface enlargement, membrane 4; (C) membrane 7; (D) membrane 8.



(c)



(d)

Fig. 4. (Continued from the previous page.)

neous, unseparable slurry is obtained as compared to the slurry formed with the zeolite and the unmodified polymer (i.e., pure PVC). Treating a zeolite/modified polymer membrane (i.e., **6**) with HCl caused complete destruction of the zeolitic component as evident from the disappearance of the typical XRD lines (Fig. 3, compare c to b). The treated membrane (i.e., **7**) exhibited a remarkable increase in thickness (Table I), and this is evidently due to the much lower density of the obtained silica. This membrane has a very low selectivity but quite high pervaporability (Table I). Treating membrane **6** with NaOH also caused destruction of zeolite A but in this case XRD lines still exist [Fig. 3(d)], and they apparently belong to a mixture of hydroxy sodalite and zeolite *P*. The treated membrane (i.e., **8**) exhibits ~25% shrinkage, low selectivity, and low pervaporability (Table I). Scanning electron micrographs of membrane **4** [see Figs. 4(a, b)] clearly show zeolite crystallites which spread evenly in the polymer bulk. These crystallites are entirely missing in the case of membrane **7** [Fig. 4(c)] and instead, large holes can be seen. On the other hand, with membrane **8** [Fig. 4(d)] zeolite crystallites still exist, and it seems that the polymer itself has somewhat changed. These findings are in accord with the XRD results (Fig. 3). Thus, the importance of NaA in the zeolite/modified polymer membrane is established.

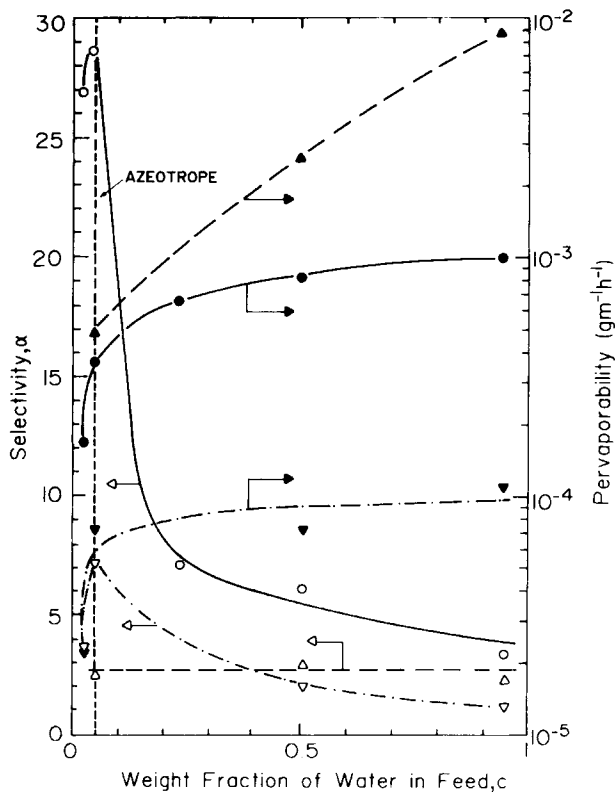


Fig. 5. Effect of ethanol-water feed composition on separation factor, α (open symbols) and pervaporability P (closed symbols): ($\nabla, \blacktriangledown$) membrane 2; (Δ, \blacktriangle) membrane 3; (\circ, \bullet) membrane 4.

The interface between the zeolite and the polymer-grafted etheric side chains apparently provides a unique "phase" through which water is transported better than ethanol. Unlike the dry-layer diffusion mechanism,¹ this transport mode is dependent on the ethanol-water solubility in the membrane hence on upstream pressure. As seen in Figure 2, introducing zeolite P_t into the modified polymer (membrane 5) causes reverse in the relative magnitude of P , and water becomes the favored component for transport in the entire pressure range. The effect of pressure on water transport is especially pronounced below 0.5 MPa. At $\sim 60\%$ zeolite, the above interfacial effect may reach saturation, and from there on the etheric groups cannot cover completely the external surface of the zeolite crystallites. As a consequence, large holes (macropores) form between the zeolite and the polymer leading to faster pervaporation rate with complete loss of selectivity. In the range of 60–70% zeolite content, the competition between the interfacial micropore and macropore transport is evident (Fig. 1). Above 70%, the transport is mainly through the nonselective macropores.

The macropore transport mechanism as proposed herein is in agreement with the fact (Table I) that unmodified (parent) PVC when mixed with zeolite A provides a membrane (i.e., 3) which is nonselective for water-ethanol separation but exhibits higher pervaporation rates as compared to the pertinent membrane made of the modified PVC (i.e., 1). The performance of membrane 3 is further demonstrated in Figure 5, in which α and P are plotted against weight fraction of water in the feed (c). As also shown, membrane 4 is selective only at and near the azeotropic point (i.e., $c \approx 0.044$). It exhibits a

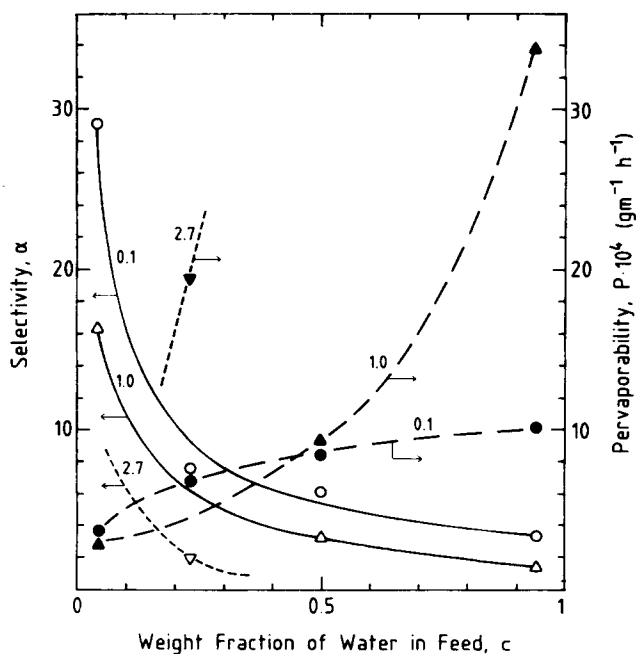


Fig. 6. Effect of upstream pressure on ethanol-water separation (open symbols) and pervaporability (closed symbols) as a function of feed composition. [Membrane 4; pressure values (MPa) are indicated near the respective curves.]

fourfold decline in α when c is increased to 0.25. We consider this finding as evidence against the possibility that the rate-determining step in the transport is intracrystalline zeolitic diffusion since the latter mode of transport should not be dependent on c in a manner as described in Figure 5. On the other hand, micropores in the zeolite/modified polymer interface are of a strong hydrophilic nature and, therefore, influenced appreciably by water concentration in the feed. As this concentration increases, considerable membrane swelling takes place, causing a sharp decline in α and a pronounced growth in P (Fig. 5). Membrane swelling is apparently also a function of upstream pressure, as indicated in Figure 6 by the change in behavior of the P vs. c plot as a function of pressure. The relation between swelling and the P vs. c plot is discussed by Yoshikawa et al.⁹ The effect of upstream pressure on the selectivity is a monotonic decrease throughout the entire feed composition range (i.e., $0.044 \leq c \leq 0.94$). This is due to the increase in membrane swelling. Below $c \approx 0.5$, both α and P are improved as upstream pressure is reduced.

In summary, adding a zeolite, such as NaA, to a suitably grafted polymer (e.g., the above modified PVC) provides a mixture from which a membrane can be fabricated, exhibiting improvement in both selectivity and transport rate in the separation of ethanol-water azeotrope, as compared to the zeolite-free membrane. We speculate that this effect results from the involvement of a unique transport mechanism employing a zeolite/modified polymer interfacial "phase." At low water concentrations, water transport through this interface is favored for ethanol transport.

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