

Pervaporation of Nonaqueous Ethanol Azeotropes Through Interpenetrating Polymer Network Membranes Prepared from Poly(4-vinylpyridine) and Poly(vinyl alcohol)

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ABSTRACT: Highly hydrophilic interpenetrating polymer network (IPN) membranes were prepared from a mixture system of poly(4-vinylpyridine) (P4VP) and poly(vinyl alcohol) (PVA) by quaternizing crosslinking of P4VP with 1,4-dibromobutane (DBB) and simultaneous crosslinking of PVA with hexamethylene diisocyanate (HMDI). The membrane performance in pervaporation (PV) for the azeotropic mixture of ethanol with a less polar organic liquid (chloroform, benzene, carbon tetrachloride, and cyclohexane) was investigated. The strength of these IPN membranes was higher than that of the cellulose acetate membrane and depended on the membrane composition. All the membranes were ethanol permselective for the azeotropic feeds and equimolar mixture feeds as well. Only the swelling degree Q of the membrane, among several physicochemical factors, showed a relationship with the separation performance for the four feeds; a lower value of Q generally corresponded to a higher separation factor and smaller permeability. The membrane composition, which exhibited an optimum membrane performance, was examined in detail for some membranes. Both the separation factor for sorption and that for diffusion far exceeded unity, but the latter was greater in most cases than was the former and dominated the overall separation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2729–2738, 2001

Key words: pervaporation; IPNs; hydrophilic polymers; membranes; poly(4-vinylpyridine)

INTRODUCTION

Pervaporation (PV) technology has gained increasing importance because it is an energy-saving process for separating various mixtures. The membranes used for PV involve many kinds of polymer materials. We reported on the PV separation of an aqueous ethanol solution using an interpenetrating polymer network (IPN) membrane composed of poly(glycidyl methacrylate)

crosslinked with tetraethylenepentamine and poly(4-vinylpyridine) (P4VP) crosslinked with dibromobutane and a semi-IPN membrane composed of crosslinked poly(glycidyl methacrylate) and P4VP.¹ An IPN has advantages of providing a variety of characteristics and functions, yielding a homogeneous membrane, by combining different types of networks, such as hydrophilic and hydrophobic components, soft and hard segments, cationic and anionic polymers, or analogous characters to enhance the affinity for one component of the feed mixture. After our publication, however, very few reports that dealt with IPN-separating membranes have appeared. They include cellu-

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lose-poly(acrylamide or acrylic acid) IPN membranes for the PV of water–ethanol mixtures² and a semi-IPN of a poly(ethylene glycol dimethacrylate) network interpenetrated with cellulose propionate or butyrate for ethanol-ethyl *t*-butyl ether,³ while active research on IPNs was directed toward IPNs themselves, mostly containing epoxy resin or urethane linkage as a crosslink component.^{4–9} PV for the separation of nonaqueous mixtures, on the other hand, becomes increasingly important from industrial and environmental viewpoints. This is apparent from recent publications dealing with the separation of methanol (or ethanol)–methyl (or ethyl) *t*-butyl ether,^{10–18} benzene–cyclohexane,^{19–22} alcohol–toluene,²³ styrene–ethylbenzene,²⁴ and acetone-chlorinated hydrocarbons,²⁵ through a variety of membranes other than those of an IPN.

In feed mixtures consisting of a polar and less polar component such as alcohol-*t*-butyl ethers and alcohol-toluene, a membrane of polar character seems to be favorable for the permeation of the more polar component because the latter is preferentially sorbed into the membrane. In our previous study, the IPN membrane, containing highly polar quaternized pyridine moieties, played a crucial role in preferential water permeation out of aqueous ethanol feeds.¹ As for nonaqueous mixture feeds, it is also likely for a more polar feed component to permeate preferentially into a polar membrane.

In this study, a highly polar quaternized P4VP was dealt with as the principal membrane material and, in addition, poly(vinyl alcohol) (PVA) of extremely hydrophilic character was employed as a partner of IPN. The aim of this study was to demonstrate the advantageous effect of highly hydrophilic IPN membranes on the separation of a polar feed component by its preferential permeation from a less polar one and to investigate how the content of each polymer material and crosslinking agent affects the strength and separating performance of those membranes in PV for nonaqueous azeotropic mixtures of ethanol, as a polar feed component, and chloroform, benzene, cyclohexane, or carbon tetrachloride, as a less polar organic feed component.

EXPERIMENTAL

Materials

P4VP was prepared, according to our previous article,¹ from freshly vacuum-distilled 4VP [kind-

ly supplied by Kohei Chemical Industries (Japan)] by emulsion polymerization with a redox initiator, potassium persulfate, and sodium hydrogen sulfite. PVA ($M = 66,000$) was purchased from Wako Jun-yaku Co. (Japan). 1,4-Dibromobutane (DBB) from Kanto Chemical Co. (Japan) and hexamethylene diisocyanate (HMDI) from Tokyo Kasei Co. (Japan) were used after vacuum-distillation. Solvents of guaranteed purity grades (ethanol, cyclohexane, and carbon tetrachloride) were used as received and those of other grades [benzene, chloroform, and dimethyl sulfoxide (DMSO)] were distilled before use.

Membrane Preparation

A determined amount of P4VP and PVA was separately dissolved in DMSO. The concentration of the two polymers was 4.5 and 7.4 wt %, respectively. A determined amount of DBB was dissolved in the P4VP solution. This solution was added to the PVA solution, and, finally, the required amount of HMDI was added. The well-stirred mixture was cast into a metal ring frame of about 8 cm diameter and 3 cm height, which was put onto a clean glass plate. The glass plate was, in advance, wetted and dried with a 1.5 wt % aqueous polyacrylamide solution for the sake of easy peeling, and the outside periphery of the frame was fixed onto the plate with an adhesive to prevent the casting solution from leaking. The cast plate was heated at 80°C in an oven. After 75 min heating, the membrane periphery was cut from the frame wall with a sharp knife to release the stress due to the shrinkage of the membrane, and heating was continued. The total heating time was 5 h. Most of the membranes were peeled off from the plate and stored in ethanol before use. Some membranes were immersed in water for more than 24 h. The thickness was measured with a thickness gauge of 1 μm accuracy. The thickness ranged from 90 to 170 μm , mostly around 150 μm .

Permeation

PV was carried out in the same apparatus as reported,²⁶ which was of the batch type with a 300-mL cell capacity and an 18.1 cm^2 effective membrane area and controlled at 25°C by circulating water in the cell jacket. The four kinds of azeotropic ethanol mixtures with cyclohexane, carbon tetrachloride, benzene, and chloroform were supplied into the cell in this order. Their

Table I Feed Composition of Ethanol Mixtures

Mixture Feed of Ethanol With	Ethanol Composition in			
	Azeotropic Mixture			Equimolar Mixture (Wt %)
	Mol %	Bp (°C)	Wt %	
(1) Chloroform	16.3	59.5	7.0	27.9
(2) Benzene	43.7	68.0	31.4	37.1
(3) Carbon Tetrachloride	38.6	66.0	15.8	23.1
(4) Cyclohexane	43.9	71.5	30.0	35.4

compositions are shown in Table I. The pressure of the permeate side was 3 mmHg (Torr). The flux J_1 was determined by the weight increase of the trap cooled in liquid nitrogen for a given time, and overall permeability was expressed in P [$\text{g cm}^{-1} \text{h}^{-1}] = J_1 x$ (membrane thickness Δx). The permeate composition was determined from the calibration curve obtained from the mixtures of known composition by gas chromatography (GC) with a Shimadzu GC-8APT equipped with a column of poly(ethylene glycol) 20M at 70°C and at an inlet temperature of 120°C. In the case of benzene-ethanol, a 200-MHz $^1\text{H-NMR}$ (Varian Gemini 200H) was used for composition determination because the GC peaks of benzene and ethanol were often too close to estimate correctly. The separation factor for ethanol α was obtained by the following equation:

$$\alpha = (Y_e/Y_s)/(X_e/X_s)$$

where X and Y are weight fractions of the feed and permeate, respectively, and the subscripts e and s denote ethanol and the partner solvent, respectively.

Sorption

A sample membrane was dried in a flask under reduced pressure at 40°C. The weight, diameter, and thickness of the dried membrane were measured and then the membrane was immersed in the azeotropic feed at room temperature ($25 \pm 3^\circ\text{C}$) for 48 h. The membrane was wiped with paper; the weight, diameter, and thickness of the swollen membrane were measured; and its swelling degree Q , defined as the weight percentage of the absorbed feed liquid against the dry membrane, was evaluated. The membrane was placed in a flask that was connected to a cold trap. Before

placing the trap in liquid nitrogen, the air of the system was pumped out for a couple of seconds to evacuate air moisture. The sorbed and penetrated components into the membrane were collected in the trap in a vacuum (3 mmHg) for 2 or 6 h. The trap was sealed with stopcocks and warmed to room temperature to avoid condensing the air moisture. The composition of the collected liquid was estimated by GC or $^1\text{H-NMR}$ and α^S for sorption was calculated according to the above equation. When a frozen feed was evacuated at 3 mmHg for 2 or 6–7 h as a control experiment, the ethanol content of the feed tended to increase by 3 to 33 %. Therefore, a correction was made by dividing the increase rate of ethanol obtained in the sorption experiment by the control rate, and corrected α^S values were used.

α^{EV} for evaporation was calculated from the vapor pressure of each component at the feed composition at 25°C according to Antoine's equation, assuming that Raoult's law is obeyed. α^D was obtained from the following equation:

$$\alpha = \alpha^S \alpha^{\text{EV}} \alpha^D$$

Measurements

Crosslinking Rate

Each crosslinking system was examined for the confirmation of the IPN formation. P4VP and PVA solutions of the same concentration as in the membrane fabrication were prepared in two flasks for each solution. One of them was heated at 80°C and the other was allowed to stand at room temperature until its fluidity was lost (gel formation). The time required for the gel formation was measured.

Table II Gelling Time for P4VP-DBB and PVA-HMDI

Crosslinking System	Temperature (°C)	Gelling Time (min)	Appearance of the Gel
P4VP-DBB	Room temperature	45	Clear, soft
	80	15	Same as above
PVA-HMDI	Room temperature	1	White, hard, and rather brittle
	80	0.5	Same as above

P4VP, 4.5 wt %, and PVA, 7.4 wt %, with 30 mol % crosslinking agent based on the polymer.

Tensile Strength

Two to four sample membranes ($0.3\text{--}1.2 \times 3$ cm) were measured with a Shinkoh TOM-5 tensiometer and the results were averaged.

RESULTS AND DISCUSSION

Rate of Crosslinking Reactions

It is favorable for IPN membrane formation that the two independent crosslinking reactions proceed at a comparable rate. Therefore, the time required for gelation or solidification in the reaction of P4VP with DBB and of PVA with HMDI was measured for the respective solutions of the same concentration as in membrane formation as shown in Table II. The concentration of P4VP was lowered because of high viscosity: Apparently, the urethane formation of PVA is completed faster than the quaternization of P4VP. Hence, HMDI

was added last in the membrane casting, and heating was continued for 5 h at 80°C, which seemed enough for complete crosslink formation. The resulting membranes were tough, flexible, and different from the appearance of the respective crosslinked polymers shown in Table II, indicating IPN formation. Although ethylene glycol diglycidyl ether (EGE) is likely to work as a crosslinking agent for PVA, other than a diisocyanate, no tough gel or solid was evident in DMSO and other aprotic solvents at an elevated temperature of 130°C for a prolonged period of 20 h even in the presence of an amine catalyst.

Dependence of Membrane Strength on the Composition

The tensile strength of the membranes was first studied because their strength and elongation seemed to depend largely on the membrane composition. The results are shown in Figures 1–3. Figure 1 shows the dependence on the polymer composition, indicating that an increasing con-

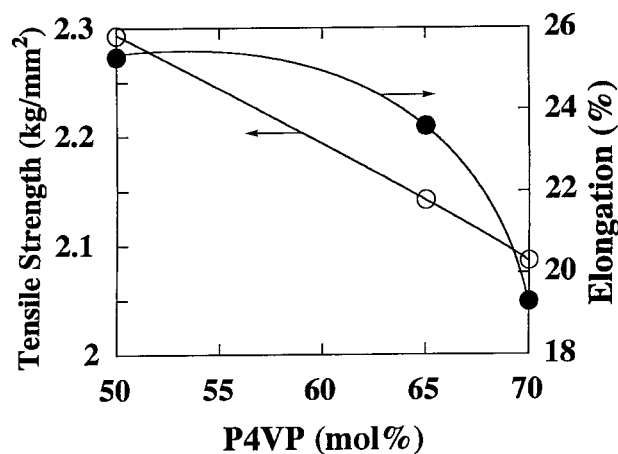


Figure 1 Tensile strength and elongation versus P4VP content for DBB30HM30 membranes containing 30 mol % DBB and HMDI based on P4VP and PVA, respectively.

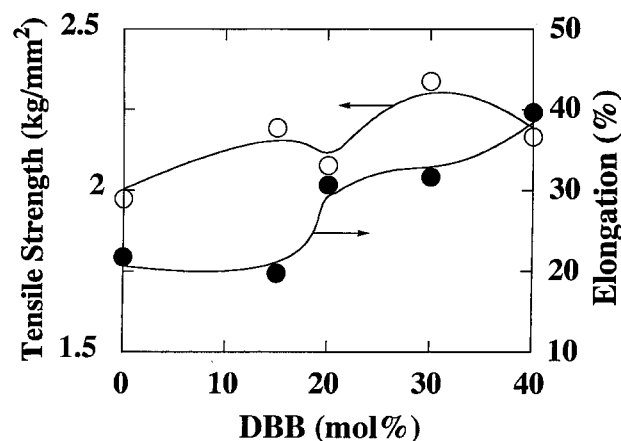


Figure 2 Tensile strength and elongation versus DBB for 4VPA50HM30 membranes. 4VPA denotes P4VP and PVA; 50, mol % of P4VP; and HM, HMDI.

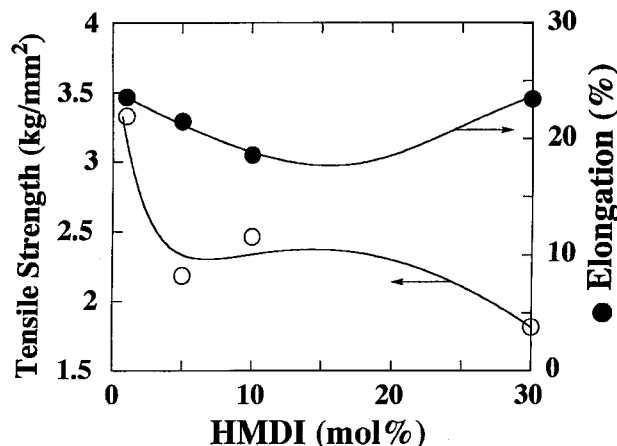


Figure 3 Tensile strength and elongation versus HMDI for 4VPA50-30 membranes. The number that follows the dash is mol percent of DBB based on P4VP.

tent of P4VP reduces the strength and elongation and that a 50 or 65 mol % P4VP content is a favorable composition. Those three membranes were stronger than was the cellulose acetate (CA) membrane since the CA membrane had a strength of 1.18 kg mm^{-1} . Figures 2 and 3 show the dependence on the DBB and HMDI composition, respectively. It is seen from Figure 2 that the strength increases with increasing DBB up to 30 mol % DBB, which shows a maximum strength. However, an increasing content of HMDI lowers the strength as seen in Figure 3. This is probably because crosslinking at an early stage restrains the segments from moving and intact isocyanate groups meanwhile react with a trace of water, increasing the fraction of incomplete crosslinking. Therefore, 1–10 mol % HMDI based on PVA is a preferable content at 30 mol % DBB. The maximum strength in Figure 3 is higher than that in

Figure 2. This fact indicates that the urethane linkage is responsible for the major portion of the strength, which is clearly demonstrated by Table III. In Table III are listed the results of strength and elongation for each crosslinked membrane after immersion in the feed. No homogeneous crosslinked membrane of PVA was obtained at a content of HMDI more than 0.5 mol % because of a striking contraction. The difference in the strength between the two membranes is distinct in Table III.

PV Performance of IPN Membranes

All the IPN membranes prepared were found to be ethanol permselective for the four kinds of feeds studied. Some conceivable factors that can control and govern the separation factor α and permeability P , such as intermolecular forces, are represented as differences in the solubility parameter $\Delta\delta$ or the hydrophobic constant Δf ,²⁷ viscosity η , and molecular size V of the feed component, and so on. However, all those factors can contribute simultaneously to α and P in the PV at a certain rate. Thus, the swelling degree Q can be regarded as a representative factor that includes most of the above factors, because α and P , and Q as well, are controlled principally by the affinity between the feed component and the membrane, although Q does not include the velocity factor of the feed molecules penetrating into the membranes. Figure 4 illustrates the dependence of α and P on Q for the membrane containing 65 mol % P4VP. A distinct dependence on Q was observed. An increase in Q reduces the selectivity and facilitates the passing of the feed through the membrane. The chloroform mixture feed gives exceptionally remarkable results, probably because of its strong affinity to P4VP. The membrane con-

Table III Tensile Strength and Elongation of Crosslinked P4VP and PVA Membranes

Mixture Feed of Ethanol with	P4VP100-30 ^a		PVA100-0.5 ^b	
	Tensile Strength (g mm^{-1})	Elongation (%)	Tensile Strength (g mm^{-1})	Elongation (%)
(1) Chloroform	51.6	49.1	3137	62.6
(2) Benzene	32.3	42.7	1553	64.7
(3) Carbon tetrachloride	470	57.1	2894	78.1
(4) Cyclohexane	251	22.4	2570	66.3

Tensile strength and elongation measured after immersion in azeotropic feed at room temperature for 24 h.

^a P4VP membrane crosslinked with 30 mol % DBB.

^b PVA membrane crosslinked with 0.5 mol % HMDI.

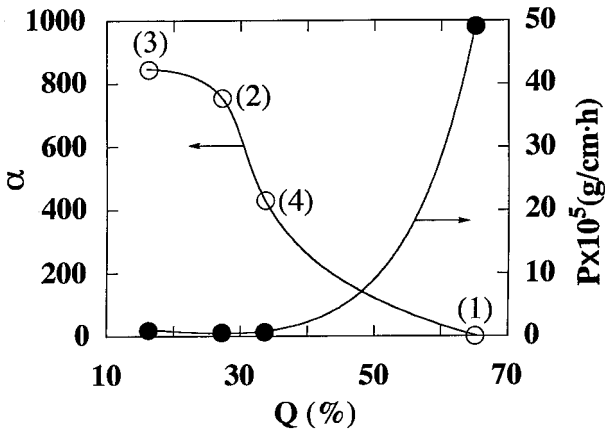


Figure 4 α and P versus Q for 4VPA65-30HM30 membrane ($\Delta x = 146 \mu\text{m}$). The numbers denote the azeotropic mixture feed of ethanol with (1) chloroform, (2) benzene, (3) carbon tetrachloride, and (4) cyclohexane.

taining 50 mol % P4VP showed a similar tendency as depicted in Figure 5, although the P of the chloroform mixture feed was unexpectedly low. It was found, from a comparison between Figures 4 and 5, that the membrane containing a higher P4VP (65 mol %) has a higher value of α and is favorable for separation with the same 10^{-6} order of P except for the chloroform mixture feed [$P = 0.62 \times 10^{-5}$ for (2), 0.98×10^{-5} for (3), and 0.69×10^{-5} for (4) in Fig. 4]. The membrane, exceeding 65 mol %, tended to be less durable, as shown in Figure 1.

When a membrane of the same composition as shown in Figure 5 was immersed in water just

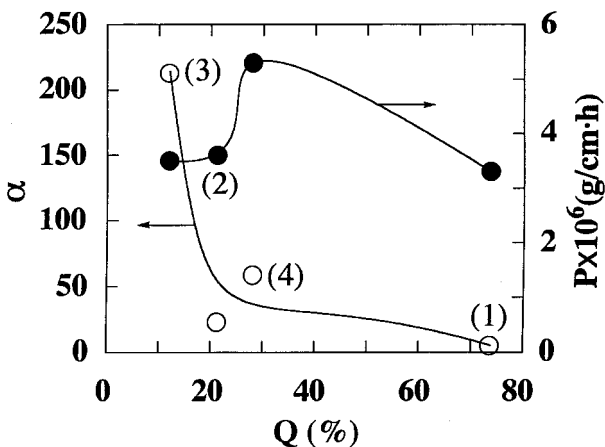


Figure 5 α and P versus Q for 4VPA50-30HM30 membrane ($\Delta x = 144 \mu\text{m}$). The number is the same as in Figure 4. The same numbers are used in Figures 6–11.

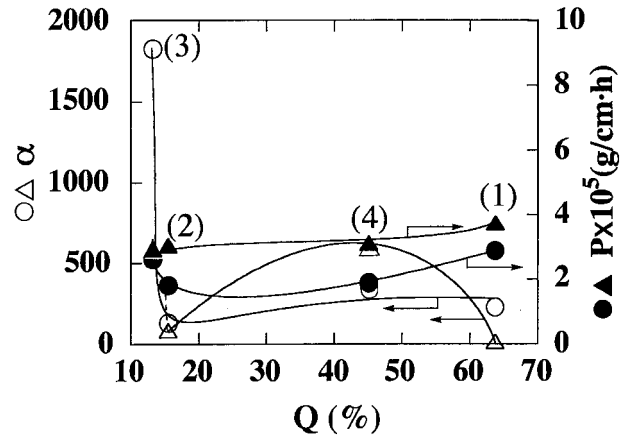


Figure 6 α and P versus Q for the 4VPA50-30HM5 membrane ($\Delta x = 146 \mu\text{m}$). (○,●) Azeotropic mixtures; (△,▲) equimolar mixtures.

after membrane preparation, the strength decreased to 1/80 and α decreased to 1/4 to 1/12 except for a twofold increase for the cyclohexane mixture feed, with a concurrent $25\text{--}10^3$ times increase in P . A similar tendency was observed for the membranes of other compositions. Water molecules bound to a membrane may act to absorb ethanol, which, in turn, accompanies more or the partner component, yielding a smaller value of α and a larger value of P . Water-immersed membranes generally had lower strength, and, eventually, their performance was inferior to those of the membranes that were not in contact with water.

The influence of the difference in the feed composition was examined between the azeotropic and equimolar feed compositions listed in Table I. The results are illustrated in Figure 6, where comparable values are obtained for the respective feeds except for the equimolar feed mixture of carbon tetrachloride (no peak was detected in GC). No other factors, $\Delta\delta$, Δf , η , and V alone, mentioned above, showed any significant relationship with α and P .

Permeation Characteristics

Dependence of α on Q

The PV process comprises three successive major steps: preferential sorption of a penetrant into the membrane on the feed side, phase transition of the penetrant from liquid to vapor, and diffusion of liquid and vapor through the membrane. Thus, the overall separation factor α should consist of α^S , α^{EV} , and α^D , that is, $\alpha = \alpha^S \times \alpha^{\text{EV}} \times \alpha^D$, where

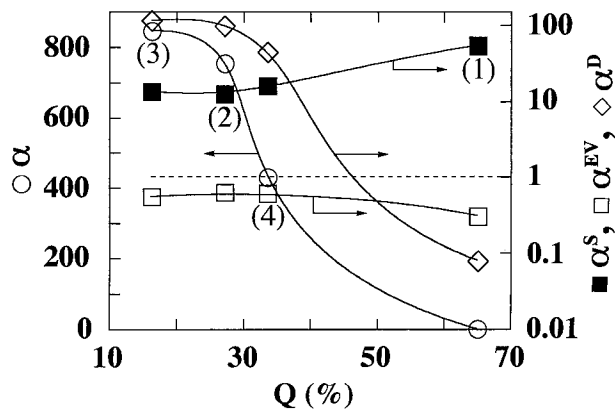


Figure 7 Separation factors versus Q for 4VPA65-30HM30 membrane.

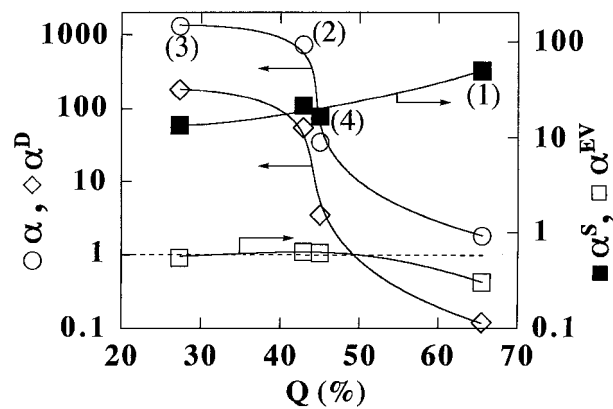


Figure 9 Separation factors versus Q for 4VPA50-30HM20 membrane.

α^S is the separation factor for the solubility of ethanol in the membrane on the feed side; α^{EV} , for evaporation of ethanol at a certain interface in the membrane; and α^D , for overall diffusion of ethanol prior to and after the evaporation.²⁸ Some of those values are shown against Q in Figures 7–11. α^{EV} shows similar values, always less than or close to unity because ethanol is less volatile at the azeotropic composition. All the α^S values are higher than unity and show a tendency to increase with increase in Q , representing that membranes permselectively absorb ethanol and a higher degree of swelling is favorable for increasing the sorption selectivity of ethanol. Most of the α^D , except for the chloroform mixture feed, are much higher than unity and compose the major portion of α , which is indicative of ethanol selectivity in the diffusion process and, as seen in Figures 7–11, α^D shows a tendency very similar to

that of α . These facts indicate that diffusion through the membrane controls the overall permeation.

In the case of the chloroform mixture feed, all α^S values obtained were somewhat higher than unity in spite of a high degree of swelling, due to a strong affinity of chloroform for P4VP. α^D values, to the contrary, were often lower than unity, indicating that chloroform tends to move through the swollen membrane faster than does ethanol. Therefore, it should be noted that the ethanol selectivity for the chloroform mixture feed is determined by sorption, but the low value of α^D crucially reduces the overall separation factor α , the product of those α fractions, and as a result, α for the chloroform mixture feed is controlled by α^D . As ethanol is the common component of the feed and is more soluble in the membrane, the difference in the diffusion rate of the partner com-

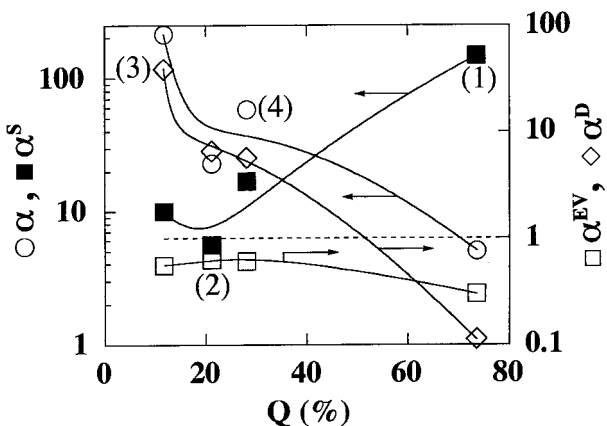


Figure 8 Separation factors versus Q for 4VPA50-30HM30 membrane.

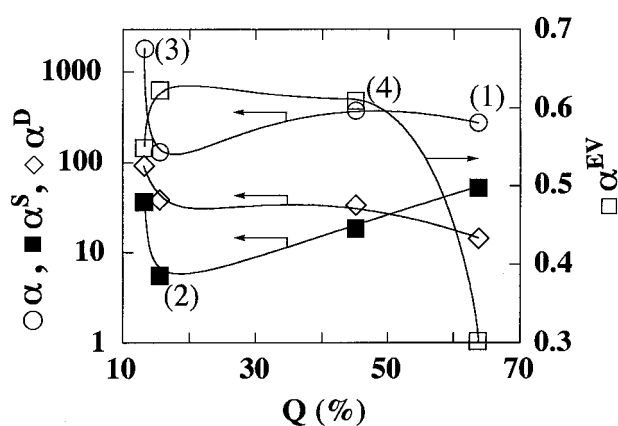


Figure 10 Separation factors versus Q for 4VPA50-30HM5 membrane.

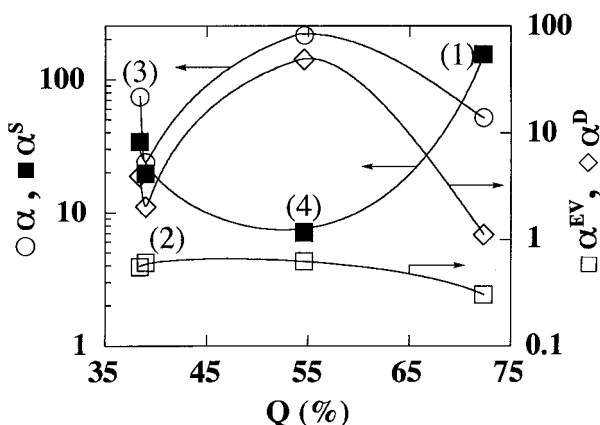


Figure 11 Separation factors versus Q for 4VPA50-10HM1 membrane.

ponent may have decided the separation behavior. A parallel relationship between α^D and α was commonly observed in the membranes of other compositions.

In the swelling power of the feed, carbon tetrachloride showed the least and chloroform the highest degree. A large quantity of sorbed chloroform and its smaller molecular size may work favorably for faster movement in the membrane. For benzene and cyclohexane, on the other hand, the latter usually had a higher degree, and, occasionally, their degrees were close to each other (Fig. 9). The increase in temperature to 30°C from 10°C gave no striking increase in Q at 48 h immersion, except for chloroform feed, which gave about a three times increase in Q .

Dependence of α on the Content of Crosslinking Agents

As seen in Figures 7–11, α values greatly depend on membranes containing different contents of crosslinking agents as well as on Q . Accordingly, the dependence of α and P values on the content of the crosslinking agent HMDI and DBB for each feed is illustrated as shown in Figures 12–14 for the three membranes of 4VP50 containing 30 mol % DBB (Fig. 12), 5 mol % HMDI (Fig. 13), and 1 mol % HMDI (Fig. 14). Those membranes had a higher strength and therefore we developed a greater number of experimental data. Commonly observed in all these figures through (a)–(d) is again a very similar dependency pattern between α (○) and α^D (◇). In Figure 12, an increase in HMDI content tended to decrease the permeability. This implies that an increasing crosslinking density disturbs the passing of penetrants and

that more residual hydroxyl groups of PVA at a smaller content of HMDI are favorable for the permeation of ethanol. In Figures 13 and 14, to the contrary, no distinct tendency of the P 's is observed, some of them increasing, invariant, and showing a maximum or minimum with increase in DBB or in crosslinking density. This may, in part, be caused by the preferential permeation of ethanol of a polar character with an increasing content of electrically charged pyridine moieties. However, a partial relation can be seen between P and α^S , for example, Figures 12(c), 13(c,d), and 14(b,d), showing that the preferential sorption of ethanol contributes to permeability.

The lack of some data for chloroform in Figures 13 and 14 and for benzene in Figure 14 is due to the break of the membrane in the course of PV operation because of the reduction of the strength

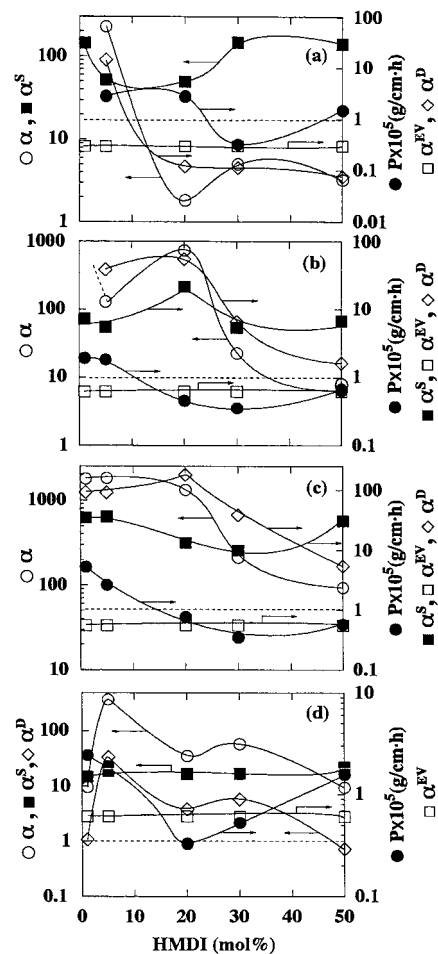


Figure 12 Separation factors and P versus HMDI content for 4VPA50-30 membranes and ethanol mixture feeds with (a) chloroform, (b) benzene, (c) carbon tetrachloride, and (d) cyclohexane.

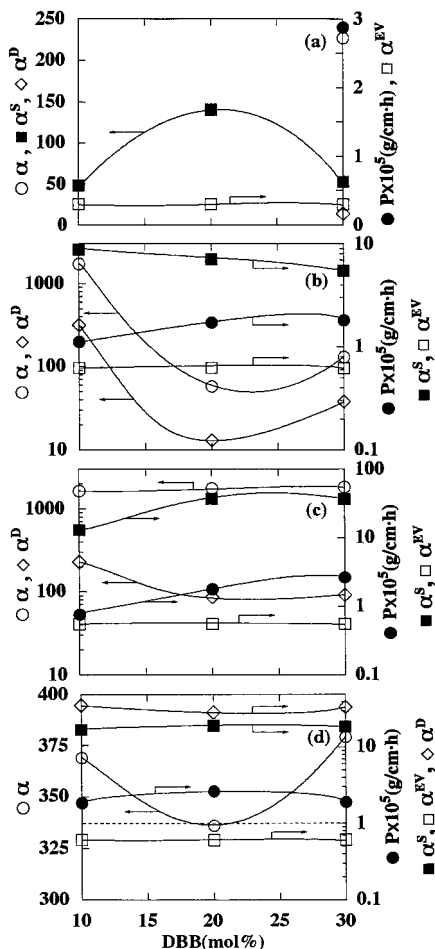


Figure 13 Separation factors and P versus DBB content for 4VPA50HM5 membranes and ethanol mixture feeds with (a) chloroform, (b) benzene, (c) carbon tetrachloride, and (d) cyclohexane.

caused by greater swelling. As for the maximal α values, each membrane has an optimum content of a crosslinking agent for the respective feeds. In Figure 12, the optimum content is 20 mol % HMDI for benzene and carbon tetrachloride and 5 mol % for chloroform and cyclohexane feeds. The optimum content, common to the four feeds, is summarized to be 5 mol %. Likewise, Figure 13 for the DBB content shows that the common optimum should be 30 mol %, but 10 mol % if chloroform is excluded, and in Figure 14, it should be 10 mol % for chloroform and 20–30 mol % for the other feeds.

CONCLUSIONS

The following conclusions can be drawn from the discussion described above:

1. Tough IPN membranes were obtained by quaternizing the crosslinking of P4VP with DBB and simultaneous crosslinking of PVA with HMDI at an elevated temperature of 80°C. The contact with water deteriorated the membrane performance.
2. The membrane composition that gave a maximum strength was 50 mol % P4VP, 30 mol % DBB based on the P4VP, and 1–10 mol % HMDI based on PVA. The strength decreased with increase in P4VP.
3. The membranes were strongly hydrophilic and displayed ethanol permselectivity in PV for azeotropic mixtures of ethanol with chloroform, benzene, cyclohexane, and carbon tetrachloride. A common tendency of the order of the separation factor was carbon tetrachloride > cyclohexane \cong benzene > chloroform.

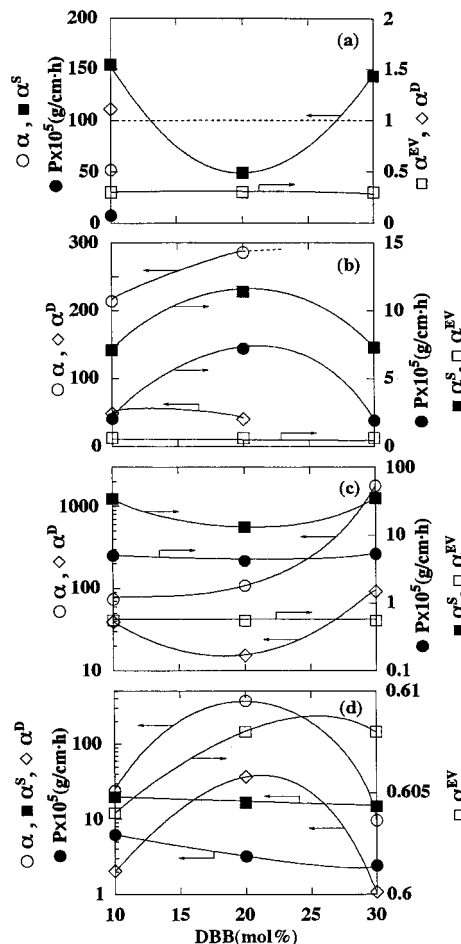


Figure 14 Separation factors and P versus DBB content for 4VPA50HM1 membranes and ethanol mixture feeds with (a) chloroform, (b) benzene, (c) carbon tetrachloride, and (d) cyclohexane.

4. The separation performances of those four feeds showed a relationship with the swelling degree of the membrane toward the feed, which may represent the actual forces between the membrane and the feed, but not with any single calculated factor of intermolecular forces, viscosity of feeds, or molecular size. Generally, a smaller swelling degree corresponded to a higher separation factor and smaller permeability.
5. The compositions which gave an optimum separation performance contained 65 mol % P4VP, with a smaller content of 5–20 mol % HMDI and 10–30 mol % DBB depending on the feed.
6. Both α^S for sorption and α^D for diffusion far exceeded unity in most cases except for α^D of the chloroform feed, indicating that both processes are ethanol selective, but the overall separation factor α for all the feeds was controlled principally by α^D .

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