

Separation of Water–Ethanol by Pervaporation Through Polyion Complex Composite Membrane*

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SYNOPSIS

For the purpose of separating alcohol–water mixtures by the use of the pervaporation technique, new composite membranes composed of polyion complexes (PIC) as a separating layer were developed. The polyion complex structure, consisting of polyacrylic acid (PAA) and polycation, provided excellent permeation rate and selectivity. Among the polycations, ionenes, which have quaternary ammonium groups in the backbone chain, were effective in giving membranes of higher permselectivities. High selectivity of PIC membranes was observed at high ethanol concentration regions in the feed mixture. For the azeotropic mixture of water/ethanol (95 wt % EtOH) at 60°C, the PAA-based PIC membrane had the following separation properties: separation factor $\sim 3,500$ and permeation rate ~ 1.6 kg/m² h.

INTRODUCTION

In recent years, membrane separation of organic liquid mixtures by the use of the pervaporation technique has been studied by many investigators. Especially, a lot of research regarding water/lower-alcohol separations has been carried out because of the practical interest in industries.¹ However, membranes which have both high selectivity and permeation rate are not commonly available.^{2,3} The object of this research is to develop a water permselective membrane having high selectivity and permeation rates.

Material Selection

The diverse membrane materials have been examined to identify high efficiency water/ethanol separation membranes. Classification of published dehydration membranes is rather difficult because of

their complexity. According to Yamada,⁴ dehydration membranes can be classified as follows:

1. Hydrophilic commercial and synthesized membranes
2. Introduction of hydrophilic group into hydrophobic membranes
3. Hydrophilic–hydrophobic block membranes

Especially, membranes having various kinds of nonionic, cationic, and anionic hydrophilic groups exhibit high water selectivity.^{5–14}

Introduction of ionized groups into the membranes enhances their water selectivity.^{14–16} This phenomenon can be accounted for by the fact that ionized groups hydrate strongly and exclude organic solvents (salting out effect¹⁴).

In this study, we focused on polyacrylic acid (PAA) as a membrane material. PAA is considered to be suitable for water selective membrane material from several points (Table I).

As shown in Table I, PAA has a high charge density based on the dissociated carboxyl group. However, when the feed solution to be separated has a low concentration of ethanol, PAA is dissolved or significantly swollen, resulting in a remarkable decline of selectivity.

Resistance to a wide range of feed composition can be achieved by converting PAA into a three-

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Table I Polyacrylic Acid as a Membrane Material

1. Polyelectrolyte—high charge density
$\left(\text{CH}_2 - \underset{\text{COOH}}{\text{CH}} \right)_n \xrightarrow{\text{Salt form}} \left(\text{CH}_2 - \underset{\text{COO}^\ominus \text{M}^\oplus}{\text{CH}} \right)_n$
2. Crosslinkable through carboxyl group
3. High molecular weight

dimensional structure by crosslinking. The carboxyl group of PAA can be used as a crosslinking site. Several kinds of crosslinking agents have been examined for this purpose.¹⁷⁻¹⁹

Finally, the high molecular weight polymer, which is effective for making thin and tough membranes, can be easily synthesized by usual radical polymerization.

Long-Term Durability

As reported earlier,¹⁷ the PAA composite membrane showed excellent separation properties, when PAA was converted into a salt form. However, it was also found that the high separation properties decrease with time. This lack of long-term stability was also observed for the PAA grafted PAN membranes.²⁰

Through quantitative analysis of the alkali ion in the membrane and IR spectrum of the membrane surface using the ATR technique, it was found that the decrease of separation properties was caused by the elution of alkali metal ion out of the membrane which led to the regeneration of a free acid form ($-\text{COOH}$).¹⁷ Thus the suppression of alkali ions out of the membrane is one of the main objects of this study.

In order to solve this problem, the following methods have been employed:

1. Keeping the feed solution at high pH²¹
2. Ionic crosslinking by polyvalent counter cation²²

The first method is not very practical, because alkali compounds are added into the feed solution. As for the second method, ionic crosslinking with a polyvalent metal ion, such as Al^{3+} , has been reported by Huang et al.²² Although the ionic crosslinking in general makes a membrane more brittle, they obtained an ionically crosslinked PAA membrane by controlling the amount of Al^{3+} ion. In order to improve mechanical properties of membranes, blending with a relatively hydrophobic polymer such as nylon 6 has been also reported.²³ But the blending is not desirable from the point of permselectivity. Furthermore, multivalent metal cations mostly yield relatively low permeation rates and low selectivity.²⁰

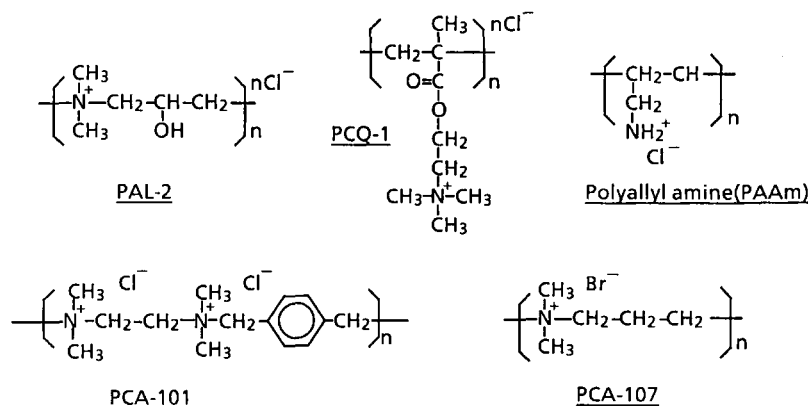
We found that PAA membranes converted into polyion complexes (PIC) by treating them in aqueous solutions of polycations provided excellent permselectivities without making them brittle.

In this study, we will discuss the separation potential of the PAA-based polyioncomplex composite membrane, and the effects of ionization and polyion complexation in some detail.

EXPERIMENTAL

Materials

PAA of molecular weight 500,000 (M_v) was obtained by the usual radical polymerization using ammonium peroxodisulfate as the initiator. PAA of molecular weight 4,000,000 (M_n) was purchased from Scientific Polymer Products Inc. Polyallylamine was supplied by Nitto Boseki Co., Ltd. PAL-2 and PCQ-1 shown in Figure 1 were supplied by Nippon Senka

**Figure 1** Chemical structures of polycations.

Chemical Industries, Ltd. Polycation PCA-101, shown in Figure 1, were synthesized through the following Menshutkin reactions.²⁴

First, 0.03 mol 1,4-bis(iodomethyl)benzen (1,3-dibromopropan) was dissolved in 80 cm³ dimethylformamide at room temperature. *N,N,N',N'*-tetramethyl-1,3-propylenediamine (0.03 mol) was added into the solution while stirring. The reaction was continued at room temperature for 4 h while stirring, and left overnight. The reaction product was filtered off, washed with ethyl acetate, and dried in a vacuum dryer at 40°C. PCA-107, shown in Figure 1, was also synthesized in similar way to above.

Polyethersulfone ultrafiltration membrane (DUS-40) as a support was supplied by Daicel Chemical Industries, Ltd. Ethylene glycol-diglycidylether (Ex-810) as a crosslinking agent was obtained from Nagase Industries, Ltd. All other materials were of reagent grade.

Membrane Preparation

PAA aqueous solutions were cast onto the supporting UF membranes with a wire-bar applicator (0.15 mm wire diameter). Coated membranes were dried under the clean air at 20°C for 30 min. In the case of crosslinked PAA membranes, the crosslinking agents such as ethylene glycol-diglycidylether were added to the PAA solution prior to casting, and crosslinking was allowed to proceed at 100°C for 10 min in a clean oven. The above procedure was repeated two or three times in order to make a pinhole-free membrane. In order to convert the PAA separating layer to the polyion complexes, these membranes were dipped in a 2.0 wt % aqueous solution of polycations at room temperature for 12 h.

Pervaporation

The pervaporation apparatus used for evaluating the separation properties consists of four cells in parallel (membrane area, 8.5 cm²), feed mixture tank, vacuum pump, and two gaschromatographs (one for feed and the other for permeate) having the sampling devices. The schematic diagram of this appa-

ratus is shown in Figure 2. In this apparatus, permeates are sent into the gaschromatograph without condensation, and the computer controls the sampling device and carries out data processing. By the use of this apparatus, evaluation results can be obtained every 20 min. Standard evaluation conditions were: feed concentration, 95 wt % EtOH; feed temperature, 60 or 70°C.

The separation factor α was calculated as below:

$$\alpha = (Y_{\text{H}_2\text{O}}/Y_{\text{EtOH}})/(X_{\text{H}_2\text{O}}/X_{\text{EtOH}})$$

where $Y_{\text{H}_2\text{O}}/Y_{\text{EtOH}}$ is the weight ratio of water to ethanol in the permeate and $X_{\text{H}_2\text{O}}/X_{\text{EtOH}}$ is the weight ratio of water to ethanol in the feed mixture.

RESULTS AND DISCUSSION

PAA Polyion Complex Membranes

As mentioned before, the counteractions of PAA elute into feed solution, and consequently both permeation rate and separation factor decrease with measuring time. The typical features of PAA-potassium salt composite membranes crosslinked with diamine and diepoxide are shown in Figure 3.

Instead of alkali metal cations, several kinds of polycations were used for ionization. Polyion complex (PIC) can be easily formed by simply immersing the PAA composite membrane into the appropriate concentration and pH of polycation solution. The PIC formation was confirmed by ATR-FTIR technique.

Figure 4 is the scanning electron micrographs of cross sections of PAA composite and PIC (PAA/PCA-101) composite membranes, respectively. It can be seen that a very thin (ca. 0.1 μm) skin layer of PAA has been formed on the surface of the supporting membrane and that the thickness of this PAA layer appreciably increases with the complexation.

This kind of PIC formation has already found wide applications in other membrane technologies

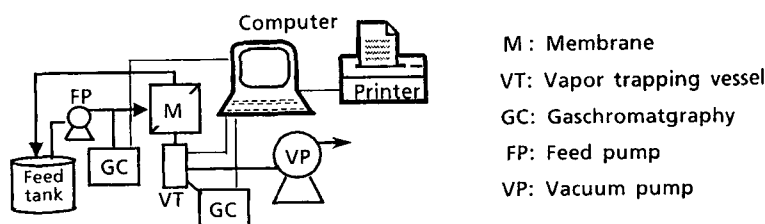


Figure 2 Pervaporation apparatus.

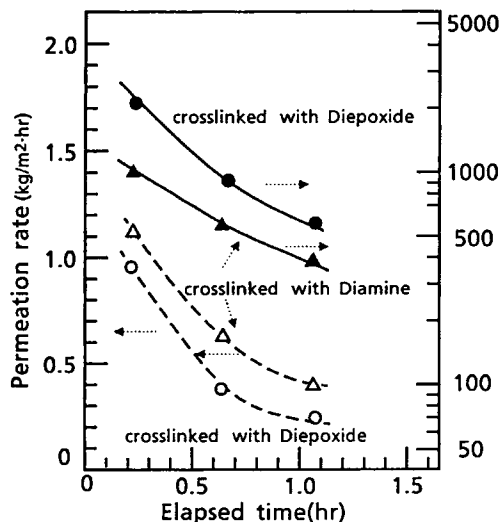


Figure 3 Separation properties of PAA-potassium salt membrane as a function of time (PAA: MW 500,000, crosslinked with ethyleneglycol-diglycidylether or 1,3-diamino, 2-hydroxypropane; evaluation: PV with 95 wt % EtOH of 70°C).

such as ultrafiltration.^{25,26} However, in this study, PIC aims at stabilizing the PAA dissociation due to the high order of interaction between oppositely charged polymers.

Figure 5 shows the separation properties of the PIC membranes in which counter polycations are polyethyleneimine and PCA-107, respectively. No prominent decline in both permeation rate and separation factor was observed. From a comparison of Figure 3 with Figure 5, it is apparent that PIC formation is quite effective to keep the separation properties of PAA membrane.

In the case of polyethyleneimine, further durability examination was carried out. As can be seen in Figure 6, the separation factor increases with time and becomes 800 during about 2 weeks measurement. Furthermore, no sign of decline in permeation rate ($\sim 0.45 \text{ kg/m}^2 \text{ h}$) was observed. These results can be explained by that PIC is no more soluble in common solvent and the ionization of PAA was stabilized by the scrambled salt structure.²⁶

Counterpolycation

Next, various weak and strong polycations were examined to elucidate the effect of polycation on the separation properties. Table II shows the separation properties of several PAA-based PICs consisting of different polycations. In this table, it should be noted that poly(ethylene glycol) forms complexes through hydrogen bonding.²⁷ Since this kind of complex membrane was reported recently,²⁸ we examined it

together. Among them, strong polycations, so called "ionenes," gave membranes of much higher separation properties compared to the weak polycations.

It has been known that PIC formation is influenced by the degree of polymerization, the ionic strength of the medium, and pH, etc.²⁹ Furthermore, Osada et al. have pointed out that chain length in addition to the coulombic forces, i.e., the number of charged sites, and the effect of hydrophobic bonds influence complexation.³⁰

Thus the overall effect affecting the dissociation of PAA and the PIC structure might be the reason why these ionenes give good separation properties.

From consideration of the solution-diffusion aspect, the separation factor can be separated into two factors qualitatively. That is, solubility and mobility terms,³¹

$$\alpha_s = \text{solubility selectivity} \\ = (C_{\text{H}_2\text{O}}^m / C_{\text{EtOH}}^m) / (C_{\text{H}_2\text{O}}^f / C_{\text{EtOH}}^f)$$

$$\alpha_m = \text{mobility selectivity} \\ = D_{\text{H}_2\text{O}} / D_{\text{EtOH}}$$

$$\alpha = \alpha_s * \alpha_m$$

where $D_{\text{H}_2\text{O}}$ and D_{EtOH} are the averaged diffusion coefficients of water and ethanol, respectively. In this system, the solubility selectivity can be considered to be more important.

Kurokawa et al.³² measured the sorption isotherms of water and some organic solvents for various PICs. Depending on the combination of polycation and polyanion, the sorption properties are quite different.

They reported that PIC consisting of poly(styrene sulfonate) ($\text{PSS}^- \text{Na}^+$) and an ionene shows the lesser adsorptivity for organic solvents such as methanol. Thus it may be considered that the present systems (PAA/ionenes) also have similar characteristics (solubility selectivity dominant) and reject ethanol more completely out of the membrane.

PAA Molecular Weight

When PAA ($M_v = 500,000$) were converted to PIC, crosslinking was necessary to keep the membrane strength. Actually, uncrosslinked membranes have not matched its performance at all.

However, by use of higher molecular weight PAA ($M_n = 4,000,000$), the crosslinking was not necessary, and furthermore, a rather thinner separation layer (ca. 0.1–0.15 μm) was easily obtained, which was attributed mainly to the high viscosity of the

PAA Composite Membrane

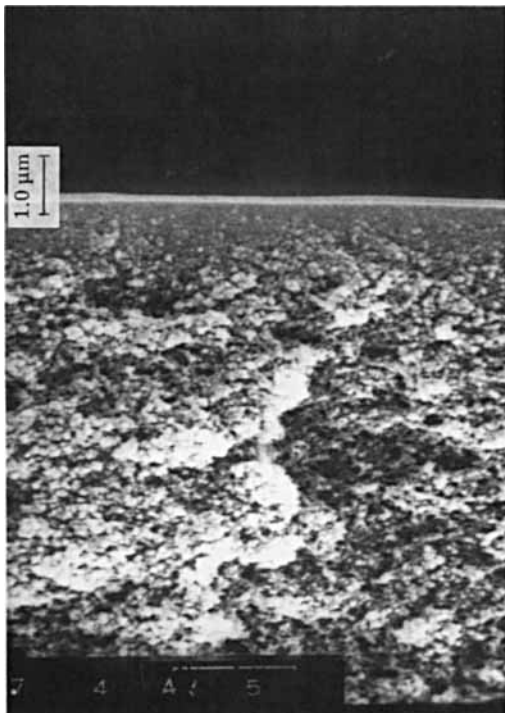
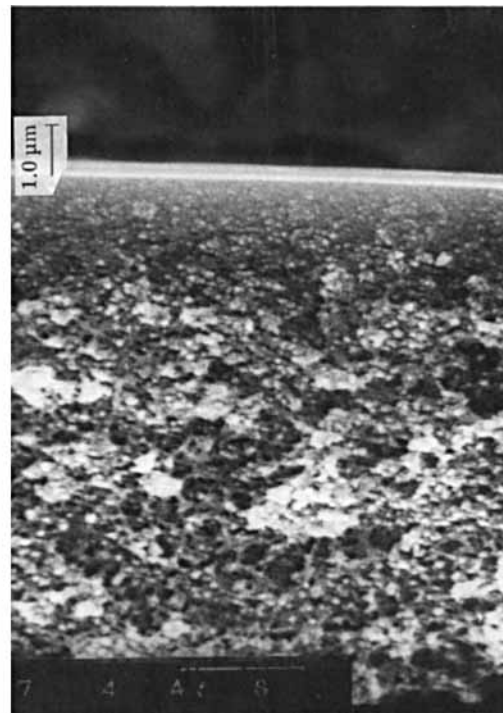
PIC(PAA/PCA-101)
Composite Membrane

Figure 4 Cross section of PAA composite membranes.

casting solution. Thus membranes prepared from higher molecular weight PAA yielded higher permeation rates.

From the above results, high molecular weight ($M_n = 4,000,000$) PAA was used in further discussion.

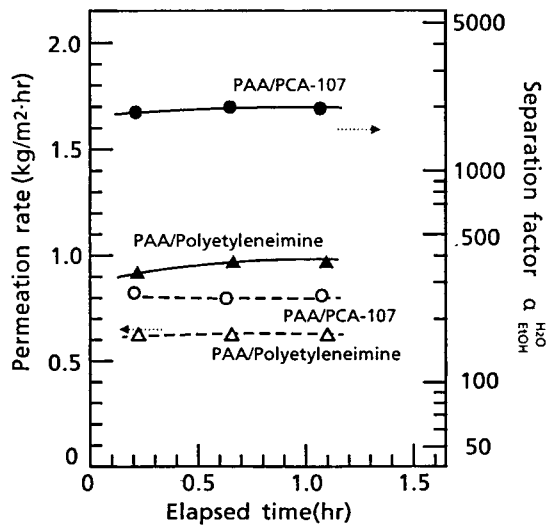


Figure 5 Separation properties of PIC membrane as a function of time (PAA: MW 500,000, crosslinked with ethyleneglycol-diglycidylether; evaluation: PV with 95 wt % EtOH of 70°C).

Separating Layer Thickness

The effect of the separating layer thickness on separation properties was shown in Figure 7. With a decrease of the separating layer thickness, the permeation rate increased and the separation factor decreased slightly. However, the permeation rate did not correlate with the reciprocal of membrane thickness above the value of approximately $2 \mu\text{m}^{-1}$. This result may be explained by the asymmetric structure of membranes during pervaporation. The upstream side of the membrane contacting with the feed mixture is swollen by feed mixture, and consequently has less permeation resistance, while the downstream side under a vacuum condition is dry, and has rather high resistance. Thus, it is supposed that, even if whole thickness is changed, the thickness of dry and high resistance layer may be little changed,^{33,34} and consequently the permeation rate does not change so much.

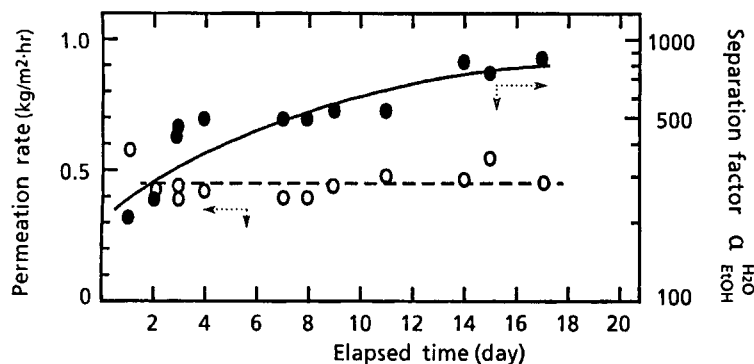


Figure 6 Separation properties of PAA/polyethyleneimine membrane as a function of time (PAA: MW 500,000, crosslinked with diepoxide; evaluation: PV with 95 wt % EtOH of 70°C).

Polycation/PAA Ratio

In the case of PIC consisting of a weak polyanion, it has been known that pH in the mixing solution affects the composition.³⁵ Tsuchida et al.³⁶ reported that, depending on degree of neutralization, the composition of the complex ($[\text{polycation}]/[\text{polyanion}]$) varies from 0.24 to 0.99.

In order to elucidate the effect of the PIC composition on the separation properties, we prepared several membranes of which PIC composition (unit molar ratio, $[\text{PCA-107}]/[\text{PAA}]$) was varied by changing pH of the polycation (PCA-107) solution. The composition of each sample was determined by element analysis. This result is shown in Figure 8.

The molar ratio $[\text{PCA}]/[\text{PAA}]$ increases with increasing pH and approaches unity at high pH regions. The dotted line in Figure 8 represents the data for the poly(methacrylic acid)-ionene system reported by Osada et al.³⁷ As can be seen, these features are quite similar.

The effects of PCA-107/PAA composition on the separation factor and permeation rates were shown in Figures 9 and 10, respectively. Separation properties, especially permeation rate, increase with increasing the amount of associated PCA-107. To clarify this result, the permeation rate, Q_{total} , is divided into two parts, i.e., Q_{H_2O} and Q_{EtOH} , in Figure 9. High water selectivity of the PIC membranes has been attributed not only to the increase of Q_{H_2O} , but also to the appreciable decrease of Q_{EtOH} .

It seems that the quantitative complexation (1 : 1 ratio) maximizing the dissociation of PAA plays a dominant role in increasing hydrophilicity and excluding ethanol out of the membrane (salting out effect).

Effect of Feed Composition

The effects of feed composition on the separation factor and permeation rate are shown in Figure 11.

Table II Separation of PAA Polyion Complex Membranes^a

Counter Cation	Permeation Rate Q (kg/m ² h)	Water in Permeate (wt %)	Separation Factor $\alpha(H_2O/EtOH)$
Polyethyleneimine	0.83	92.05	220
Polyallylamine	0.51	97.53	750
PCA-101	0.79	98.90	1710
PCA-107	0.82	99.03	1940
PAL-2	0.34	97.76	830
PCQ-1	0.22	95.24	380
Poly(ethylene glycol) ^b	0.23	89.95	170

^a PAA: MW 500,000, crosslinked with epoxide. Evaluation: PV with 95 wt % EtOH of 70°C.

^b Polycomplex through hydrogen bonding.

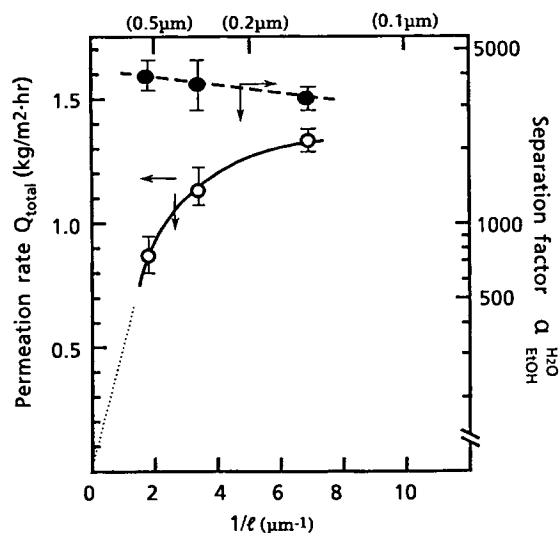


Figure 7 Effect of separating layer thickness (PAA: MW 4,000,000, uncrosslinked, PIC with PCA-107; evaluation: PV with 95 wt % EtOH of 70°C).

In Figure 12, the ethanol concentration in permeates was plotted against that in feed mixtures. The permeation rate increases monotonously with water content in the feed mixture, and selectivity decreases. Around 40 wt % EtOH, the separation factor became unity. This may be explained by the membrane swelling so much to enhance the diffusivity of ethanol at high water content region. This tendency is similar to that reported for the composite GFT membrane.³³

Effect of Evaluation Temperature

The effect of evaluation temperature on the separation properties for 95 wt % EtOH is shown in Ta-

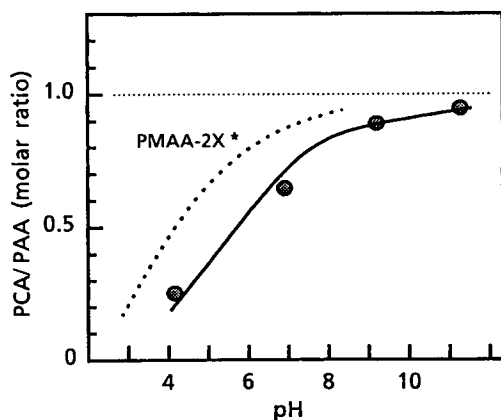


Figure 8 The proportion of PCA-107 to PAA in the PIC treated with different pH (PAA: MW 4,000,000; *: PMAA-2X PIC³⁷).

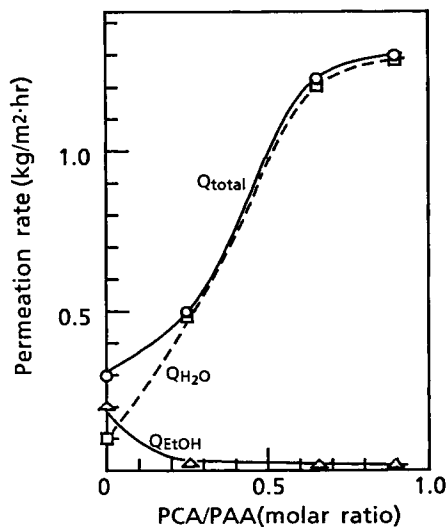


Figure 9 Effect of PCA/PAA ratio on permeation rate (PAA: MW 4,000,000, uncrosslinked, PIC with PCA-107; evaluation: PV with 95 wt % EtOH of 70°C).

ble III and Figure 13. With increase of temperature, the permeation rate and separation factor changed little. As shown in Figure 14, the apparent activation energy ΔE_{app} is 6.2 kcal/mol for water and 9.2 kcal/mol for the ethanol component. This value for water is in rough accordance with those obtained by Nafion membranes.³⁸ However, as pointed out by Reineke et al.,¹⁴ the increase in the permeation rate is partly due to the increased vapor pressures resulting in larger driving for permeation.

To eliminate this effect, the permeability coefficients for each component were evaluated by calculating the vapor pressures at the azeotropic

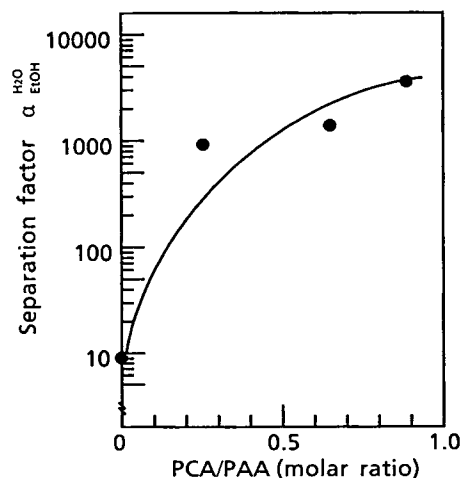


Figure 10 Effect of PCA/PAA ratio on separation factor (PAA: MW 4,000,000, uncrosslinked, PIC with PCA-107; evaluation: PV with 95 wt % EtOH of 70°C).

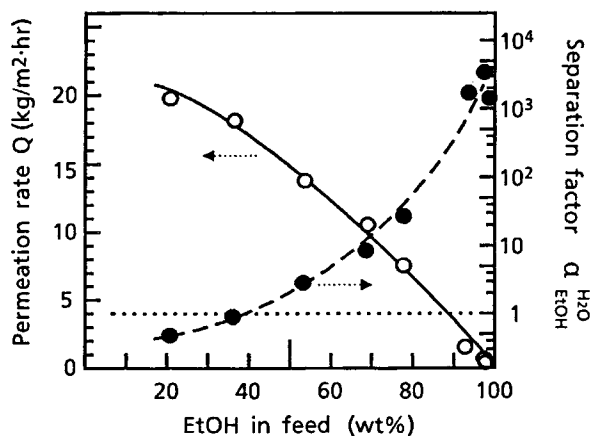


Figure 11 Effect of feed composition on separation properties (PAA: MW 4,000,000, uncrosslinked, PIC with PCA-107; evaluation: PV of 70°C).

point.³⁹ These results are shown in Figure 15 and Table III. In contrast with the permeation rate, the activation energies for permeability coefficients have negative values. This might come from the fact that the absolute value of the sorption enthalpy is larger than the activation energy for diffusion.

Effect of Downstream Pressure

Figure 16 shows the effect of downstream pressure on separation properties for 95 wt % EtOH. Both permeation rate and separation factor decreased with the increase of downstream pressure. However, as shown in Figure 16, this mainly comes from the decrease of the permeation rate of water. This result

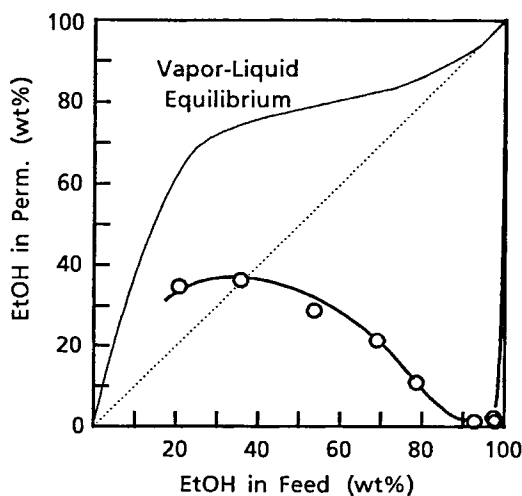


Figure 12 Effect of feed composition on permeates composition (PAA: MW 4,000,000, uncrosslinked, PIC with PCA-107; evaluation: PV of 70°C).

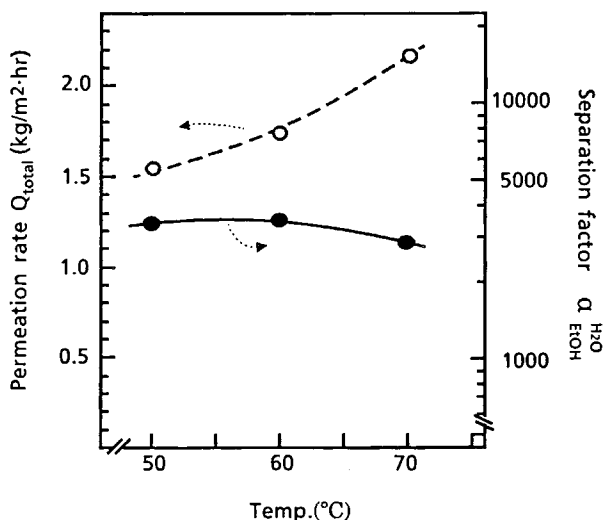


Figure 13 Effect of evaluation temperature on separation properties (PAA: MW 4,000,000, uncrosslinked, PIC with PCA-107; evaluation: PV with 95 wt % EtOH).

can be explained by the permeation rate's correlation with partial pressure differences across the membrane. The partial pressure of water (39 mm Hg in 95 wt % at 60°C) is close to the downstream pressure compared to that of ethanol (321 mm Hg) in the feed mixture so that the partial pressure difference of water across the membrane, which results in the driving force of permeation, is more affected by the variation of downstream pressure than that of ethanol.

In this system, the permeation rate of ethanol (Q_{EtOH}) increases slightly with an increase of downstream pressure. Similar results have been reported for H₂O/THF separation with cuprophan membranes and for H₂O/*i*-PrOH with cellulose membranes.³⁴ It has been supposed that, as the downstream pressure increases, the downstream side of the separating layer swells, so that the ethanol diffusivity is enhanced.

Separation Potential of PIC Membranes

Generally, the membrane property is characterized by permeation rate, Q (kg/m² h), and separation factor α . However, in order to evaluate the productivity of the membrane, other parameters such as $Q(\beta - 1)$ or $\alpha \cdot Q$ have been proposed.⁴⁰⁻⁴²

β is a new parameter defined by

$$\beta = C_{\text{H}_2\text{O}}^p / C_{\text{H}_2\text{O}}^f$$

When one judges whether pervaporation is economical or not compared with existing distillation, great concern exists about the needed separation

Table III Effect of Temperature on Separation Properties for the PIC Membrane^a

Temp (°C)	Separation Factor α (H ₂ O/EtOH)	Q_{total} (kg/m ² h)	$Q_{\text{H}_2\text{O}}$ (kg/m ² h)	Q_{EtOH} (kg/m ² h)	$P_{\text{H}_2\text{O}} \times 10^{10}$ (g cm/cm ² s cm Hg)	$P_{\text{EtOH}} \times 10^{13}$ (g cm/cm ² s cm Hg)
50	3320	1.23	1.22	0.0061	2.17	1.28
60	3510	1.63	1.62	0.0083	1.73	1.08
70	2890	2.17	2.15	0.0141	1.54	1.21

^a PAA: MW 4,000,000, uncrosslinked, PIC with PCA-107, skinlayer ca. 0.15 μm . Evaluation: PV with 95 wt %.

factor and permeation rate. Through pilot plant operations, Sander et al.² confirmed that the GFT (crosslinked PVA composite) membrane had sufficient performance, that is, $\alpha \sim 1000$, $Q \sim 0.5 \text{ kg/m}^2 \text{ h}$ and thus $\alpha \cdot Q \sim 500$ at 95% EtOH and 100°C. Therefore, this value can be considered to be the target value for material selection and membrane preparation.

In Table IV, the highly water permselective pervaporation membranes are cited from the literature, and compared with the performance obtained in this study. Regarding separation factor, poly(hydroxymethylene) and alginic acid-CO²⁺ salt membranes in particular yield high values which can be considered to be the highest level achieved so far. It is noted that, except for PVA and polyhydroxymethylene, most of the membrane materials are derived from polyelectrolytes, either polyanion or polycation.

With regard to the productivity of membranes, the PIC composite membrane optimized in this study has achieved the highest value. Through these

comparisons, it has been proven that this PAA-based polyion complex membrane has a high separation potential for the dehydration of alcohol, i.e., azeotropic mixture of alcohols, etc.

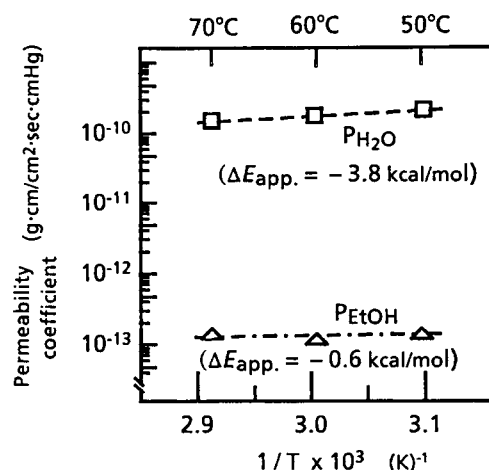


Figure 15 Effect of permeate pressure on separation factor (PAA: MW 4,000,000, uncrosslinked, PIC with PCA-107; evaluation: PV with 95 wt % EtOH of 70°C).

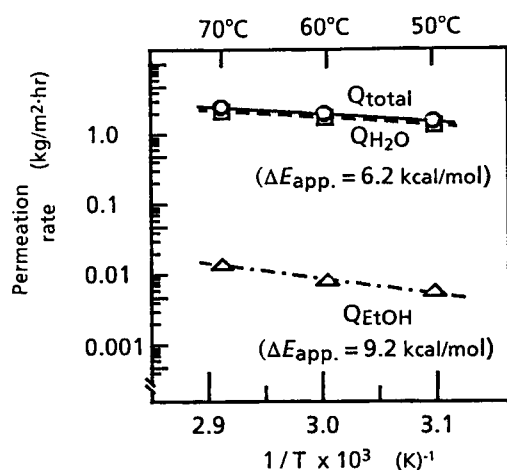


Figure 14 Effect of evaluation temperature on separation properties (PAA: MW 4,000,000, uncrosslinked, PIC with PCA-107; evaluation: PV with 95 wt % EtOH of 70°C).

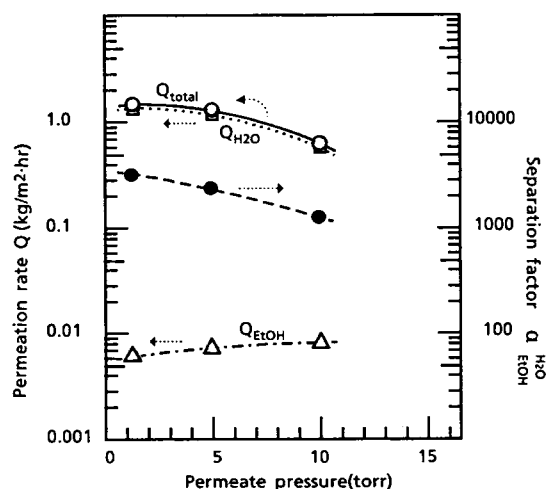


Figure 16 Effect of permeate pressure on separation properties (PAA: MW 4,000,000, uncrosslinked, PIC with PCA-107; evaluation: PV with 95 wt % EtOH of 70°C).

Table IV Separation of Other Hydrophilic Membranes

Material	Ethanol in Feed (wt %)	Temp. (°C)	Separation Factor α (H ₂ O/EtOH)	Permeation Rate Q (kg/m ² h)	$Q \times \alpha$	Ref.
Crosslinked PVA	95	80	9500	0.01	95	3
Poly(hydroxy methylene)	95	60	> 8950	0.013	116	5, 6
Chitosan (crosslinked with H ₂ SO ₄)	90	60	6500	0.1	650	9
Sulfonated polyethylene						
Cs ⁺	85.4	26	725	0.152	110	13
Na ⁺	85.4	26	671	0.080	54	13
CMC(DS 0.8, Na ⁺)	90	30	2430	0.052 ^a	126	14
Alginic acid (crosslinked with Co ²⁺)	90	60	5000	0.15	750	9
PAA/PCA-107	95	60	3510	1.63	5720	This study
		70	2890	2.17	6270	

^a Permeation rate: kg · mil/m² hr.

CONCLUSION

The following conclusions have been drawn from the present investigation. The alkali salt form PAA membrane showed higher water selectivity compared with the acid form, but the high separation properties declined within a few hours because of the elution of counter ions. Instead of alkali metal, various polycations were used to ionize PAA and to form polyion complexes. PIC structure was quite effective in stabilizing the separation properties. Among the polycations, "ionenes" were found to be the best. Using the high molecular weight of PAA, the separating layer thickness can be decreased (ca. 0.1 μ m) resulting in high permeation rates.

In this manner, membranes having very high separation properties ($Q \sim 1.6$ kg/m² h and $\alpha \sim 3500$ for a feed mixture of 95 wt % EtOH at 60°C) have been developed. High selectivity was observed at a rather high ethanol concentration region (> 90 wt % EtOH). These separation characteristics are anticipated to be valuable if we use this membrane for dehydration of high concentration ethanols, such as azeotropic mixture (95 wt % EtOH).

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