

# Selective Separation of Water from Water–Ethanol Solution through Quarternized Poly(4-Vinylpyridine-Co-Acrylonitrile) Membranes by Pervaporation Technique

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## Synopsis

Polymer membranes having cationic charge site, poly(1-alkyl-4-vinylpyridinium iodide-co-acrylonitrile) (alkyl: methyl, butyl, or octyl) were prepared in terms of coulombic interaction for separation of water–ethanol mixtures. The incorporation of cationic charge site into the membrane led to improve not only separation factors (selectivity toward water) but also flux number in the separation of aqueous ethanol solution by pervaporation technique. Target values, which were requested to have from the viewpoint of industrial utilization for separation of aqueous ethanol solution were attained as follows: separation factor toward water over 50 and flux value over  $500 \text{ g m}^{-2} \text{ h}^{-1}$ , through poly(1-methyl-4-vinylpyridinium iodide-co-acrylonitrile) (membrane 3) (quarternized fraction of pyridinium moiety, 89.5%; mol fraction of pyridinium moiety, 0.034) and poly(1-butyl-4-vinylpyridinium iodide-co-acrylonitrile) (membrane 5) (quarternized fraction, 100%; mol fraction of pyridinium moiety, 0.038). It was found that the introduction of cationic charge site into the membrane was one of feasible methods to obtain suitable membranes for water permselective membranes in the separation of water–ethanol mixtures.

## INTRODUCTION

Synthesis and separation processes are very important ones in chemical industry. In the distant future, the reaction membrane<sup>†</sup> which simultaneously carries out not only chemical reaction but also separation (purification) of the product will be developed as an ideal process in chemical industries. An approach to the reaction membrane is to survey membrane separation technique with artificial membranes, especially synthetic polymer membranes. We have been studying membrane separation technique from the viewpoint of chemistry; in other words, we have been preparing synthetic polymers as membrane materials and investigating their membrane performance.<sup>2–15</sup>

Separation carried out by membranes is considered to be one of the most promising processes as energy-saving separation technology. Especially, mem-

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<sup>†</sup>A preliminary experiment of such a reaction membrane (ester synthesis membrane) was reported by Yoshikawa and Shimidzu.<sup>1</sup>

brane separation technique has been attracting our attention since the energy crisis. When membrane separation technology is realized, it might be possible to attain separation of a number of organic liquid mixtures, which are difficult to separate, such as azeotropic mixtures, mixtures having nearly the same boiling point, structural isomers, or heat-sensitive compounds, by means of membrane instead of distillation, which consumes much heat energy.

Pervaporation technique is one of the potential methods to separate specifically and selectively organic liquid mixtures, where a membrane separates an upstream solution in the liquid state from downstream permeates in the gaseous state and the downstream side is maintained at a reduced pressure to ensure the gaseous state, which was named by Kober<sup>16</sup> and suggested by Binning and Lee.<sup>17</sup>

Formation of ethanol via fermentation of biomasses<sup>18,19</sup> could be an important industrial process in connection with energy problems. The liquid product is an aqueous solution that contains around 5 wt % ethanol, which is separated by distillation to give 95.6 wt % ethanol; this distillation process is an energy-intensive step that accounts for a large portion of the cost of ethanol production from biomass. Therefore, pervaporation technique is thought to be economical and energy-saving alternative processes for water-ethanol separation.

There are two ways to separate water-ethanol solution by pervaporation technique. One way is that ethanol is separated through membranes,<sup>12, 15, 20-24</sup> while the other one is that water is selectively permeated through membranes.<sup>3-14, 25-38</sup> The separation of aqueous ethanol solution by the former way was studied in terms of membrane polarity value  $E_T$  (25°C), which was evaluated by photoresponsive uni-univalent salt transport carrier,<sup>39</sup> 1-octadecyl-3,3-dimethyl-6'-nitrospiro(indoline-2,2'-2H-benzopyran) as the indicator. Membrane polarity value proposed by one of the authors<sup>40</sup> is one of the possible parameters to explain membrane performance.<sup>4, 6, 11, 41</sup> As for our work on water-ethanol separation by the latter way, that is, survey of water-permeable membranes, we have been studying pervaporation through synthetic polymer membranes in terms of hydrogen-bonding interaction<sup>3-12, 15</sup> or Coulombic interaction.<sup>13, 14</sup> In general, such water-permeable membranes are classified into three categories as follows<sup>8</sup>: (a) commercially available membranes;<sup>25-31</sup> (b) membranes incorporated hydrophilic moiety into membrane matrix (hydrophobic polymer);<sup>32-36</sup> (c) membranes from hydrophilic-hydrophobic multiblock copolymers.<sup>37, 38</sup> All membranes reported by us belonged to the group (b) category. Synthetic polymer membranes having imide group,<sup>3, 4, 6</sup> *N*-substituted imide group,<sup>7</sup> carboxylic acid moiety,<sup>5, 8, 12</sup> or *N*-substituted imide group and ester group,<sup>9, 10</sup> selectively permeated water from aqueous ethanol (alcohol) or aqueous acetic acid solution by pervaporation technique by making use of hydrogen-bonding interaction. Especially, poly{1-(2-methylpropenyloxy)succinimide-co-acrylonitrile} membrane had a high separation factor, which reached over 2000 toward water.<sup>10</sup> Although these membranes permeated water preferentially, flux values were less than 100 g m<sup>-2</sup> h<sup>-1</sup>. From the viewpoint of industrial utilization of synthetic

<sup>8</sup>This classification was proposed by Yamada.<sup>42</sup>

polymer membranes for separation of water-ethanol solution, the membrane is requested to have following properties: Separation factor toward water is over 50 and flux value reaches over 500 g m<sup>-2</sup> h<sup>-1</sup>.<sup>43</sup>

Separation of water from water-ethanol solution was attempted through ion exchange membranes by pervaporation technique by making use of a Coulombic interaction instead of a hydrogen-bonding interaction.<sup>29,36</sup> There is another attempt of pervaporation of water through partially quarternized poly(4-vinylpyridine) membrane.<sup>44</sup>

Based on an industrial viewpoint, synthetic polymer membranes having cationic charge site, poly(1-alkyl-4-vinylpyridinium iodide-co-acrylonitrile) (alkyl: methyl, butyl, or octyl) membranes were prepared, and the selective separation of water-ethanol mixtures through the present membranes were investigated. Preliminary experiments<sup>13,14</sup> showed the possibility that these membranes might be applicable to industrial utilization. The present article deals with a study of selective separation of water from water-ethanol through quarternized poly(4-vinylpyridine-co-acrylonitrile) membranes.

## EXPERIMENTAL

### Materials

4-Vinylpyridine, acrylonitrile, 2,2'-azobis(2-methylpropionitrile) (AIBN), and *N,N*-dimethylformamide (DMF) were purified in the usual manner. Diethyl ether, iodomethane, iodobutane, iodoctane, and ethanol were used without further purification. The water employed here was distilled once.

### Syntheses of Membrane Materials

Poly(4-vinylpyridine-co-acrylonitrile) (1 and 7), with a mol fraction of 4-vinylpyridine unit of either 0.038 or 0.098, was synthesized by the usual radical copolymerization of 4-vinylpyridine and acrylonitrile initiated by AIBN as described previously.<sup>45</sup> Poly(1-methyl-4-vinylpyridinium iodide-co-acrylonitrile) (2, 3, and 8), poly(1-butyl-4-vinylpyridinium iodide-co-acrylonitrile) (4, 5, and 9), and poly(1-octyl-4-vinylpyridinium iodide-co-acrylonitrile) (6) were prepared by the reaction of 1 or 7 with corresponding alkyl iodide in DMF solution. The chemical compositions of 2-6, 8, and 9 were determined by <sup>1</sup>H-NMR spectra recorded on JEOL FX200 (199.5 MHz) as reported previously.<sup>2</sup> The reaction conditions and the results are summarized in Tables I and II.

All membranes were obtained by casting from DMF solution. The solutions were poured onto glass plates with applicators (casting thickness, 0.254 mm), and the solvent was allowed to evaporate at 40 °C for ca. 3 h. Concentrations of casting DMF solutions and membrane thickness are summarized in Table III.

### Determination of Membrane Polarity Values

Membrane polarity values, Dimroth's solvent polarity values [ $E_T$  (25 °C)], of these membranes were measured as described previously, using 1-octadecyl-3,3-dimethyl-6'-nitrospiro(indoline-2,2'-2H-benzopyran) as the indicator.<sup>40</sup> A

TABLE I  
 Results of Polymer Syntheses

Polymer	—R	Amount of 038 (g)	Amount of RI (g)	DMF (cm <sup>3</sup> )	Reaction temp (°C)	Reaction time (h)	<i>m</i>	<i>n</i>	$\eta_{sp}/C^a$ (dm <sup>3</sup> g <sup>-1</sup> )
2 038-Me-018	—CH <sub>3</sub>	3.0	1.1	300	30	28	0.018	0.020	0.342
3 038-Me-034	—CH <sub>3</sub>	5.0	2.7	150	30	21	0.034	0.004	0.150
4 038-Bu-015	—(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	5.0	3.2	150	60	60	0.015	0.023	0.288
5 038-Bu-038	—(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	3.0	64.6	200	70	115	0.038	0	0.252
6 038-Oc-015	—(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	4.0	25.0	250	80	90	0.015	0.023	0.171

<sup>a</sup>Reduced viscosity was measured at  $C = 1.0 \text{ g dm}^{-3}$ , DMF at 30°C.

 TABLE II  
 Results of Polymer Syntheses

Polymer	—R	Amount of 098 (g)	Amount of RI (g)	DMF (cm <sup>3</sup> )	Reaction temp (°C)	Reaction time (h)	<i>m</i>	<i>n</i>	$\eta_{sp}/C^a$ (dm <sup>3</sup> g <sup>-1</sup> )
8 098-Me-098	—CH <sub>3</sub>	3.0	50.0	200	55	71	0.098	0	0.034
9 098-Bu-077	—(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	3.8	60.0	200	80	70	0.077	0.021	0.112

<sup>a</sup>Reduced viscosity was measured at  $C = 1.0 \text{ g dm}^{-3}$ , DMF at 30°C.

 TABLE III  
 Results of Membrane Preparation

Membrane	Conc. of casting DMF soln (g dm <sup>-3</sup> )	Thickness (μm)
1 038	88	20
2 038-Me-018	118	19
3 038-Me-034	132	15
4 038-Bu-015	130	23
5 038-Bu-038	102	14
6 038-Oc-015	154	21
7 098	140	18
8 098-Me-098	120	15
9 098-Bu-077 <sup>a</sup>	—	—

<sup>a</sup>Membrane 9 was not able to be obtained.

250-W high-pressure mercury lamp was used as a light source. Absorption spectra were measured with a Shimadzu UV-240 UV-visible spectrophotometer.

## Evaluation of Charge Density of Membranes

### Measurement of Membrane Potential

The schematic diagram of the apparatus used for measuring membrane potentials is shown in Figure 1. The electromotive force which across between the bulk solutions was conducted by saturated KCl bridges and calomel

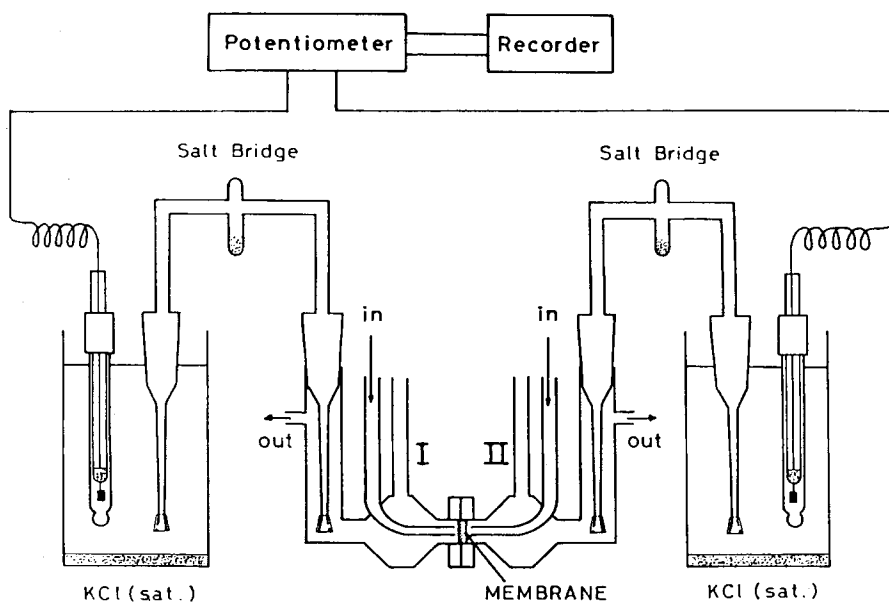


Fig. 1. Schematic diagram of the cell used for the measurement of membrane potentials.

electrodes and measured by a potentiometer (Hokuto Denko Ltd. HE-101A or HE-104). The bulk solutions of both sides of the membrane were stirred by the flow of themselves.

Anion transport number ( $t_-$ ) of the membranes were determined by the concentration-membrane potentials  $\epsilon$  ( $E_I - E_{II}$ ) at 15°C with aqueous solutions of KCl, using<sup>46</sup>

$$\epsilon = E_I - E_{II} = (2t_- - 1) \frac{RT}{F} \ln \frac{C_I}{C_{II}} \quad (1)$$

Here  $C_I$  and  $C_{II}$  represented the concentrations of the solution on either side of the membrane (0.2 and 0.1 mol dm<sup>-3</sup>, respectively);  $F$  is the Faraday constant;  $R$  is the gas constant;  $T$  is the absolute temperature.

In order to estimate charge density ( $\theta$ ) of the membrane, we measured membrane potentials as a function of  $C_{II}$  (from  $1 \times 10^{-4}$  to  $1 \times 10^{-1}$  mol dm<sup>-3</sup>). The ratio of concentration of solution on either side I or II,  $\gamma = C_I/C_{II}$ , was fixed at 2. A membrane potential  $\epsilon$  of a charged membrane is represented by eq. (2) when  $C_I$  of a uni-univalent electrolyte is contacted with one side of the membrane, and  $C_{II}$  of the same uni-univalent electrolyte is in contact with the other side of the membrane at equal pressure and temperature:<sup>47-50</sup>

$$\epsilon = E_I - E_{II} = \frac{RT}{F} \left\{ -\ln 2 + \ln \frac{-\theta + \sqrt{\theta^2 + 16C_{II}^2}}{-\theta + \sqrt{\theta^2 + 4C_{II}^2}} + (2t_- - 1) \ln \frac{(2t_- - 1)\theta + \sqrt{\theta^2 + 16C_{II}^2}}{(2t_- - 1)\theta + \sqrt{\theta^2 + 4C_{II}^2}} \right\} \quad (2)$$

Unit activity coefficients have been assumed. Trial and error methods were applied to equation (2) in order to estimate charge densities.

### Pervaporation

Permeation of water-ethanol mixture was carried out through the membranes as described previously.<sup>12</sup> The membrane area in contact with liquid was 12.6 cm<sup>2</sup>. The downstream pressure was maintained 400 Pa (3.0 torr). Pervaporation experiments were carried out at various prescribed temperatures.

The separation analysis was carried out on a Shimadzu GC-8A gas chromatograph equipped with a 1-m-long column packed with Porapak Q.

The separation factor  $\alpha$  is defined as

$$\alpha = \frac{Y_{\text{water}}/Y_{\text{ethanol}}}{X_{\text{water}}/X_{\text{ethanol}}} \quad (3)$$

where the  $Y_i$ 's are the weight fractions of permeates and the  $X_i$ 's are those of feeds, respectively.

## RESULTS AND DISCUSSION

### Characterization of Membranes

Membrane polarity values,  $E_T$  (25°C) values, of present membranes are summarized in Table IV. Absorption spectra of membranes 6 and 9 were too broad to allow for identification. Comparing membranes 1 and 7, which were parent membranes, the membrane polarity value of membrane 1 was higher than that of membrane 7. The increase of pyridine moiety fraction in the membrane led to the decrease in membrane polarity as expected from the fact that the polarity of pyridine moiety is less than that of nitrile moiety.<sup>51, 52</sup> Comparing membranes 1-5, parent membrane whose unit mol fraction of 4-vinylpyridine was 0.038 and its derivative membranes, every quarternized membrane had a higher membrane polarity value than membrane 1. The

TABLE IV  
Composition,  $\lambda_{\text{max}}^{\text{Vis}}$ , and Dimroth's solvent polarity values [ $E_T$ (25°C)]  
of Synthetic Polymer Membranes

Polymer membrane	-R	X	Y	Fraction of quarternization (%)	$\lambda_{\text{max}}^{\text{Vis}}$ (nm)	$E_T$ (25°C) (kcal mol <sup>-1</sup> )
1 038	—	0	0.038	0	543	54.0
2 038-Me-018	CH <sub>3</sub> —	0.018	0.020	47.4	540	55.1
3 038-Me-034	CH <sub>3</sub> —	0.034	0.004	89.5	535	57.0
4 038-Bu-015	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> —	0.015	0.023	39.5	542	54.4
5 038-Bu-038	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> —	0.038	0	100	536	56.6
6 038-Oc-015	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> —	0.015	0.023	39.5	—	—
7 098	—	0	0.098	0	545	53.3
8 098-Me-098	CH <sub>3</sub> —	0.098	0	100	540	55.1
9 098-Bu-077	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> —	0.077	0.021	79.6	—	—

TABLE V  
Membrane Potential and Transport Number of Synthetic Polymer Membranes<sup>a</sup>

Membrane	Membrane potential (mV)	Transport number ( $t^*$ )
1 038	-2.23	0.44
2 038-Me-018	9.38	0.77
3 038-Me-034	12.7	0.87
4 038-Bu-015	11.1	0.82
5 038-Bu-038	9.42	0.77
6 038-Oc-015	—	—
7 098	-1.50	0.46
8 098-Me-098	5.20	0.65
9 098-Bu-077	—	—

<sup>a</sup>Operating temp 15° C; 0.2/0.1 mol dm<sup>-3</sup> KCl solution.

increase of quarternization fraction, comparing membranes 2 and 3, or 4 and 5, led the increase in membrane polarity. When we made a comparison between membranes having nearly the same quarternization fraction, membranes 2 and 4, or membranes 3 and 5, membranes having methyl group as a quarternization reagent had a higher membrane polarity value than those having butyl group. This might be due to the following reason: The shielding ability of butyl group toward cationic charge was higher than that of methyl group since butyl group is more hydrophobic than methyl one. Comparing membranes 7 and 8, the introduction of cationic charge into membrane led the increase of membrane polarity value as observed in the case of membranes 1-6. From results summarized in Table III, it was concluded that the membrane polarity in the present paper was able to be controlled by the fraction of 4-vinylpyridine, quarternization fraction, and quarternization reagent.

The obtained anion transport number of present membranes are summarized in Table V. Those of parent membranes, membranes 1 and 7, were close to 0.5 as was expected from the fact that these membranes had no cationic charge site. The anion transport number of quarternized membranes were higher than those of respective parent membranes. This was a natural result from the fact that pyridine moiety in these membranes were all or partly quarternized. The anion transport number of membrane 3 was higher than that of membrane 2 with increase of quarternization fraction, while the anion transport number of membrane 5 was slightly lower than that of membrane 4, although the quarternization fraction of membrane 5 was higher than that of membrane 4. Comparing the difference in quarternization reagent, membranes quarternized by iodomethane (membranes 2 and 3) tended to have a higher anion transport number than those by iodobutane (membranes 4 and 5). This was due to the difference in shielding effect of alkyl group toward cationic charge, in other words, the difference in hydrophobicity or hydrophilicity of alkyl group. As described above, this difference in the alkyl group was also reflected in the membrane polarity value.

An example of the relationship between membrane potential and  $C_{II}$  is shown in Figure 2. Such plots were conducted in order to estimate the charge density. As shown in Figure 2, the observed membrane potentials deviated

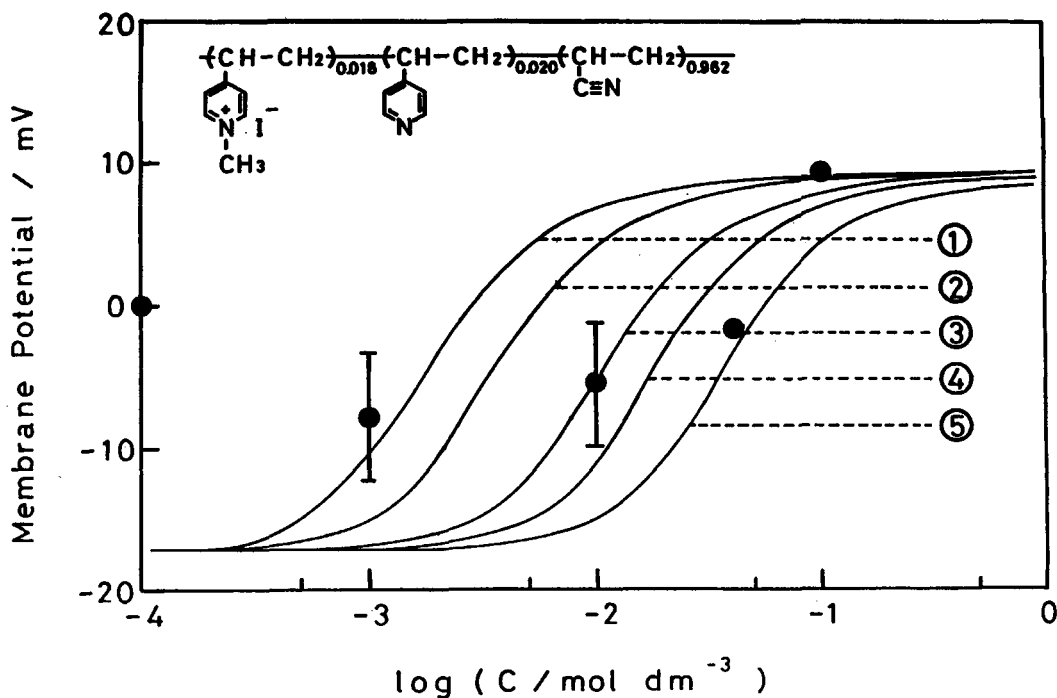


Fig. 2. Plots of membrane potentials at  $\gamma = C_I/C_{II} = 2$  against  $\log C_{II}$  at  $15^\circ\text{C}$ . KCl with membrane 2,  $\theta$  ( $\text{mol dm}^{-3}$ ): (①)  $-5 \times 10^{-3}$ ; (②)  $-1 \times 10^{-2}$ ; (③)  $-3 \times 10^{-2}$ ; (④)  $-5 \times 10^{-2}$ ; (⑤)  $-1 \times 10^{-1}$ .

from the theoretical profile so that we evaluated only the order of charge density. All membranes quarternized gave charge densities of around  $-1 \times 10^{-2} \text{ mol dm}^{-3}$ . This serious deviation might be mainly due to the fact that we substituted the constant anion transport number summarized in Table III in eq. (2) to evaluate the charge density.

### Selective Separation of Water-Ethanol Mixtures

#### *Pervaporation through Membranes 1-6*

Figure 3 gives results of pervaporation experiments, where the weight fraction of water in permeates were plotted against those in feeds. These experiments were carried out at  $15^\circ\text{C}$ . The flux value through membrane 3 at the point where the feed composition was around 0.18 was too small to allow for separation analysis. Figure 3 clearly disclosed that the selective separation of water was attained through these membranes 1-5 except membrane 6. Selectivity of membrane 6 toward water was low. When the operating temperature was  $15^\circ\text{C}$ , the swelling of the membrane, such as change of weight, area, or thickness, was scarcely observed.

Figures 4-6 indicate the effect of feed composition on separation factor  $\alpha$  and flux at  $15^\circ\text{C}$ . As shown in Figures 4 and 5, the incorporation of ionic charge into the membrane seemed to lead both the increase in selectivity toward water and flux values as we expected. Especially, marked effect was



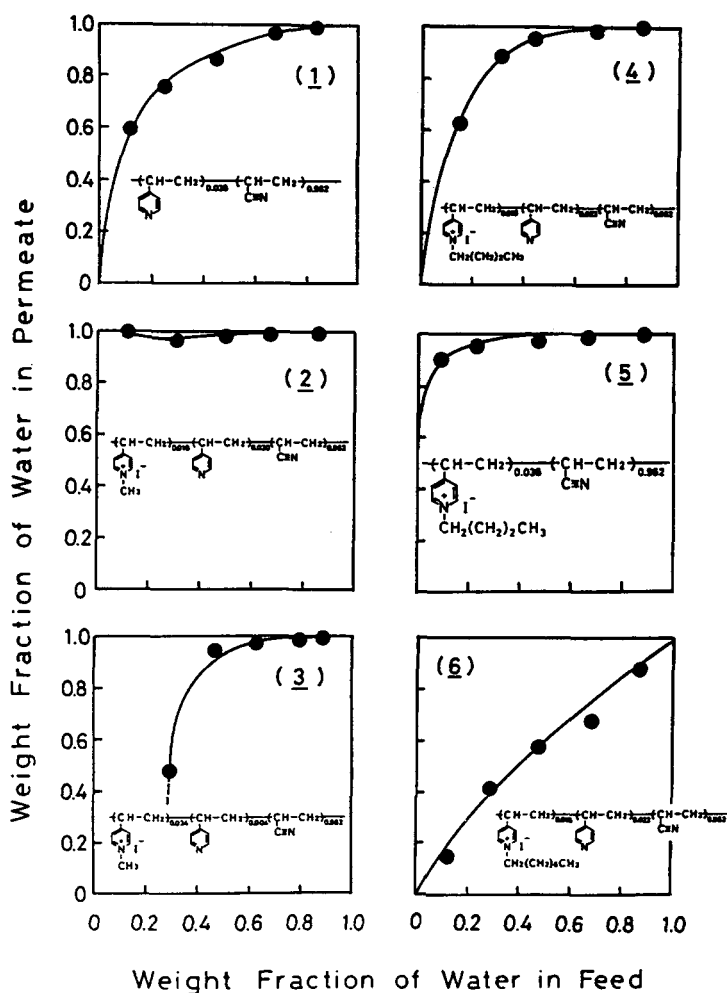


Fig. 3. Effect of feed composition on the separation of water-ethanol mixture through membranes 1-6 at 15°C. Downstream pressure, 400 Pa (3.0 torr).

observed in the permeation through membranes quarternized by iodobutane (membranes 4 and 5). On the other hand, membrane 6 gave a high flux value. The selectivity toward water through membrane 6, however, was close to unity as it is often observed in the membrane phenomenon that the selectivity is inversely proportional to the flux value.

In our previous experiments, a spectroscopic approach was carried out to detect the selective interaction between water and imide units in a poly(maleimide-co-acrylonitrile) membrane<sup>6</sup> or carboxylic acids in poly(acrylic acid-co-acrylonitrile) membrane.<sup>12</sup> In the present paper, it was impossible to carry out a spectroscopic approach. In order to study the permeation mechanism, we separated water and ethanol components, so that each component flux was able to be plotted against its feed concentration. These separated fluxes are shown in Figures 7-9.

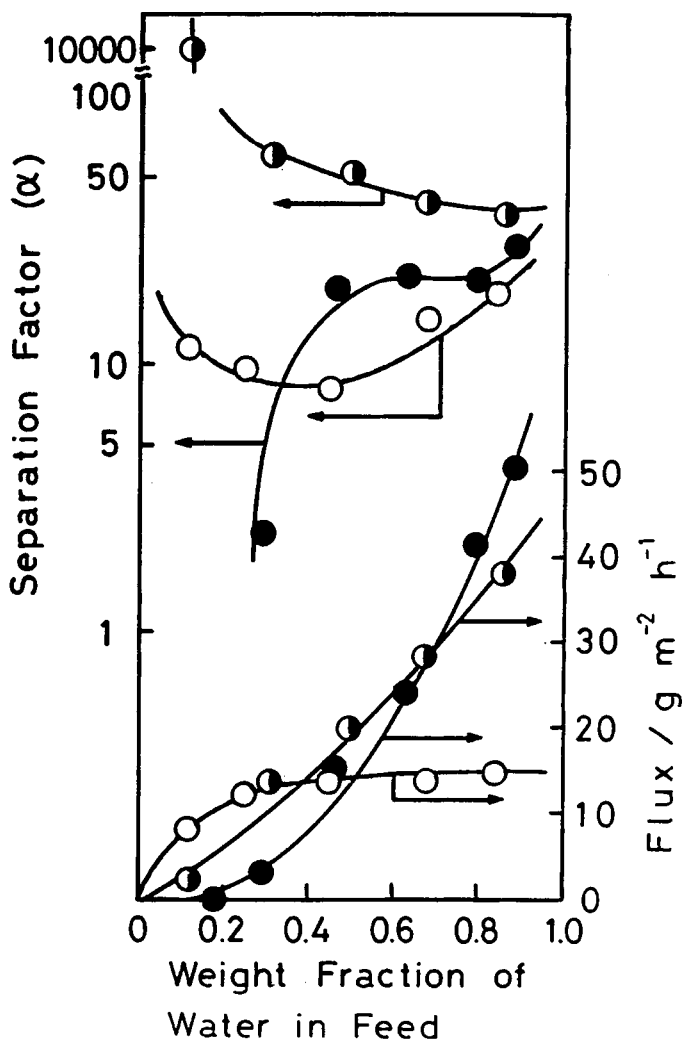


Fig. 4. Effect of feed composition on flux and separation factor ( $\alpha$ ) in water-ethanol pervaporation through membranes 1, 2, and 3 at 15°C. Downstream pressure, 400 Pa (3.0 torr): (○) membrane 1; (◐) membrane 2; (●) membrane 3.

The water flux through membranes 1, 4, 5, and 6 approached an asymptotic limit as water concentration in feed increased, that is, a typical Michaelis-Menten profile was observed. This suggests that water might be permeated through membranes 1, 4, 5, and 6 by a carrier mechanism. In the present paper, however, a carrier (pyridine moiety or pyridinium cationic charge site) was immobilized in the membrane. In this case, the water flux may be represented by the following equation<sup>9,10,12</sup>:

$$J = \frac{D K [C]_0 [H_2O]_{\text{feed}}}{l (1 + K [H_2O]_{\text{feed}})} \quad (4)$$

In this equation,  $D$  is the diffusion coefficient in the membrane for water;  $l$  is

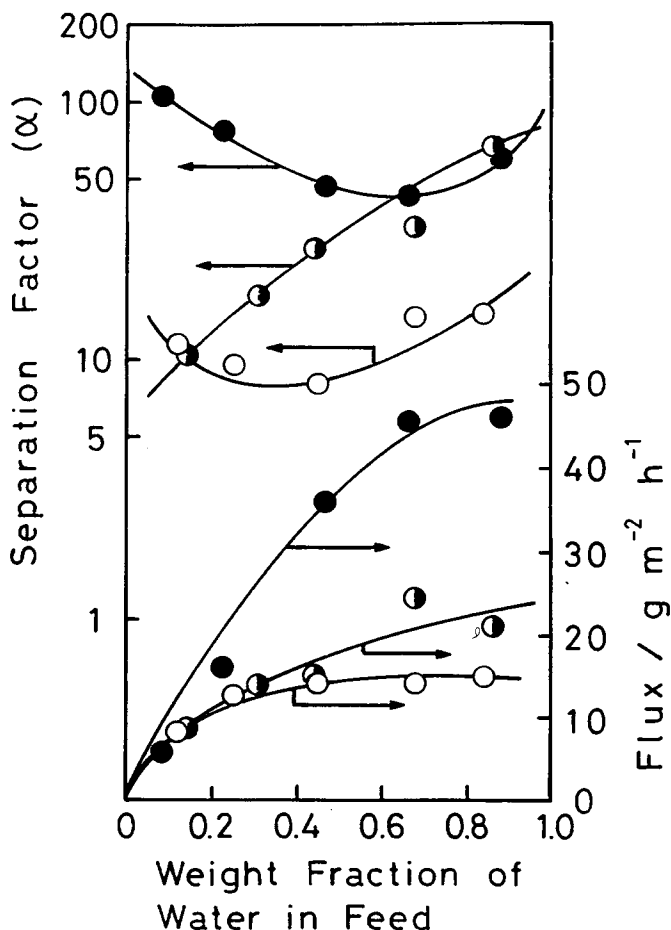


Fig. 5. Effect of feed composition on flux and separation factor ( $\alpha$ ) in water-ethanol pervaporation through membranes 1, 4, and 5 at 15°C. Downstream pressure, 400 Pa (3.0 torr): (○) membrane 1; (◐) membrane 4; (●) membrane 5.

the membrane thickness;  $K$  is the complex formation constant between carrier (fixed carrier) and water;  $[C]_0$  denotes the carrier concentration in the membrane;  $[H_2O]_{\text{feed}}$  is the water concentration in the feed. The slope and the intercept in a Lineweaver-Burk plot using the data for water permeation through membranes 1, 4, 5, and 6 gave values  $K$  and  $D$  for water. Obtained values are summarized in the tables in Figures 7-9. Membranes 4 and 6 had two different kinds of carrier for water in the membrane, that is, pyridine moiety and pyridinium cationic charge site. Since superposition of two kinds of Michaelis-Menten profiles apparently make another Michaelis-Menten one, we analyzed water permeation data of membranes 4 and 6 as one Michaelis-Menten profile by using eq. (4). When we theoretically calculated water flux through membrane 4 by making use of  $D$  and  $K$  values for membranes 1 and 5 [see the dotted line in Fig. 8(a)], calculated flux did not coincide with the observed one. From this, we concluded that the membrane in the present paper did not show the additivity of membrane property.

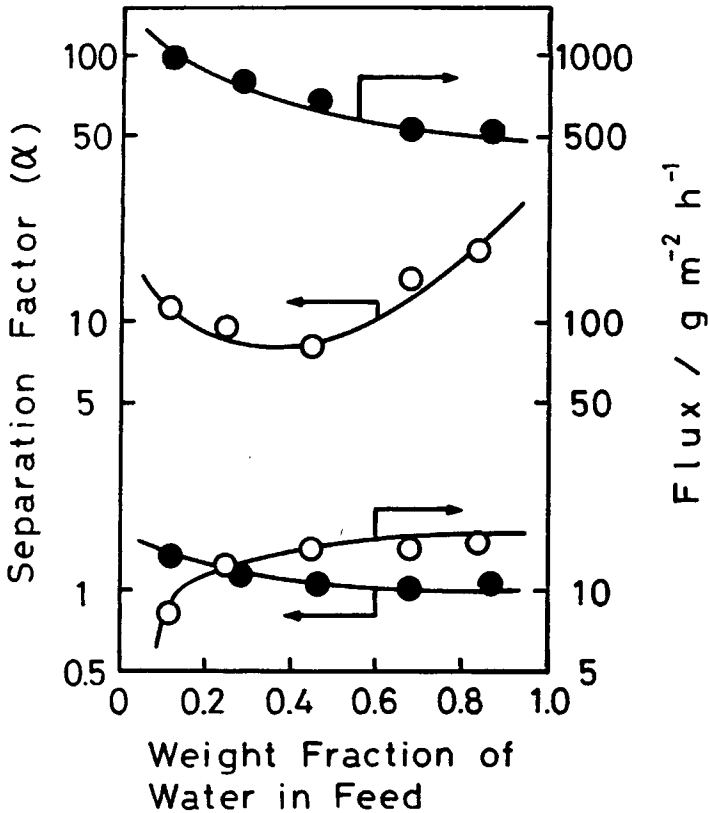


Fig. 6. Effect of feed composition on flux and separation factor ( $\alpha$ ) in water-ethanol pervaporation through membranes 1 and 6 at 15°C. Downstream pressure, 400 Pa (3.0 torr): (○) membrane 1; (●) membrane 6.

On the other hand, water permeation through membranes 2 and 3 did not obey a Michaelis-Menten type profile; that through membrane 2 gave a straight line passing through origin and that through membrane 3 showed an exponential profile. These led to the following two conclusions: Water permeated through membrane 2 without any specific interaction with membrane; water permeation through membrane 3 was much dependent on water concentration in the feed. In the water permeation through membrane 2, the water flux may be represented by the following equation<sup>53,54</sup>:

$$J = (P/l) [\text{H}_2\text{O}]_{\text{feed}} \quad (5)$$

In this equation,  $P$  is the permeability coefficient, which is the product of diffusion coefficient and solubility. For permeation of water through membrane 3, which was swollen with water itself, however, it may be microscopic swelling as mentioned above, and the diffusion coefficient  $D$  is usually dependent on the local concentration of water.<sup>55-62</sup> In some cases the concentration dependence of the diffusion coefficient has been reported to be

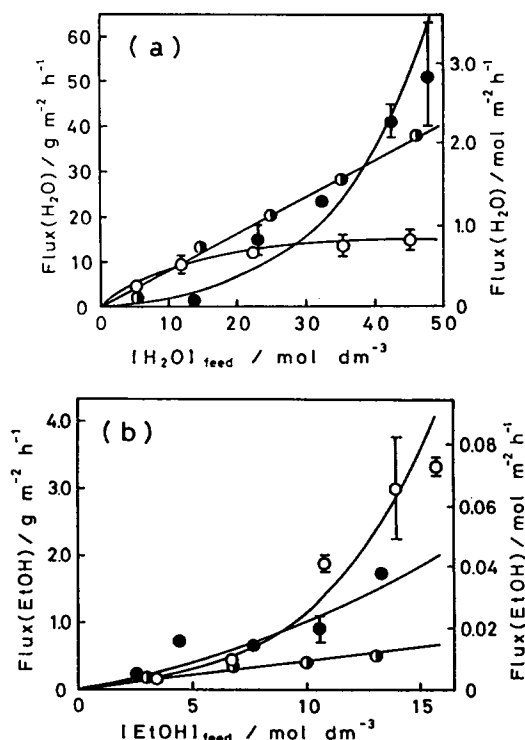


Fig. 7. Relationship between water (a) and ethanol (b) fluxes of pervaporation through membranes 1, 2, and 3, and their concentration in the feed. Downstream pressure, 400 Pa (3.0 torr); operating temperature, 15°C; (○) membrane 1; (◐) membrane 2; (●) membrane 3.

(a)

	Membrane 1	Membrane 2	Membrane 3
$D$ ( $\text{m}^2 \text{h}^{-1}$ )	$3.63 \pm 0.41 \times 10^{-8}$	—	—
$K$ ( $\text{mol}^{-1} \text{m}^3$ )	$5.75 \pm 1.29 \times 10^{-5}$	—	—
$P$ ( $\text{m}^2 \text{h}^{-1}$ )	—	$8.77 \pm 1.44 \times 10^{-10}$	—
$D_0$ ( $\text{m}^2 \text{h}^{-1}$ )	—	—	$1.58 \pm 0.00 \times 10^{-10}$
$b$ ( $\text{mol}^{-1} \text{m}^3$ )	—	—	$7.41 \pm 0.00 \times 10^{-5}$

(b)

	Membrane 1	Membrane 2	Membrane 3
$D_0$ ( $\text{m}^2 \text{h}^{-1}$ )	$2.10 \pm 0.00 \times 10^{-11}$	—	$3.22 \pm 0.00 \times 10^{-11}$
$b$ ( $\text{mol}^{-1} \text{m}^3$ )	$2.04 \pm 0.00 \times 10^{-4}$	—	$6.14 \pm 0.00 \times 10^{-5}$
$P$ ( $\text{m}^2 \text{h}^{-1}$ )	—	$1.56 \pm 0.42 \times 10^{-11}$	—

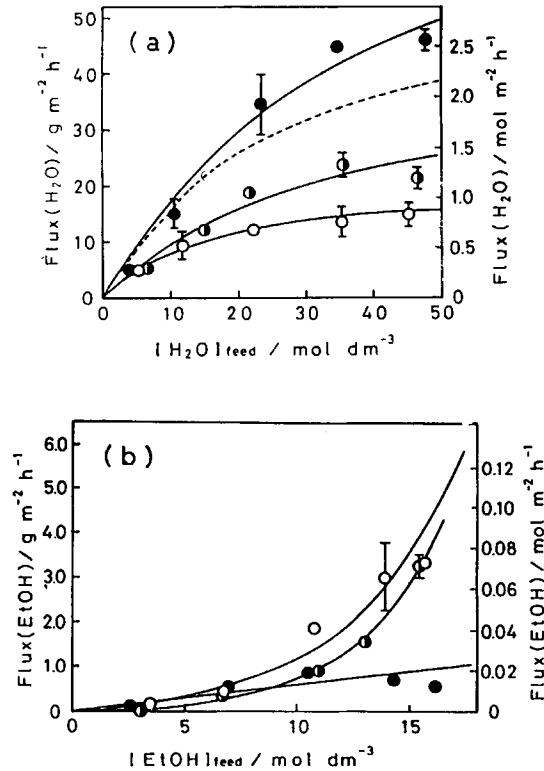


Fig. 8. Relationship between water (a) and ethanol (b) fluxes of pervaporation through membranes 1, 4, and 5, and their concentration in the feed. Downstream pressure, 400 Pa (3.0 torr); operating temperature, 15°C; (○) membrane 1; (◐) membrane 4; (●) membrane 5; (---) calculated flux through membrane 4.

(a)

	Membrane 1	Membrane 4	Membrane 5
$D$ ( $\text{m}^2 \text{h}^{-1}$ )	$3.63 \pm 0.41 \times 10^{-8}$	$3.40 \pm 0.63 \times 10^{-8}$	$6.09 \pm 0.98 \times 10^{-8}$
$K$ ( $\text{mol}^{-1} \text{m}^3$ )	$5.75 \pm 1.29 \times 10^{-5}$	$2.66 \pm 0.98 \times 10^{-5}$	$2.35 \pm 0.76 \times 10^{-5}$

(b)

	Membrane 1	Membrane 4	Membrane 5
$D_0$ ( $\text{m}^2 \text{h}^{-1}$ )	$2.10 \pm 0.00 \times 10^{-11}$	$5.62 \pm 0.00 \times 10^{-12}$	—
$b$ ( $\text{mol}^{-1} \text{m}^3$ )	$2.04 \pm 0.00 \times 10^{-4}$	$2.67 \pm 0.00 \times 10^{-4}$	—
$P$ ( $\text{m}^2 \text{h}^{-1}$ )	—	—	$1.16 \pm 0.89 \times 10^{-8}$

linear,

$$D = D_0(1 + ac) \quad (6)$$

and in others it was observed to have an exponential form,

$$D = D_0 \exp(bc) \quad (7)$$

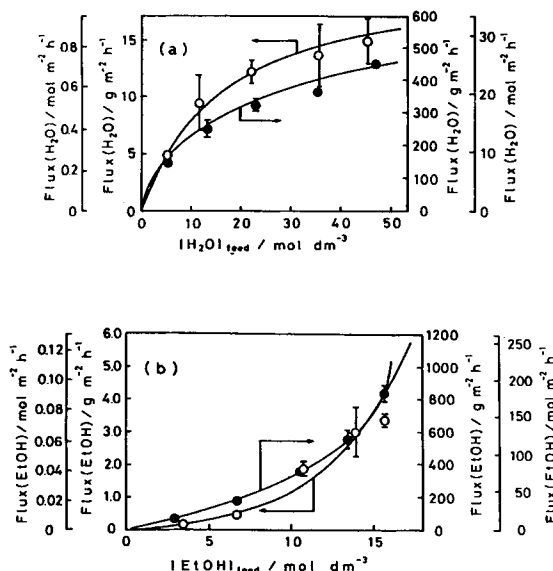


Fig. 9. Relationship between water (a) and ethanol (b) fluxes of pervaporation through membranes 1 and 6, and their concentration in the feed. Downstream pressure, 400 Pa (3.0 torr); operating temperature, 15°C; (○) membrane 1; (●) membrane 6.

(a)

	Membrane 1	Membrane 6
$D$ ( $\text{m}^2 \text{h}^{-1}$ )	$3.63 \pm 0.41 \times 10^{-8}$	$4.05 \pm 0.43 \times 10^{-7}$
$K$ ( $\text{mol}^{-1} \text{m}^3$ )	$5.75 \pm 1.29 \times 10^{-5}$	$7.31 \pm 1.55 \times 10^{-5}$

(b)

	Membrane 1	Membrane 6
$D_0$ ( $\text{m}^2 \text{h}^{-1}$ )	$2.10 \pm 0.00 \times 10^{-11}$	$8.05 \pm 0.00 \times 10^{-9}$
$b$ ( $\text{mol}^{-1} \text{m}^3$ )	$2.04 \pm 0.00 \times 10^{-4}$	$1.18 \pm 0.00 \times 10^{-4}$

In these two equations,  $D_0$  is the  $D$  in the limit of zero permeant concentration;  $c$  represents penetrant concentration;  $a$  and  $b$  are coefficients characteristic of the membrane/permeant interaction. Equation (7) will be used here, since it is more suitable in cases where the diffusion coefficient is more strongly dependent on concentration. For water permeation through membrane 2, eq. (7) was derived to be

$$D = D_0 \exp(b[\text{H}_2\text{O}]_{\text{feed}}) \quad (8)$$

From eq. (8), we obtained

$$J = (D_0/bl) \{ \exp(b[\text{H}_2\text{O}]_{\text{feed}}) - 1 \} \quad (9)$$

Obtained values of various constants in eqs. (5) and (9) are summarized in the

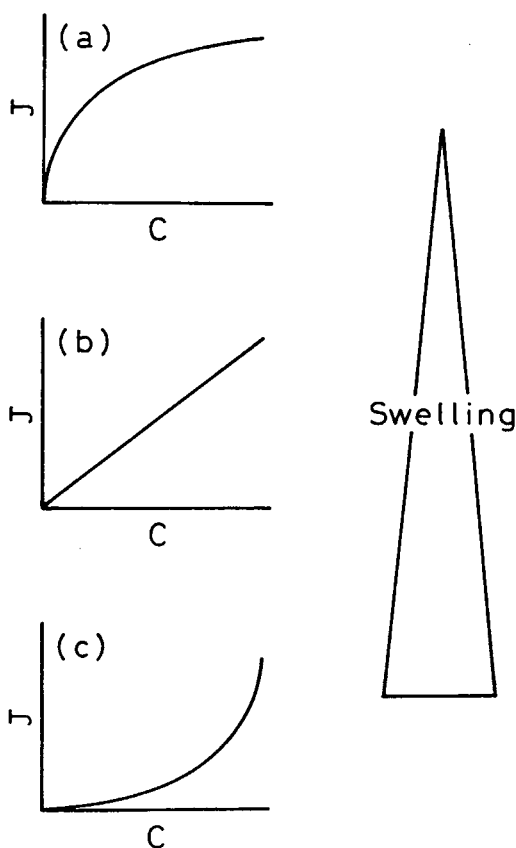


Fig. 10. Schematic profile change of permeation through membranes.

tables in Figures 6 and 7. Profile change of water permeation through membranes 1–3 are summarized schematically in Figure 10. Permeation profiles changed from (a) to (c) via (b) with increase of degree of membrane swelling by  $H_2O$ . When the membrane, membrane 1, was scarcely swollen with  $H_2O$ , pyridine moiety played an important role as a fixed carrier for water permeation. As a result, the relationship between water flux and water concentration in feed gave a typical Michaelis–Menten profile. In the case that, the degree of membrane swelling being medium because of the introduction of cationic charge site, this was the case of membrane 2, the relationship between water flux and its feed concentration obeyed eq. (5) as often observed in the membrane permeation phenomena. When the membrane, such as membrane 3, was swollen with water because of about 90% of pyridine moiety to be converted into pyridinium cationic charge site in the membrane, the water flux may be represented by eq. (9).

Next, we describe about the ethanol permeation through membranes 1–6. An ethanol permeation profile through membrane 1 showed an ethanol-feed concentration-dependent one. So the profile might be interpreted by eq. (10), which was the similar to eq. (9):

$$J = (D_0/bl) \{ \exp(b[\text{EtOH}]_{\text{feed}}) - 1 \} \quad (10)$$



The conversion of about 50% of pyridine moiety into pyridinium cation by iodomethane caused the suppression of membrane swelling by ethanol, which was not detectable by change of area, thickness, or weight, so that the flux profile was simulated by eq. (11), which was the similar form to eq. (5):

$$J = (D/l)[\text{EtOH}]_{\text{feed}} \quad (11)$$

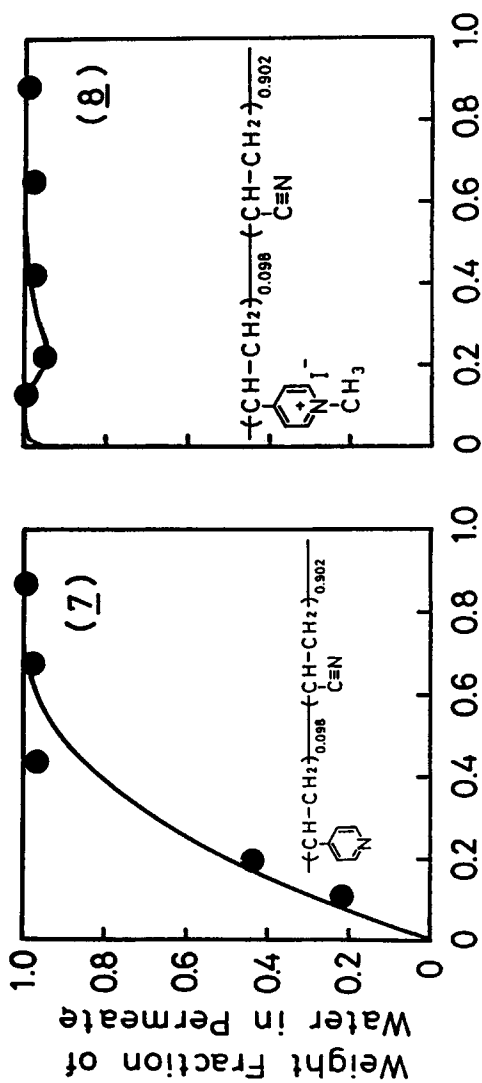
The fraction of quarternization was increased further; the ethanol flux again came to depend on ethanol feed concentration as observed in the ethanol permeation through membrane 3 in Figure 7. This was due to the swelling of membrane with H<sub>2</sub>O by the introduction of the pyridinium cationic charge site (ca. 90% of pyridine moiety in membrane 1) into the membrane [see Fig. 7(a)]. On the other hand, in the ethanol permeation through membranes quarternized by iodobutane, membranes 4 and 5, the magnitude of ethanol flux dependence on its feed concentration seemed to get higher with increase in the fraction of quarternization till around 40%. But in membrane 5, all of which pyridine moiety was quarternized by iodomethane, the membrane swelling by ethanol was suppressed, and the ethanol flux obeyed eq. (11). As for ethanol permeation through membrane 6, ethanol flux was dependent on its feed concentration and simulated by eq. (10), although water permeation obeyed eq. (4). When the quarternization reagent was iodoctane, its hydrophobicity might attract ethanol, which is more hydrophobic than water. As a result, the relationship between ethanol flux through membrane 6 and its feed concentration gave a feed-concentration-dependent profile.

#### *Pervaporation through Membranes 7 and 8*

Figure 11 gives results of pervaporation experiments, where weight fractions of water permeates through membranes 7 and 8 were plotted against those in feeds. Figure 12 shows the effect of feed composition on the separation factor  $\alpha$  and total fluxes. These experiments were carried out at 15°C. Swelling of the membrane, which meant detectable membrane swelling, was scarcely observed during the pervaporation experiments. These two membranes preferentially permeated water. Especially, the introduction of the pyridinium cationic charge site into the membrane led to both the increase in selectivity toward water and that in flux value, as we expected.

In order to study the permeation mechanism, we separated water and ethanol components as done in the previous chapter, so that each component flux could be plotted against its feed concentration. These separated fluxes are shown in Figure 13.

The relationship between ethanol flux through membrane 7 and its feed concentration gave a straight line, which passed through the origin [Fig. 13(b)] at the low ethanol concentration, where the ethanol concentration was below ca. 10 mol dm<sup>-3</sup>. This implies that ethanol was permeated through membrane 7 without any specific interaction between ethanol and the membrane. The ethanol flux, however, increased abruptly in the high ethanol concentration region, where the ethanol concentration was over ca. 10 mol dm<sup>-3</sup>. This sudden increase of ethanol flux was attributed to the swelling of the membrane. The effect of swelling of the membrane must be cancelled in order to



### Weight Fraction of Water in Feed

Fig. 11. Effect of feed composition on the separation of water-ethanol mixture through membranes 7 and 8 at 15° C. Downstream pressure, 400 Pa (3.0 torr).

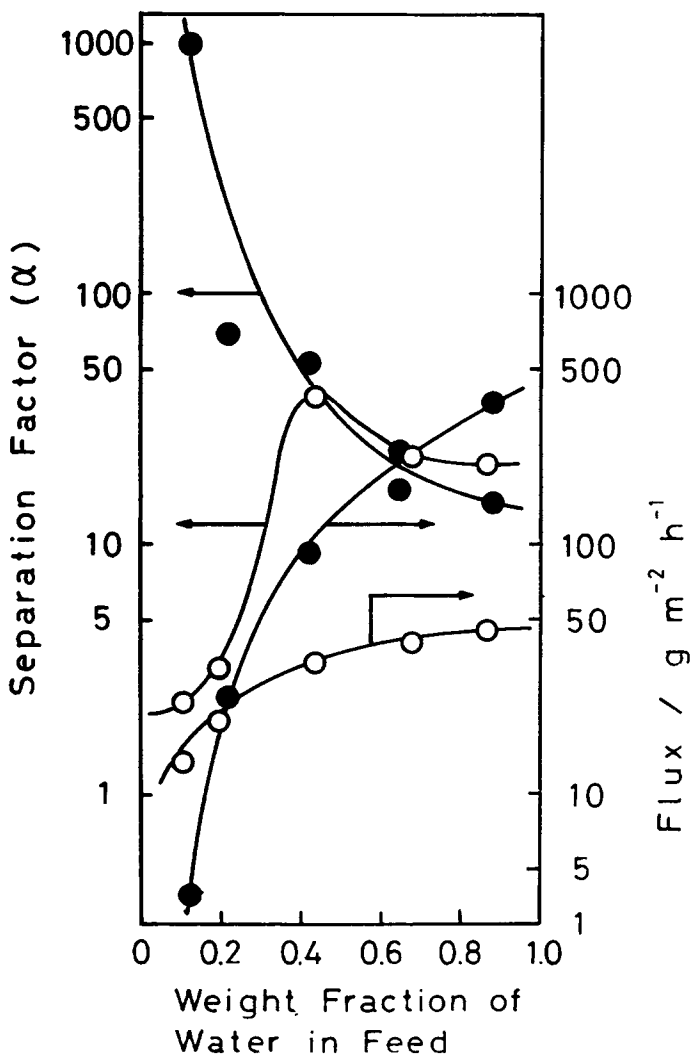


Fig. 12. Effect of feed composition on flux and separation factor ( $\alpha$ ) in water-ethanol pervaporation through membranes 7 and 8 at 15°C. Downstream pressure, 400 Pa (3.0 torr); (○) membrane 7; (●) membrane 8.

evaluate membrane permeation properties. Ethanol fluxes through membrane 7 in Figure 13(b) allowed us to correct the swelling effect. Assuming the fluxes obtained by the nonswelling membranes obey the solid line in Fig. 13(b), ethanol fluxes deviated from the straight line were forced to conform to a straight line. The corrected water fluxes were calculated by<sup>7,8,12</sup>

corrected water flux = observed water flux

$$\times (\text{corrected ethanol flux} / \text{observed ethanol flux}) \quad (13)$$

Such corrected water fluxes are shown in Figure 13(a). These corrected fluxes imply that the permeation of water through membrane 7 does not obey eqs.

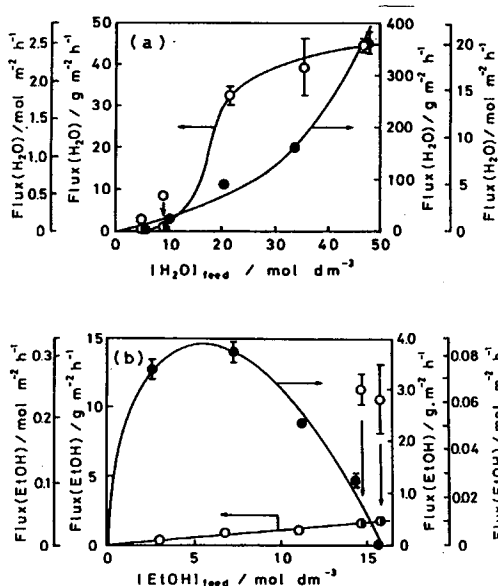


Fig. 13. Relationship between water (a) and ethanol (b) fluxes of pervaporation through membranes 7 and 8, and their concentration in the feed. Downstream pressure, 400 Pa (3.0 torr); operating temperature, 15°C; (○) membrane 7; (●) corrected flux through membrane 7; (●) membrane 8.

(a)

	Membrane 7	Membrane 8
$D_0$ ( $m^2\ h^{-1}$ )	—	$1.72 \pm 0.00 \times 10^{-9}$
$b$ ( $mol^{-1}\ m^3$ )	—	$5.64 \pm 0.00 \times 10^{-6}$

(b)

	Membrane 7	Membrane 8
$P$ ( $m^2\ h^{-1}$ )	$4.33 \pm 2.17 \times 10^{-8}$	—

(4), (5), or (9), and show Type II mechanism<sup>12</sup> as observed in a permeation of water through poly(acrylic acid-co-acrylonitrile) membrane.

On the other hand, the water flux dependence on its feed concentration through membrane 8 [Fig. 13(a)] showed a concentration-dependent profile and was represented by eq. (9). The ethanol permeation through membrane 8 gave a curious profile. All through the present article, only this flux profile is impossible to explain.

### How To Obtain Membranes for Industrial Application

Our final object in the present article is to obtain novel membranes which can be used for industrial utilization. In this case, the membrane is requested to have the following properties as we described in the Introduction: Separation factor toward water must be over 50 and the flux value must reach over  $500\ g\ m^{-2}\ h^{-1}$ .<sup>43</sup> Comparing our obtained results under the operating

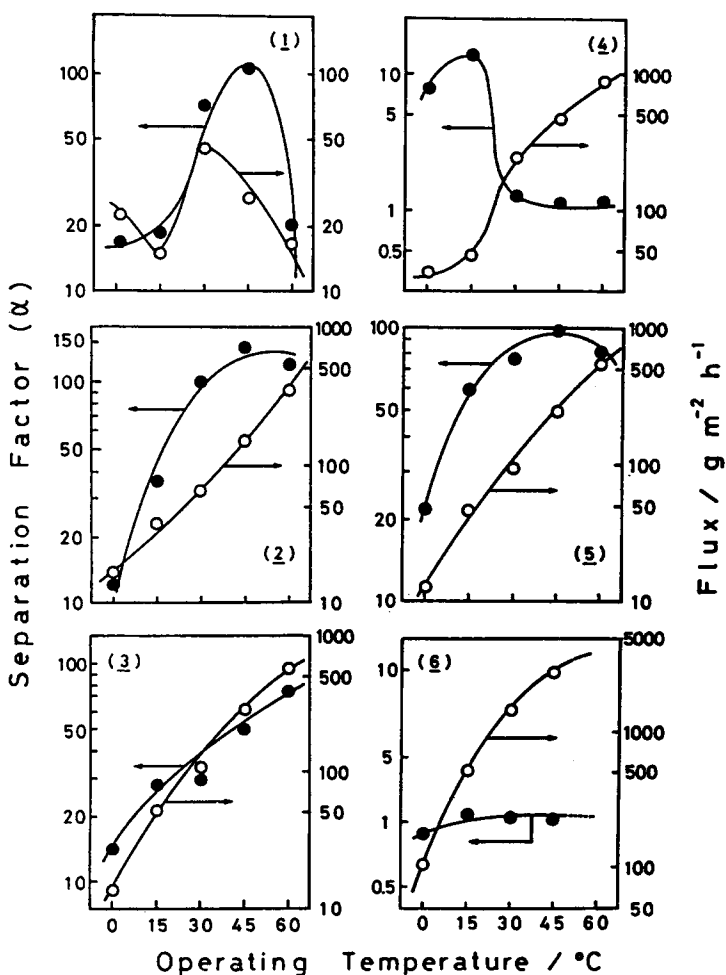


Fig. 14. Effect of operating temperature on water-ethanol pervaporation through membranes 1-6. Weight fraction of water in feed, around 0.87; downstream pressure, 400 Pa (3.0 torr).

temperature of 15°C in Figs. 4, 5, 6, and 12 with these two target values, some membranes satisfied target values of separation factor but not flux value. The others reached target flux value but were still short of their goal of separation factor.

We previously reported that the membrane performance, such as the selectivity and the flux value, is dependent on the operating temperature.<sup>3,5,6,9,10,12,13</sup> Many researchers also reported the dependence of pervaporation results on the operating temperature.<sup>63-66</sup> Accordingly, changing the operating temperature is one of the plausible ways to improve the membrane performance. On the basis of this idea, the effect of operating temperatures on the permeation through present membranes was investigated. The dependence of the membrane permeabilities on the operating temperatures is summarized in Figures 14 and 15.

To conclude, pervaporation results through membranes 3 and 5 under the operation temperature of 60°C hit the target. Hereafter we survey the effect

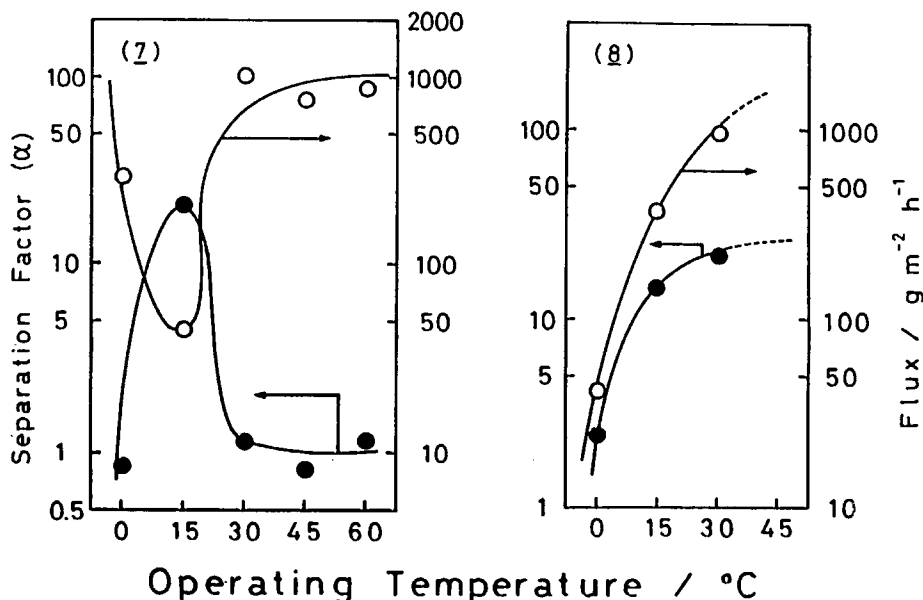


Fig. 15. Effect of operating temperature on water-ethanol pervaporation through membranes 7 and 8. Weight fraction of water in feed, around 0.88; downstream pressure, 400 Pa (3.0 torr).

of the operating temperature on membrane performance. The flux value through quarternized membranes increased monotonously with raising the operating temperature, while that through membranes 1 and 7, which were parent membranes having no cationic charge site, showed a complicated profile. As for the explanation of this difference, we considered it as follows: As for membranes 1 and 7, the raising of the operating temperature caused the increase of diffusivity, and the decrease of solubility or (and) the decrease of interaction, such as hydrogen-bonding interaction, between fixed carrier (pyridine moiety) and water (or ethanol). These two or three effects gave such a complicated profile as shown in Figures 14 and 15. On the other hand, quarternized membranes were anticipated to form a partial ionomer structure in the membrane since they had a pyridinium cationic charge site, while membranes 1 and 7 did not. However, such an ionomer structure of quarternized membrane was not able to be detected by our electron microscopic technique. Temperature dependence of the storage ( $E'$ ) and loss ( $E''$ ) moduli obtained by dynamic-mechanical analysis might prove the presence of ionomer structure in the membrane; however, we did not measure those. With rising operating temperature, the ionomer structure in the membrane broke to dilate the polymer lattice. As a result, the flux values increased in membranes quarternized. On the other hand, such dilation of the polymer lattice might be insufficient for decrease of selectivity toward water under those conditions through membranes 2, 3, 5, and 8. Selectivity of membranes 2 and 5 seemed to show the profile which gave the maximum value at around 45°C, which indicated that the dilation of polymer was effective toward selectivity of membranes 2 and 5 over around 45°C. Especially, selectivity of membrane 4 was very sensitive toward operating temperature; in other words, the dilation

effect of polymer might be more effective toward membrane 4 than any other membranes quarternized. Considering both the separation factor (selectivity toward water) and the flux number, membranes 3 and 5 may be more suitable membranes for separation of water from water-ethanol mixture among present membranes in this article at the operating temperature at 60°C.

### CONCLUSION

The incorporation of cationic charge site into poly(4-vinylpyridine-co-acrylonitrile) membrane attained to not only improvement of separation factor (selectivity toward water) but also that of flux value in the separation of water-ethanol mixture by pervaporation technique as reported on charge-mosaic membranes<sup>67,68</sup> or some ion-exchange membranes.<sup>29,36</sup> Especially, poly(1-methyl-4-vinylpyridinium iodide-co-acrylonitrile) (membrane 3) (quarternization fraction, 89.5%; mol fraction of pyridinium moiety, 0.034) and poly(1-butyl-4-vinylpyridinium iodide-co-acrylonitrile) (membrane 5) (quarternization fraction, 100%; mol fraction of pyridinium moiety, 0.038) attained target values, such as the separation factor toward water being over 50 and the flux number over 500 g m<sup>-2</sup> h<sup>-1</sup>). The incorporation of cationic charge site into the membrane is one of feasible methods of obtaining suitable membranes for water-permeable membrane in the separation of water-ethanol mixture as reported by Wenzlaff et al.<sup>29</sup> and Cabasso et al.<sup>36</sup>

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