

Dehydration of Water/Ethanol Mixtures by Pervaporation Using Modified Poly(vinyl alcohol) Membrane

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ABSTRACT: Dehydration of organic compounds can be achieved economically with pervaporation process. For example, in an ethanol plant, applying a fermentation, distillation-pervaporation combined process has clear advantage against the pure distillation for saving energy. The purpose of this paper is to develop new membranes with high selectivity and acceptable permeation rate for the separation of alcohol/water systems. Novel composite membranes were prepared by casting an aqueous solution of poly(vinyl alcohol) and poly(styrenesulfonic acid) in ultrathin film on a microporous polyacrylonitrile supporting membrane, evaporating the solvent, and heat-curing at 120°C for 2 h. The composite membranes were soaked in an aqueous solution of multi-valent metal salts and ionic cross-linked. The novel composite membranes were found to have high separation factor of 1000—2000, and also good permeation rate of 0.1—0.2 kg m⁻² h⁻¹ by pervaporation for 95 wt% ethanol aqueous solution at 60°C, and also 43 as separation factor for methanol/water system, 13900 as separation factor for iso-propanol/water system, 17900 as separation factor for *t*-butanol/water system using 95 wt% alcohol concentration at 60°C.

KEY WORDS Dehydration / Pervaporation / Poly(vinyl alcohol) Membrane / Intermolecular Cross-Link / Ionic Cross-Link / Ethanol / Differential Scanning Calorimetry Measurement /

In recent years there has been increased interest in the use of the pervaporation membrane process¹⁻³ for separation of organic liquid mixtures. A major advantage of this process is the ability of separation of azeotropic mixtures such as water/ethanol system.⁴⁻⁷ Many hydrophilic polymer membranes, such as poly(vinyl alcohol) (PVA),⁸⁻¹⁰ cellulose,¹¹ polysaccharide,¹²⁻¹⁶ polyion complex consisting of poly(acrylic acid) and polycation,¹⁷ sulfonated polyethylene,¹⁸ poly(hydroxymethylene),¹⁹ poly(maleimide-*co*-acrylonitrile),^{20,21} and poly(sulfone-amide)²² etc. have been investigated for the dehydration of water/ethanol azeotropic mixture. The composite membrane (named GFT membrane) prepared by casting an aqueous solution of poly(vinyl alcohol) and maleic acid in ultrathin film

on a microporous polyacrylonitrile supporting membrane, evaporating the solvent, and heat-curing, has been only commercialized by GFT Gesellschaft Fur Trenntechnik mbH Germany.^{23,24} The object of this research is to develop a water permselective membrane having high selectivity and good permeation rate, and long-term durability in order to save energy cost.

We investigated in detail the composite membrane obtained from PVA and poly(styrenesulfonic acid) (PSSA) and found that the intermolecular cross-links between PVA and PSSA and ionic cross-links with multi-valent metal ions increased significantly the selectivity of membrane for water/ethanol by pervaporation. In this paper, we report the effects of intermolecular cross-links and ionic

cross-links with metal ions on the pervaporation performance, and discuss a reason for the marked increase of the permselectivity.

EXPERIMENTAL

Materials

PVA having a polymerization degree of 2000 was obtained from Nacalai Tesque Inc. PSSA was prepared by sulfonation of polystyrene. Polystyrene having a polymerization degree of 1000–1400 obtained from Nacalai Tesque Inc. was dissolved in carbon tetrachloride and concentrated sulfonic acid was added under nitrogen atmosphere. The mixture was reacted at 60°C for 4 h.

The reaction mixture was added to dehydrated ether and formed a yellow gummy precipitate. Carbon tetrachloride was added to the precipitate for dissolving it. The solution was added to dehydrated ether to form a precipitate. This procedure was repeated four times to purify the reaction product. An ultrafiltration membrane (DUY-L) composed of polyacrylonitrile was obtained from Daicel Chemical Ind. Ltd. Ethanol and other reagents were of reagent grade and were used without further purification.

Membrane Preparation

PVA (1.8 g) and PSSA (1.2 g) were dissolved in distilled water (24 g) at 80°C and the solution was cooled at room temperature, and then ethanol (14 g) was mixed to coat homogeneously. The solution was coated on an ultrafiltration membrane composed of polyacrylonitrile by a spin coating machine (800 rpm). The coated membrane was dried at 40°C for 1 h and then subjected to heat-curing at 120°C for 2 h to effect cross-linking structure. The membrane was soaked in an ethanol aqueous solution for 1 h and a 0.1 N BaCl₂ aqueous solution for 1 h, and dried at room temperature.²⁵

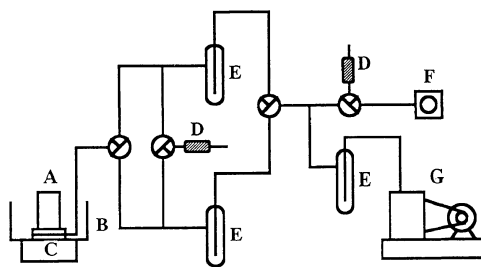


Figure 1. Schematic pervaporation apparatus: A, permeation cell; B, thermostated water bath; C, magnetic stirrer; D, vent to atmosphere; E, collection trap; F, pirani gauge; G, vacuum pump.

Prevaporation

The schematic pervaporation apparatus is shown in Figure 1. The permeation cell was made of stainless steel. The membrane was supported on a sintered stainless steel disc. The effective membrane area was 15.2 cm². Pervaporation experiments were carried out by maintaining one side of a membrane to which a mixture of water/ethanol was fed batch-wise at atmosphere pressure and the other permeate side at reduced pressure not more than 0.3 mmHg (40 Pa). The active surface of the membrane was directed to the feed side and the feed mixture was added on the surface and stirred at constant temperature.

The permeated vapor was collected in liquid nitrogen traps and *n*-propanol was added as an internal standard. The composition of the feed mixture and permeate were determined by gas chromatograph equipped with 1-m long columns packed with Polapak Q.

The separation factor of water to ethanol ($\alpha_{\text{EtOH}}^{\text{H}_2\text{O}}$) is defined as follows.

$$\alpha_{\text{EtOH}}^{\text{H}_2\text{O}} = \frac{Y_{\text{H}_2\text{O}}/Y_{\text{EtOH}}}{X_{\text{H}_2\text{O}}/X_{\text{EtOH}}} \quad (1)$$

where X_{EtOH} and $X_{\text{H}_2\text{O}}$ are ethanol and water contents (wt%) in the feed mixture, respectively and Y_{EtOH} and $Y_{\text{H}_2\text{O}}$ are ethanol and water contents (wt%) in the permeate, respectively.

Degree of Hydration

The membrane was immersed in distilled water in flask, and the flask was placed in a thermostated bath at 25°C. After 20 h, the membrane was quickly taken out, wiped with tissue paper and weighed in a pre-weighed closed flask. The membrane was dried under reduced pressure at 60°C for 24 h and weighed again. The degree of hydration ($H\%$) was expressed as a relative weight increase.

Differential Scanning Calorimetry (DSC) Measurement

The membrane was immersed in distilled water in flask, and the flask was placed in a thermostated bath at 25°C. After 20 h, the membrane was removed, wiped with tissue paper, and about 8 mg of the water-swollen membrane were sealed in aluminum pan.

DSC measurement of the sealed sample was performed by heating from -60°C to 20°C at the rate of $2.5^\circ\text{C min}^{-1}$ after cooling to -60°C and holding for 10 min by using a Perkin Elmer Inc. Model 7 DSC.

RESULTS AND DISCUSSION

Preparation of PVA/PSSA Composite Membrane

The composite membrane can be prepared by casting the solution consisting of PVA and PSSA on a polyacrylonitrile ultrafiltration membrane and subjecting it to heat-curing to produce intermolecular cross-links between PVA and PSSA. The infrared spectra of a heat-cured membranes were observed, and new absorption bands were found at 1170 cm^{-1} and 1460 cm^{-1} . These two absorption bands became stronger with increasing the heat-curing period, and the absorption band attributable to hydroxyl groups was reduced as reported by Nishimura *et al.*²⁵ They reported that the $\text{R-O-SO}_2\text{-R}'$ bond is formed by dehydration between two polymers under heat-curing, and the interpolymer is cross-linked and water-insoluble. The effects of

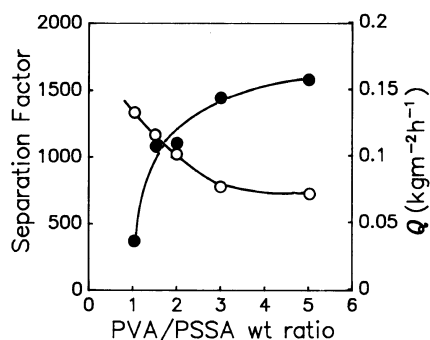


Figure 2. Effects of PVA/PSSA polymer composition in casting solution on pervaporation performance for 95 wt% ethanol aqueous solution at 60°C with Na^+ counter ion: ●, separation factor; ○, Q ($\text{kgm}^{-2}\text{h}^{-1}$).

composition and concentration of a casting solution, temperature and period of heat-curing and revolution speed of spin coating machine on the pervaporation performance of PVA/PSSA composite membranes have been investigated.

The effects of PVA/PSSA composition ratio on the separation factor and permeation rate for 95 wt% ethanol aqueous solution at 60°C by pervaporation are shown in Figure 2. The separation factor increased considerably with an increase of PVA/PSSA composition ratio. The permeation rate decreased with increase of the ratio of PVA/PSSA composition. These results can be explained by increase of hydrophilicity and hydration with decrease of PVA/PSSA composition ratio. The PVA/PSSA composition ratio of 1.5 (wt ratio) seems to be the best condition in consideration of the separation factor and permeation rate, because a compact and rational separation system can be realized by using the membrane having larger permeation rate and adequate separation factor ($\alpha > 1000$) and it is possible to decrease cost. A PVA/PSSA composition ratio of 1.5 (wt ratio) was used in further experiments.

It is interesting that the composite membrane coated by only PVA exhibits a high separation factor of approximate 1600. Huang *et al.* have described that the separation factor

of PVA membrane, not composite membrane was approximate 50 for 95 wt% ethanol aqueous solution at 40°C.⁹ The separation factor of PVA composite membrane is very high compared with that of PVA membrane. The reason for this is considered the high separation factor of PVA composite membrane due to a composite structure. PVA/PSSA membrane prepared by non-coating did not exhibit high separation factor.

The pervaporation performance of this membrane was compared with GFT membrane. The separation factor and permeation rate of GFT membrane have been reported to be 9500 and $0.01 \text{ kg m}^{-2} \text{ h}^{-1}$ for 95 wt% ethanol aqueous solution at 80°C, respectively.²³ The separation factor of GFT membrane is higher and permeation rate lower than PVA/PSSA membrane. PVA/PSSA membrane having larger permeation rate and adequate separation factor ($\alpha > 1000$) is favorable to be put to practical use, because the membrane area can make smaller and a smaller apparatus is required for industrial use, which decreases cost.

Figure 3 shows the effect of heat-curing temperature on both separation factor and permeation rate for 95 wt% ethanol aqueous solution at 60°C. The heat-curing period was 2 h. The heat-curing temperature has strong influence on pervaporation performance. At low temperature of 100–120°C, a smaller separation factor and much larger permeation rate were obtained. This behavior is expected for poor cross-links and large hydration of the membrane. With increasing the temperature, the permeation rate decreased and the separation factor increased markedly, due to increase of cross-links in membrane. At 120°C, the separation factor had a maximum value, and at higher temperature than 120°C, both the separation temperature and the permeation rate decreased. The reason seems that the amount of SO_3H groups decrease immoderately by the excess intermolecular cross-linking reaction. The heat-curing tem-

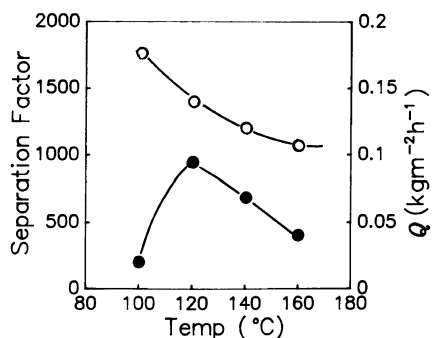


Figure 3. Effects of heat-curing temperature on pervaporation performance for 95 wt% ethanol aqueous solution at 60°C with Na^+ counter ion and the heat-curing period was fixed 2 h: ●, separation factor; ○, Q ($\text{kg m}^{-2} \text{ h}^{-1}$).

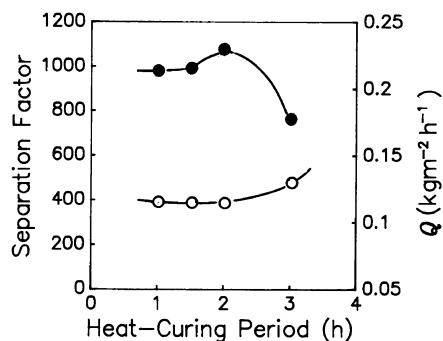


Figure 4. Effects of heat-curing period on pervaporation performance for 95 wt% ethanol aqueous solution at 60°C with Na^+ counter ion: ●, separation factor; ○, Q ($\text{kg m}^{-2} \text{ h}^{-1}$).

perature of 120°C was used in further experiments.

The effect of heat-curing period on the pervaporation performance was investigated at 120°C. The results obtained are shown in Figure 4. Membrane performance did not change significantly with heat-curing period of 1–2 h, but with heat-curing period of 3 h separation factor decreased slightly. A heat-curing period of 2 h was used in further experiments.

The effect of polymer concentration in the casting solution on the pervaporation performances for 95 wt% ethanol aqueous solution at 60°C was investigated at various concentra-

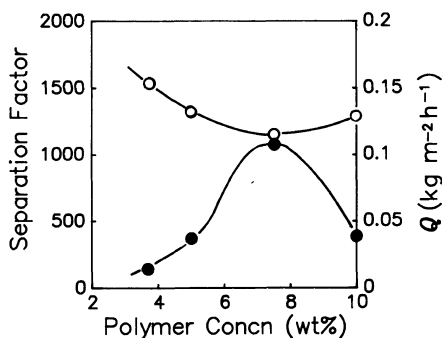


Figure 5. Effects of polymer concentration in the casting solution on pervaporation performance for 95 wt% ethanol aqueous solution at 60°C with Na⁺ counter ion: ●, separation factor; ○, Q (kg m⁻² h⁻¹).

tions in the casting solution with polymer composition of PVA/PSSA wt ratio 1.5 and heat-cured at 120°C for 2 h. The results are shown in Figure 5. When the polymer concentration was 3.5–7.5 wt%, the separation factor increased markedly and permeation rate decreased slightly. For 7.5 wt% polymer concentration, the separation factor was maximum. In order to decrease the thickness of coating layer, it is necessary that the polymer concentration decreases as possible, but these results indicate that pinholes exist in the coating layer for the region of less than 7.5 wt%.

When the polymer concentration was 10 wt%, the separation factor decreased and permeation rate increased. The behavior will be caused by pinholes in the coating layer, because the viscosity of polymer solution is very high and not preferable for coating by a spin coating machine. The polymer concentration of 7.5 wt% was used in further experiments.

The effects of revolution speed of a spin coating machine on pervaporation performance were examined and are shown in Figure 6. When the revolution speed was 800–1000 rpm, the separation factor was maximum. At more than 1000 rpm it is considered that the pinholes form in the coating layer. A revolution speed of 800 rpm was used in

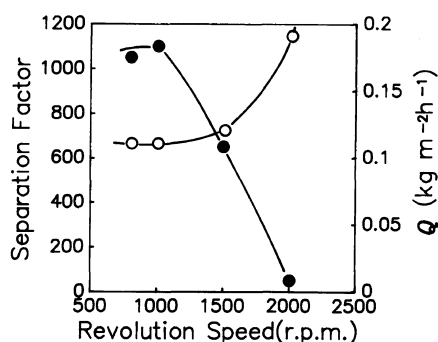


Figure 6. Effects of revolution speed of spin coating machine on pervaporation performance for 95 wt% ethanol aqueous solution at 60°C with Na⁺ counter ion: ●, separation factor; ○, Q (kg m⁻² h⁻¹).

further experiments.

DSC Investigation of the State of Water

DSC analysis has been often used to estimate the amounts of free, freezable bound and non-freezing water in water-swollen membranes.^{26–35} Free water is defined as water which has the same phase transition temperature as bulk water.²⁸ Freezable bound water is water having a phase transition temperature lower than 237 K. This depression is usually ascribed to the weak interaction of the water with the polymer chain of membrane²⁹ and/or capillary condensation in the membranes.^{30,31} Non-freezing water is defined as water which has no detectable phase transition from 273 to 200 K.³² Water is supposed to be influenced by strong interaction with the polar moieties of the polymer chain.

In most investigations,^{28–30,33} the melting enthalpy of water at 273 K has been used to calculate the amount of freezable bound water in membranes, although the transition temperature is clearly lowered.³⁴ For supercooled bulk water, the crystallization enthalpy, $\Delta H(T)$, is known to be lower than that of bulk water at 273 K,³⁵ as expressed by:

$$\Delta H(T) = \Delta H(273) - \int_T^{273} \Delta C_p dT \quad (2)$$

Where ΔC_p is the difference of heat capacity of ice and super-cooled water. The same relation may be applied to freezable bound water.

Figure 7 shows DSC heating curves of water-swollen PVA/PSSA membranes (not composite membrane) prepared at various heat-curing temperatures. Table I shows the degree of hydration and amounts of free, freezable bound and non-freezing water.

Below 100°C of heat-curing temperature, the isolated peaks of around 273 K and near 263 K were found. This indicates that there

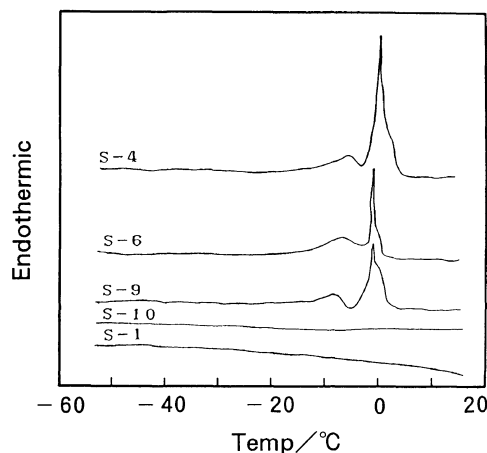


Figure 7. DSC heating curves of water-swollen PVA/PSSA membranes: heating rate, $2.5^\circ\text{C}\cdot\text{m}^{-1}$.

are at least two states of freezable water in the membrane. *i.e.*, free water (T_1 , 273 K) and freezable bound water (T_2 , near 263 K). With increasing heat-curing temperature, the two peak were not observed. Table I shows also the phase transition temperature for free water and freezable bound water observed in the heating process. With increasing heat-curing temperature, T_1 did not change but T_2 became lower; the degree of hydration and the amounts of the freezable and non-freezing water decreased, but the weight ratio of non-freezing water to total water in membrane increased.

The states of water in PVA membranes were investigated by Higuchi *et al.*,²⁶ and it has been reported that the weight ratio of non-freezing water to total water increases with decrease of the degree of hydration ($H\%$) and all water in the membrane of $H \leq 35\%$ becomes non-freezing water. These results are consistent with our results observed in PVA/PSSA membranes. Moreover, it is interesting that the amount of freezable bound water in the ionic cross-links membrane with Ba^{2+} (S-6) decreases and the weight ratio of non-freezing water to total water increases.

On the other hand, in studies on solute permeation through hydrogel membrane, free volume theory^{36,37} or pore theory³⁸ has been

Table I. Characteristics and phase transition temperature of water-swollen PVA/PSSA membrane

Sample No.	Heat-curing	Ion	H wt%	Freezable water				N.F. ^c V_3^b	PV Performance ^d
				T_1^a	T_2^a	V_1^b	V_2^b		
S-4	80°C × 2 h	H ⁺	87.8	0	-8.4	38.9	10.3	38.7	$\alpha=96, Q=0.16$
S-6	80°C × 2 h	Ba ²⁺	57.1	0	-8.9	10.4	7.9	38.8	$\alpha=222, Q=0.12$
S-9	120°C × 2 h	H ⁺	57.1	0	-13.9	26.4	16.4	14.4	$\alpha=116, Q=0.14$
S-10	110°C × 2 h	H ⁺	17.4	—	—	0	0	17.4	$\alpha=179, Q=0.14$
S-1	120°C × 2 h	H ⁺	13.8	—	—	0	0	13.8	$\alpha=209, Q=0.14$

^a T_1 , melting temp (°C) of free water; T_2 , melting temp (°C) of freezable bound water.

^b V_1 , concn (wt%) of free water; V_2 , concn (wt%) of freezable bound water; V_3 , concn (wt%) of non-freezable bound water.

^c N.F., Non-freezing water.

^d Pervaporation performance for 95 wt% ethanol aqueous solution at 60°C through PVA/PSSA composite membrane; Q ($\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$).

applied assuming, incorrectly that the water in the membranes is in a single state. There are only a few works on gas^{27,39,40} or solute permeation taking such water states into account.^{29,41} The few works on solute permeation are the studies on the reverse osmosis membrane used for desalination. An inquiry with regard to the relationship between states of water and pervaporation phenomena has not been scrutinized.

Horigome *et al.* have reported that the active layer of the membrane, used for desalination, has only non-freezing water within it, and the solubility of NaCl in the non-freezing water is close to zero,^{29,41} and it is concluded that non-freezing water has a selectivity for the solute such as NaCl and that the properties of the freezable bound water are similar to those of the pure bulk water. Toprak *et al.* proposed from infrared spectra of cellulose acetate membrane that water sorbed in the membrane has a low degree of association and that bonds between water and membrane are considerably weaker than those in liquid water, and the weak bonding of water to membrane is consistent with high mobility, while its low degree of association explains the low solubility of ions and hence the low permeability of membrane to salts.⁴¹

Considering these two reports, our results in Table I can be explained as follows. With increasing heat-curing temperature or introducing the ionic cross-links with Ba²⁺, the amount of freezable water decreases and the weight ratio of non-freezing water to total water in membrane increases. This causes low solubility and low mobility of alcohol in membrane, similar to NaCl, and hence high selectivity for water/alcohol mixtures.

Effects of Metal Salts

By pretreatment of PVA/PSSA composite membrane with the water solution containing metal salts, SO₃H groups in the composite membrane change into metal salts. The effects of the metal salts on the membrane perfor-

Table II. Effects of metal ions on membrane performance for 95 wt% ethanol aqueous solution at 60°C

Metal ions	$Q/\text{kg m}^{-2} \text{h}^{-1}$	$\alpha_{\text{EtOH}}^{\text{H}_2\text{O}}$
H ⁺	0.14	140
Na ⁺	0.11	1040
K ⁺	0.16	780
Cs ⁺	0.15	700
Mg ²⁺	0.11	740
Ca ²⁺	0.12	1090
Ba ²⁺	0.12	1870
Al ³⁺	0.08	1500

mance of PVA/PSSA composite membrane were investigated. The results are shown in Table II.

The separation of alcohol/water mixtures by Nafion hollow fiber membranes was reported by Cabbaso *et al.*⁴² They showed that the permeation rate and separation factor by pervaporation were highly dependent on type of metal ion and for the alkali cation series, the separation factors increased in the following order: H⁺ < Li⁺ < Na⁺ < K⁺ < Cs⁺, but the permeation rates decreased reversely: H⁺ > Li⁺ > Na⁺ > K⁺ > Cs⁺.

However, the separation factors of PVA/PSSA composite membrane for the alkali cation series slightly decreased in the following order: Na⁺ > K⁺ > Cs⁺, and the permeation rate increased reversely: Na⁺ < K⁺ < Cs⁺. Mochizuki *et al.* investigated the separation of water/alcohol mixtures through alginate membrane and reported the influence of alkali cations on the permeation rate.¹⁵ The permeation rate increased in the following order: Li⁺ < Na⁺ < K⁺ < Rb⁺ < Cs⁺, but hardly had any affect on selectivity. This behavior can be explained well by the conformation change and mobility of alginate molecules investigated by CP/MAS ¹³C NMR, water mobility within the alginate membrane, and crystallinity of the membrane. The dependence of the permeation rates of PVA/PSSA composite membrane on alkali cations may be explained by the same reason, and slight decrease of

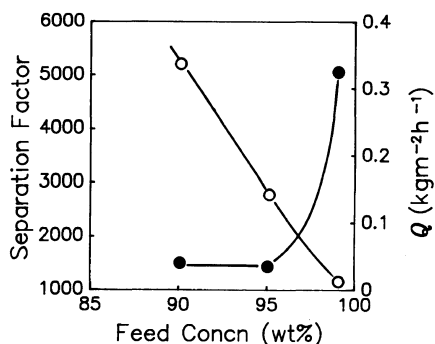


Figure 8. Dependence of separation factor and permeation rate on ethanol concentration at 60°C with Ba²⁺ counter ion: ●, separation factor; ○, Q (kgm⁻²h⁻¹).

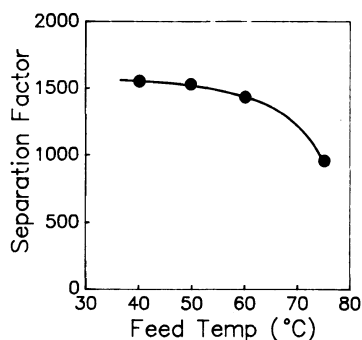


Figure 9. Dependence of separation factor on temperature of 95 wt% ethanol aqueous solution with Ba²⁺ counter ion.

separation factor seems to be reasonable in consideration of the general relationship between permeation rate and separation factor; that is, the separation factor decreases with increasing permeation rate.

For multi-valent counter ions, higher separation factors than potassium or sodium ions were obtained. For the alkali earth cation series, the separation factors markedly increased in the following order: Mg²⁺ < Ca²⁺ < Ba²⁺, since the separation factors increase with increasing electronegativity of metal ions.¹² It is not clear, however, why the divalent metal salts are more effective than the trivalent salt. The reason may be correlated with the conformation of a ionic cross-links between SO₃H groups and divalent metal ions. Ba²⁺ was the most suitable counter ion for selective separation.

Dependence of Permselectivity on Ethanol Concentration

Figure 8 shows the dependence of the separation factor and permeation rate on the composition of ethanol in feed at 60°C. High separation factors were obtained at a high ethanol concentration of more than 95 wt%, and at 99 wt% ethanol aqueous solution, the separation factor of approximate 5000 was obtained. The permeation rate decreases proportionally to water concentration in feed

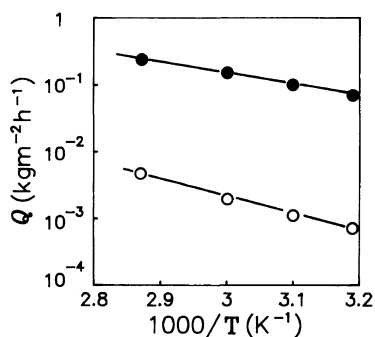


Figure 10. Semi-log plots of partial permeation rates for 95 wt% ethanol aqueous solution with Na⁺ counter ion vs. reciprocal of absolute temperature: ●, water permeation rate (kgm⁻²h⁻¹); ○, ethanol permeation rate (kgm⁻²h⁻¹).

solution.

Effects of Temperature

The effects of temperature on the separation factor and permeation rate for 95 wt% ethanol aqueous solution were investigated. The results are shown in Figures 9 and 10. With increase of temperature, the separation factor decreased a little, and the permeation rates of water and ethanol increased. Temperature increments of 10°C increased the permeation rates by 1.5–2 times. The temperature dependence of permeation rate for each component was expressed by Arrhenius equation. From the Arrhenius equation, the

apparent activation energies for water and ethanol were calculated and the value for water was $7.8 \text{ kcal mol}^{-1}$ and for ethanol $11.6 \text{ kcal mol}^{-1}$. The decrease of separation factor with increase of temperature is due to the higher activation energy for ethanol than that for water. The apparent activation energy $7.8 \text{ kcal mol}^{-1}$ for water is very close to those of PVA membranes cross-linked with amic acid,¹⁰ *i.e.*, $8.8 \text{ kcal mol}^{-1}$ for pure water and about $7.5 \text{ kcal mol}^{-1}$ for 90 wt% ethanol aqueous solution, respectively. The apparent activation energy $11.6 \text{ kcal mol}^{-1}$ for ethanol is close to those in PVA membrane cross-linked with amic acid, about 9 kcal mol^{-1} .

These results indicate that the permeation mechanism is the same for these PVA membranes. That is, according to the free volume theory, the thermal motion of polymer chains in the amorphous regions randomly produces free volume. As temperature increases, the frequency and amplitude of chain jumping increase and the resulting free volume becomes larger, and the diffusion rates of individual permeating molecules and associated permeating molecules are high, so that the total permeation rate is high and separation factor low.

Effects of Down Stream Pressure

Figures 11 and 12 show the effects of the downstream pressure on membrane performance for 95 and 99 wt% ethanol aqueous solution at 60°C , respectively.

The separation factor was not sensitive to the pressure at low downstream pressure, but decreased abruptly with increasing downstream pressure. The separation factor for 99 wt% ethanol aqueous solution decreased more sharply than that for 95 wt% ethanol aqueous solution with increasing downstream pressure. The region of sharp transition of separation factor shifted towards lower downstream pressure with increasing ethanol concentration in the feed solution. Similar to the separation factor, the permeation rate

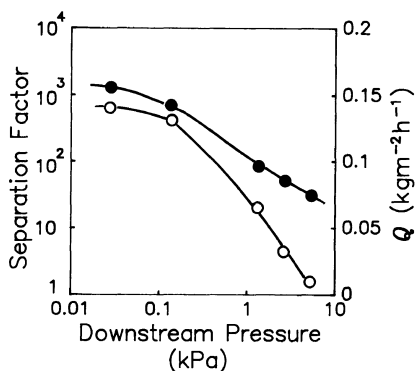


Figure 11. Effects of downstream pressure on membrane performance for 95 wt% ethanol aqueous solution at 60°C with Na^+ counter ion: ●, separation factor; ○, Q ($\text{kg m}^{-2} \text{h}^{-1}$).

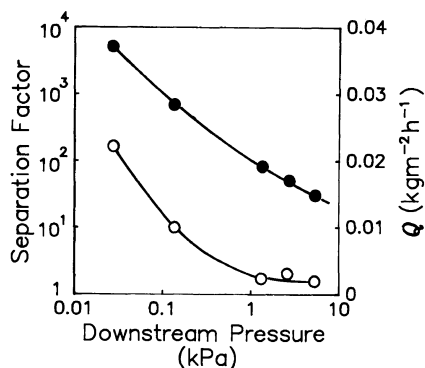


Figure 12. Effects of downstream pressure on membrane performance for 99 wt% ethanol aqueous solution at 60°C with Na^+ counter ion: ●, separation factor; ○, Q ($\text{kg m}^{-2} \text{h}^{-1}$).

decreased with increasing of the downstream pressure. With increasing the ethanol concentration, the region of sharp transition of permeation rate shifted towards lower downstream pressure.

These results can be explained by the partial pressure difference between feed side and permeate side. The partial pressures of water and ethanol for 95 wt% ethanol aqueous solution at 60°C are 5.2 and 42.8 kPa, and for 99 wt% at 60°C , 1.3 and 37 kPa, respectively. When pervaporation is carried out for 95 wt% aqueous solution, the partial pressure of water is close to the downstream pressure, compared

Table III. Separation factors and permeation rates for alcohol and many other organic aqueous solutions with Ba^{2+}

Organic	Organic concn	Temp	$\alpha_{\text{org}}^{\text{H}_2\text{O}}$	Q
	wt%	$^{\circ}\text{C}$		$\text{kg m}^{-2} \text{h}^{-1}$
Methanol	95.5	60	43	0.17
Ethanol	95.3	60	1570	0.15
Iso-propanol	96.0	60	13900	0.15
<i>n</i> -Butanol	95.0	60	18600	0.23
Iso-butanol	95.0	60 </td <td>32800</td> <td>0.20</td>	32800	0.20
<i>t</i> -Butanol	95.0	60	17900	0.21
Acetone	94.9	40	7700	0.14
MEK	95.0	60	17500	0.39
Acetic acid	95.0	60	4700	0.014

to that of ethanol in the feed solution. So that the partial pressure difference of water across the membrane, which results in the driving force of permeation, is more affected by the downstream pressure than that of ethanol. Thus, both the separation factor and permeation rate decrease with increase of downstream pressure.

Similar results have been reported for water/tetrahydrofuran (THF) separation with cuprophane membranes and for water/iso-propanol with cellulose membrane.⁴³⁻⁴⁵

Effects of Molecular Size and Shape of Water Soluble Organic Compounds

Table III shows the separation factors and permeation rates of alcohols and many other organic aqueous solutions by pervaporation. The water selectivities for higher molecular weight alcohol/water mixtures were much higher than that for the ethanol/water system, with nearly complete separation in many cases. This is no doubt due to lower diffusivity because of the large molecular size of these alcohols and their lower solubility in the highly polar membrane environments, and their lower volatility.

Figure 13 shows the relationship between logarithm of separation factors and stoke's radius of organic compounds. Separation factors increased as stoke's radius of the

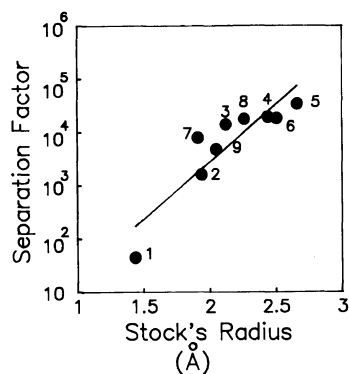


Figure 13. Relationship between separation factor for 95 wt% organic aqueous solution at 60°C with Ba^{2+} counter ion and stoke's radius of various organic compounds: 1, methanol; 2, ethanol; 3, iso-propanol; 4, *n*-butanol; 5, iso-butanol; 6, *t*-butanol; 7, acetone; 8, methyl ethyl ketone (MEK); 9, acetic acid.

alcohols and other organic compounds increased. The correlation coefficient between logarithm of separation factors and stoke's radius of organic compounds was calculated to be 0.915, an adequate correlation.

Long-Term Durability

In order to put PVA/PSSA composite membrane to practical use, long-term durability of pervaporation performance is very important, but it has been reported that the separation factor and permeation rate of the polyacrylic acid-potassium salt composite membrane

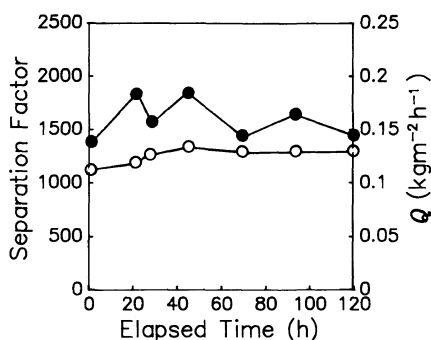


Figure 14. Long-term durability of membrane performance for 95 wt% ethanol aqueous solution at 60°C with Ba²⁺ counter ion: ●, separation factor; ○, Q (kgm⁻²h⁻¹).

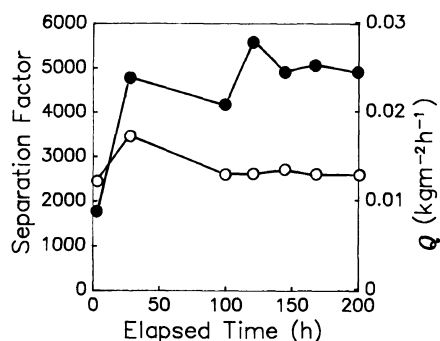


Figure 15. Long-term durability of membrane performance for 99 wt% ethanol aqueous solution at 60°C with Ba²⁺ counter ion: ●, separation factor; ○, Q (kgm⁻²h⁻¹).

cross-linked with diamine and diepoxide decrease with measuring time about 1.5 h.¹⁷ Therefore, the durability of pervaporation performance was investigated for 95 and 99 wt% ethanol solutions at 60°C. These results are shown in Figures 14 and 15, respectively.

The pervaporation performance for 95 wt% at 60°C was kept approximately 1450 as the separation factor and 0.13 kgm⁻²h⁻¹ as the permeation rate after 120 h. For 99 wt% at 60°C, the separation factor increased markedly from the start of experiment to 27 h, and was kept around 5000 after 200 h and the permeation rate did not change significantly

and was kept about 0.013 kgm⁻²h⁻¹. This confirms that the separation factor and permeation rate did not decrease in a short time as did the polyacrylic acid-potassium salt composite membrane cross-linked with diamine and diepoxide.

CONCLUSIONS

The experimental results can be summarized as follows:

(1) Composite membranes were prepared by coating an aqueous solution of PVA and PSSA polymer mixture on polyacrylonitrile porous membrane, cross-linking the coating layer with heat-curing, and soaking in aqueous solution of metal salts.

(2) The membranes were found to have high separation factors by pervaporation, ranging from 1000–2000, and good permeation rates of 0.1–0.2 kgm⁻²h⁻¹ for 95 wt% ethanol aqueous solution at 60°C, and 43 as the separation factor for methanol/water system, 13900 as the separation factor for isopropanol/water system, 17900 as the separation factor for *t*-butanol/water system using approximate 95 wt% aqueous solution at 60°C.

(3) Ba²⁺ was the most suitable counter ion among the many kinds of cations for selective separation.

(4) This membrane indicated sufficient long-term durability in 95 and 99 wt% ethanol aqueous solutions at 60°C.

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