물-에탄올 혼합물의 투과증발용 분리막 제조

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Preparation of Pervaporation Membranes for Separation of Water-Ethanol Mixture

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요 약 : 가교된 poly(vinyl alcohol) (PVA) 막에 의한 물-에탄올 혼합물의 투과증발실험을 수행하였다. 물에 대한 선택투과성을 높이기 위하여 단순 가교 PVA막의 한쪽 표면을 monochloroacetic acid나 propane sultone과 반응시켜 표면이 물에 대한 친화력이 높도록 하였다. 그 결과 mono-chloroacetic acid로 개질된 막 (나트륨염형)의 성능은 표면 개질되지 않은 막에 비하여 투과도 및 선택투과도가 각각 2배 및 4배 이상 증가하였다. 그러나 propane sultone으로 개질된 막의 성능은 기대와는 달리 크게 변하지 않았다.

Abstract : Pervaporation of water-ethanol mixture through crosslinked poly(vinyl alcohol) (PVA) membranes was performed. In order to enhance the permselectivity of water, one side of the crosslinked PVA membrane was hydrophilically modified by reacting either monochloroacetic acid or propane sultone. The membrane (sodium carboxylate form) modified by monochloroacetic acid exhibited that the flux and permselectivity increase more than two and four times, respectively, compared to those of the simply crosslinked PVA membrane. However, the membrane modified by propane sultone showed that the transport properties remain almost unchanged.

INTRODUCTION

Pervaporation is a membrane separation process where a liquid mixture is directly brought into contact a semipermeable membrane and the permeate is removed as a vapor by applying either vacuum or carrier gas. Since evaporation of liquid penetrant takes place in pervaporation process, it is a rather energy consuming process. However, pervaporation is still beneficial compared to the conventional separation processes such as distillation, extraction etc, in so far as a highly permselec-

tive membrane is employed. Therefore, the high permselectivity is essential in the pervaporation process, which is accordingly applied to remove minor component of a liquid mixture.

Transport in pervaporation membrane takes place through the following three steps : i) dissolution of penetrant into the membrane, ii) diffusion across the membrane due to the concentration gradient developed, and iii) finally evaporation at the down stream side. Transport behavior described above is termed commonly as a solution-diffusion model.[1] The permselectivity depends upon the first two steps while the last step does not influence the permselectivity as long as the partial pressure in the permeate side is kept low.[2~5] Thus, in order to achieve high permselectivity, the solubility and diffusivity of corresponding penetrants should be controlled.

On the basis cited above, in preparation of highly separable membrane for water-ethanol mixture, poly(vinyl alcohol) (PVA) has been chosen due to its high water solubility. Diffusion rate may be controlled by suppressing the chain mobility with crosslinking the PVA membrane. Furthermore, one side of the crosslinked PVA membrane surfaces was modified more hydrophilically for enhancing preferential sorption at the liquid-membrane interface.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) used was Elvanol (E.I. Du Pont De Nemours) with number and weight average molecular weight of $M_n = 52,800$ and $M_w = 113,000$, respectively, and 99.8% hydrolyzed and atactic.[6] Water was double-distilled, and the all chemicals used were of EP grade and used without further purification.

Preparation of Crosslinked Membrane

10 wt% aqueous PVA solution was mixed with aqueous solutions of glutaraldehyde as a crosslinking agent, sulfuric acid as a catalyst for the crosslinking reaction, acetic acid as a buffer, and

methanol as a quencher for the reaction.[6] The mixed solution was cast on a Petri dish at room temperature and the crosslinked membranes were prepared followed by being washed with water. The amount of glutaraldehyde was varied to control the crosslinking density. Thickness of the dry membrane was about 135 μm $\pm$ 5.

Surface Modification with Monochloroacetic Acid (MCA)

A specially designed reaction cell (Fig. 1) was used. for surface modification of one side of the membrane surfaces A crosslinked PVA membrane (Fig. 1-a, approximate membrane surface area = 40 cm^2) was sandwiched between a Teflon O-ring (Fig. 1-d) and a Teflon sheet (Fig. 1-b) such that only one side of the membrane surfaces was able to contact with reaction medium. The sandwiched membrane was again clamped by two stainless steel rings (Fig. 1-c) making a reaction cell. A mixture of ethanol and 20% aqueous NaOH solution (8 : 2 by weight, respectively) as well as sodium ethoxide (0.023 g-mole) in ethanol were added into the reaction cell. The reaction was carried out at 80°C for 2 hrs. After washing with water three times, 2.18g of monochloroacetic acid (0.023 g-mole) dissolved in 5ml ethanol was added into the reaction cell and reacted at 80°C for varying reaction time. The reacted surface was converted either COOH−COONa form by treating HCl or NaOH solution, respectively, as shown in reaction Scheme 1. The sodium content for −COONa form membrane was measured with an atomic absorp-
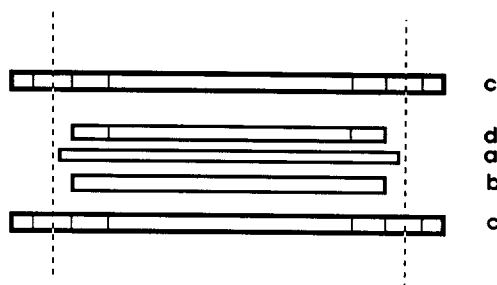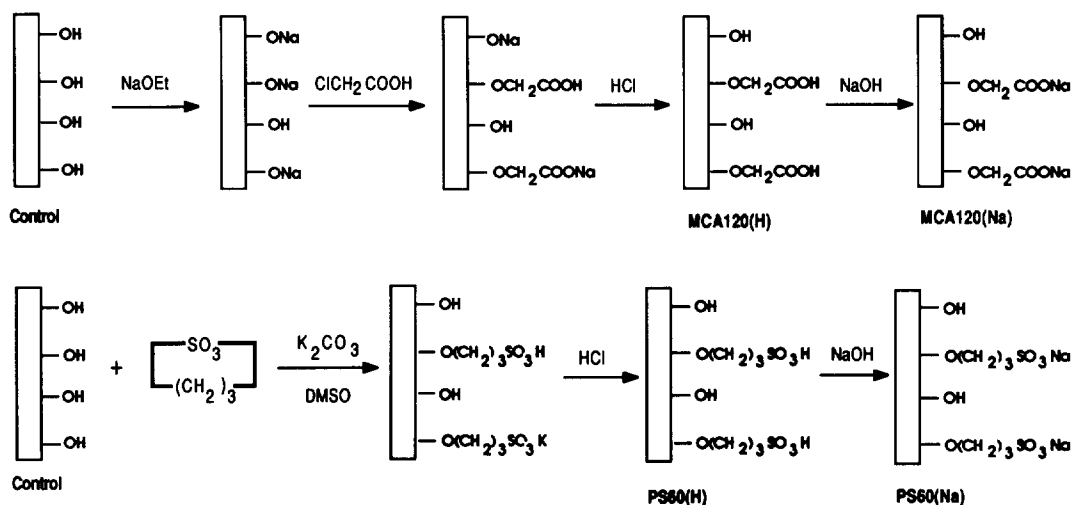

Fig. 1. Schematic diagram of the one-side reaction cell : a, membrane ; b, Teflon sheet ; c, stainless steel ring ; d, Teflon O-ring.

Reaction Scheme. 1.

tion spectrometer (Perkin Elmer 3030 B).

Surface Modification with Propane Sultone[7]

K$_2$CO$_3$ (0.77g, 0.0056mole) and propane sultone (1.37g, 0.0112mole) dissolved in a mixture of dimethyl sulfoxide and methyl ethyl ketone (2/8 by volume) were introduced into the reaction cell described previously. The reaction was carried out at either 40°C or 60°C for 16 hrs. The sulfonic acids introduced on the membrane surface were converted to sodium sulfonate by treating with NaOH solution. The sodium content of-SO$_3$Na form membrane was measured with the same method described previously

Degree of Crystallinity

The degree of crystallinity of crosslinked PVA membrane was obtained by measuring densities with a density gradient column (solvent : carbontetrachloride and cyclohexane) at 25°C. The degree of crystallinity, x, was calculated by the following equation (1)

$$\frac{1}{\rho} = \frac{x}{\rho_c} + \frac{1-x}{\rho_a} \tag{1}$$

where ρ is the sample density, ρ_c and ρ_a are the densities of complete crystalline PVA ($\rho_c = 1.269$ g/cm^3) and amorphous PVA ($\rho_a = 1.345$ g/cm^3), respectively.[6,8]

Swelling Experiments

The degree of swelling, S$_m$, was obtained by weighing the dry sample and the swollen sample, fully equilibrated with water for 7 days at 40°C.

$$S_m = (W_s - W_d)/W_s \tag{2}$$

where W$_s$ and W$_d$ denote the weights of the water-swollen sample and the dry sample, respectively.

Pervaporation Experiments

Pervaporation of water-ethanol mixture was carried out at 40°C by using an ordinary pervaporation technique.[9] The effective membrane area for pervaporation was 22.9 cm^2. The down stream pressure was kept between 4 to 5 Torr. The permeate composition was analyzed by the gas chromatograph. pervaporation performance was characterized in terms of the steady state flux and the separation factor or permselectivity. The steady state flux, J, was obtained as

$$J = Q / At \tag{3}$$

where Q is the total amount permeated during the experimental time interval t at steady state, and A is the effective membrane surface area. The separation factor, α, as a measure of the permselectivity, is defined as[3]

$$\alpha = \frac{(X_w^p / X_e^p)}{(X_w^f / X_e^f)} \qquad (4)$$

where X is the weight fraction, the superscripts p and f stand for permeate and feed, respectively, and the subscripts w and e for water and ethanol.

RESULTS AND DISCUSSION

Membrane Characterization

The volume fractions of PVA in the relaxed, $v_{2,r}$, and the swollen membrane, $v_{2,s}$, are[6]

$$v_{2,r} = V_p / V_{g,r} = (W_p / \rho_p) / V_{g,r} \qquad (5)$$

$$v_{2,s} = V_p / V_{g,s} = (W_p / \rho_p) / V_{g,s} \qquad (6)$$

where V_p and W_p are the volume and the weight of dry polymer, and $V_{g,r}$ and $V_{g,s}$ the volumes of membranes at the relaxed and swollen states, respectively. The relaxed state is defined as the state immediately after the crosslinking but before swelling.[6]

The number average molecular weight, $\overline{M}_c$, between two crosslinks is[6]

$$\frac{1}{\overline{M}_c} = \frac{1}{\overline{M}_n} - \frac{(\overline{v} / \overline{V}_1)\left[\ln(1-v_{2,s}) + v_{2,s} + \chi v_{2,s}^2\right]}{v_{2,r}\left[(\frac{v_{2,s}}{v_{2,r}})^{1/3} - \frac{1}{2}(\frac{v_{2,s}}{v_{2,r}})\right]} \qquad (7)$$

and the crosslinking density, ρ_x, is[6]

$$\rho_x = 1/\overline{v}\,\overline{M}_c \qquad (8)$$

where $\overline{v}$ is the specific volume of 100% amorphous PVA ($\overline{v} = 0.788\,cm^3/g$) and $\overline{V}_1$ the molar volume of water ($\overline{V}_1 = 18\,cm^3/mol$), and $\overline{M}_n$ the number average molecular weight of PVA($\overline{M}_n = 52,800$). χ is the Flory-Huggins interaction parameter. The theoretical crosslinking density $\rho_{x,t}$ was calculated by assuming that 100% of glutaraldehyde was reacted with hydroxyl group of PVA

$$\rho_{x,t} = \frac{1/\overline{v}}{M_{va}/R_{cr}} \qquad (9)$$

where R_{cr} is the crosslinking ratio (moles of glutaraldehyde / moles of PVA repeating unit) and M_{va} is the molecular weight of repeating unit of PVA($M_{va} = 44$). Table 1 lists physical properties of the crosslinked PVA membranes. Experimental crosslinking density, ρ_x, increases with increasing amount of glutaraldehyde as expected. Furthermore, the ρ_x values are comparable with the $\rho_{x,t}$ values. This implies that glutaraldehyde stoichiometrically reacts with hydroxyl groups of PVA. The samples 1-4 of Table 1 denote the membranes prepared by crosslinking and then drying, and the samples 5-8 the membranes prepared by crosslinking and drying simultaneously. The crosslinking density and the degree of swelling of two methods are in agreement within the experimental error. From these facts it may be concluded that the crosslinking density of PVA membrane may be readily controlled by simply adjusting the amount of glutaraldehyde. As increasing R_{cr}, both x and S_m decrease. This is ascribed to the fact that the mobility of PVA chain segments is suppressed when the polymer chain molecules were crosslinked.

Table 1. Properties of Crosslinked Poly(vinyl alcohol) Membranes

Sample	R_{cr}	$x(\times 10^2)$	S_m	$\rho_x(\times 10^4)$	$\rho_{x,t}(\times 10^4)$
1	0.5	—	14.7	1.73	1.44
2	1.0	—	10.4	2.76	2.88
3	1.5	—	8.7	3.33	4.33
4	2.0	—	8.0	5.76	5.77
5	0.5	37.9	12.4	1.42	1.44
6	1.0	29.9	9.5	3.26	2.88
7	1.5	28.3	8.4	4.60	4.33
8	2.0	25.0	7.1	4.68	5.77

R_{cr} : crosslinking ratio (moles of glutaraldehyde/moles of PVA repeating unit).

x : degree of crystallinity

S_m : degree of swelling

ρ_x : experimental crosslinking density(mol/cm³)

$\rho_{x,t}$: theoretical crosslinking density(mol/cm³)

Pervaporation Characteristics

Pervaporation properties of the crosslinked PVA membranes with different amount of glutaraldehyde were measured. As shown in Table 2, the permselectivity increases and the flux decreases with increasing the crosslinking ratio. As increasing the crosslinking ratio, chain mobility and swellability of PVA membrane are suppressed. Thus, both the equilibrium solubility and diffusivity of water and ethanol decrease,[12] which results in low flux. In particular, diffusivity of

Table 2. Transport Properties of Crosslinked Poly (vinyl alcohol) Membranes

R_{cr}	J	J_w	α	X_w^p
0.0	0.222	0.104	8.0	0.47
0.5	0.047	0.028	13.5	0.60
1.0	0.023	0.017	27.0	0.75

R_{cr} : crosslinking ratio (moles of glutaraldehyde/moles of PVA repeating unit).

J : total flux(kg/m^{2}h) with 135 μm thick membrane

J_w : water flux(kg/m^{2}h) with 135 μm thick membrane

α : permselectivity of water

X_w^p : weight fraction of water in the permeate

ethanol is reduced markedly compared to that of water since ethanol having larger size is hindered more than water in the environment of the suppressed chain mobility. Thus, the permselectivity of water increases with increasing amount of the crosslinking agent used.

The physicochemical interaction between penetrant and membrane plays an important role in determining the pervaporation characteristics.[3,10~16] For example, the hydrogen-bonding interaction markedly increases the permselectivity of water.[13,16] Yoshikawa et al.[16] demonstrated that hydrogen bonding interaction of carboxylic acids decreases as following order : water>ethanol>acetonitrile. On this basis, in this study, carboxylic acids and sulfonic acids groups were introduced on the one side of the membrane surfaces.

Transport properties of the crosslinked PVA membranes modified with monochloroacetic acid were listed in Table 3. Comparing the results of the crosslinked membrane and the crosslinked and surface-modified membrane, −COOH form the permselectivity increases substantially while the flux decreases. The permselectivity of carboxylic acid form membranes decreases slightly with

Table 3. Transport Properties of Crosslinked and Surface-Modified Poly(vinyl alcohol) Membranes by Monochloroacetic Acid : Feed 10 wt% Water

Sample	t	J	J_w	α	X_w^p	w_{Na}
Control	0	0.023	0.017	27.0	0.75	
MCA20(H)[a]	20	0.016	0.014	51.0	0.85	
MCA20(Na)[b]	20	0.022	0.019	66.0	0.88	0.08
MCA60(H)[a]	60	0.015	0.012	38.4	0.81	
MCA60(Na)[b]	60	0.024	0.021	55.3	0.86	0.12
MCA120(H)[a]	120	0.016	0.012	31.9	0.78	
MCA120(Na)[b]	120	0.053	0.049	120.0	0.93	0.14

[a]−COOH form membrane ; [b]−COONa form membrane

t : reaction time(min)

J : total flux(kg/m^{2}h) with 135 μm thick membrane

J_w : water flux(kg/m^{2}h) with 135 μm thick membrane

α : permselectivity of water

X_w^p : weight fraction of water in the permeate

w_{Na} : weight % of sodium in the −COON$_a$ form membrane

Table 4. Transport Properties of Crosslinked and Surface-Modified Poly(vinyl alcohol) Membranes by Propane Sultone : Feed 10 wt% Water

Sample	T	J	J_w	α	X_w^p	w_{Na}
Control		0.023	0.017	27.0	0.75	
PS40(H)[a]	40	0.061	0.025	6.3	0.41	
PS40(Na)[b]	40	0.069	0.047	19.1	0.68	0.11
PS60(H)[a]	60	0.027	0.021	30.1	0.77	
PS60(Na)[b]	60	0.036	0.027	25.6	0.74	0.20

[a] $-SO_3H$ form membrane ; [b] $-SO_3Na$ form membrane

T : reaction temperature(℃)

J : total flux(kg/m²h) with 135μm thick membrane

J_w : water flux(kg/m²h) with 135μm thick membrane

α : permselectivity of water

X_w^p : weight fraction of water in the permeate

w_{Na} : weight % of sodium in the $-SO_3Na$ form membrane

increasing reaction time, while the flux remains almost constant. In order to obtain more hydrophilic surface, the carboxylic acids on the surface are converted to the sodium carboxylate. The sodium carboxylate membrane exhibits that both the flux and the permselectivity increase markedly compared to those of acid form membrane. In particular, comparing the results of the "Control" membrane and MCA120(Na) membrane, the flux and the permselectivity are increased by more than 2 times and 4 times, respectively. This is ascribed to the fact that the carboxylic group at the liquid-membrane interface preferentially interacts with water than ethanol. This result is very surprising since the flux and the permselectivity are in conflict in common membrane transport. Thus, the surface modification technique could be a useful method in improving the pervaporation characteristics.

In the case of the membranes modified by propane sultone, the transport properties are rather disappointed as shown in Table 4. For the sample reacted at 40℃, the flux increases at the expense of the permselectivity. When the reaction temperature is 60℃, transport properties do not change very much. However, the transport properties of sodium sulfonate membrane are always better than those of sulfonic acid membrane, which is consistent with the carboxylic acid case.

CONCLUSIONS

Crosslinked membranes were prepared by adjusting the amount of the crosslinking agent, glutaraldehyde. As expected, the flux decreases and the permselectivity of water increases. Further, one side of the crosslinked PVA membrane surfaces was modified by either reacting with monochloroacetic acid or propane sultone. When carboxylic acids groups are introduced, the flux maintains almost unchanged and the permselectivity increases substantially. In addition, when acids are converted to sodium carboxylate, both the flux and the permselectivity increase simultaneously. Thus, we may conclude that the surface modification technique is a useful means to improve the transport properties in pervaporation. However, when the surface was modified by propane sultone, the results were rather disappointed and the reasons are not clear at this moment.

REFERENCES

1. M. H. V. Mulder, T. Franken, and C. A. Smolders, *J. Memb. Sci.,* **22,** 155 (1985).

2. P. Aptel, N. Challard, J. Cuny, and J. Neel, *J. Memb. Sci.,* **1,** 271 (1976).

3. I. Cabasso, *Ind. Eng. Chem. Prod. Res. Dev.,* **22,** 313 (1983).

4. M. H. V. Mulder, J. Oude Hendrikman, H. Hegeman, and C. A. Smolders, *J. Memb. Sci.,* **16,** 269 (1983).

5. E. Nagy, O. Borlai, and J. Stelmaszek, *J. Memb. Sci.,* **16,** 79 (1983).

6. C. T. Reinhart and N. A. Peppas, *J. Memb. Sci.,* **18,** 227 (1984).

7. E. J. Goethals and G. Natus, *Die Makromol. Chem.,* **116,** 152 (1968).

8. J. Brandrup and E. H. Immergut, Editors, Polymer Handbook, 2nd Ed., John Wiley and Sons, New York, 1975.

9. M. H. V. Mulder, F. Kruitz, and C. A. Smolders, *J. Memb. Sci.,* **11,** 349 (1982).

10. Y. F. Xu and R. Y. M. Huang, *J. Appl. Polym. Sci.,* **36,** 1121 (1988).

11. Q. T. Nguyen, L. Le Blanc, and J. Neel, *J. Memb. Sci.,* **22,** 245 (1985).

12. P. Schissel and R. A. Orth, *J. Memb. Sci.,* **17,** 109 (1984).

13. P. Aptel, J. Cuny, J. Jozefonvicz, G. Morel, and J. Neel, *J. Appl. Polym. Sci.,* **18,** 365 (1974).

14. M. Yoshikawa, H. Yokoi, K. Sanui, N. Ogata, and T. Shimidzu, *Polymer J.,* **16,** 653 (1984).

15. S. Yamada and T. Hamaya, *J. Memb. Sci.,* **17,** 125 (1984).

16. M. Yoshikawa, T. Yukoshi, K. Sanui and N. Ogata, *J. Polym. Sci. Part A.,* **24,** 1585 (1986).