

Polyacrylonitrile과 Poly(vinyl pyridine)으로부터 제조한 고분자 복합체막의 물-에탄올 투과증발분리

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Pervaporation of Water-Ethanol through Polyion Complex Membrane from Polyacrylonitrile and Poly(vinyl pyridine)

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요 약 : 본 연구에서는 폴리아크릴로니트릴(PAN)을 기질로 고분자 복합체막을 제조하고 투과증발 공정을 이용해 물과 에탄올 이성분혼합액의 분리를 행하였다. PAN은 물과의 친화성이 높아서 고분자기질로 선택하였다. 치밀한 PAN막을 알칼리 용액에서 가수분해하고 이것을 poly(4-vinyl pyridine)과 반응시켜 고분자복합체막을 제조하였다. 이 고분자복합체막은 치밀한 PAN막에 비해 유량이 약 20배가량 증가하였다. 또한 이 막은 온도에 무관한 선택도를 유지한 반면 유량은 온도에 따라 증가하였다.

Abstract : In the present work the separation of water-ethanol binary mixture through polyion complex membranes based on polyacrylonitrile(PAN) was studied using pervaporation processes. PAN was chosen as a base polymer because of its high affinity with water. It was hydrolysed with alkaline solution followed by the reaction with poly(4-vinyl pyridine) to make polyion complex membranes. Polyion complexation of PAN with quarternized poly(4-vinyl pyridine) enhances the pervaporation flux about 20 times to that of homogeneous and dense PAN membranes. Polyion complex membranes maintain temperature-independent separation factor while the flux increases with temperature.

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INTRODUCTION

Pervaporation is a membrane separation process that can be applied to separate organic-water mixtures. Particularly for ethanol-water solution, ethanol selective membranes were sought.^{1,2} However, a great deal of research efforts has been focused on the separation near the azeotropic composition. For this application, we have reported the pervaporation performance of homogeneous and modified polyacrylonitrile(PAN) membrane.² A lot of work has been done to develop more efficient membranes.³⁻⁷ Good selectivities for water have been obtained using hydrophilic groups or by the inclusion of this group in the membrane structure.⁸⁻¹⁰

Increasing hydrophilicity, however, normally induces an increase of the solubility of the polymer in water, and as a consequence the membrane may dissolve in water solution. It is possible to decrease the polymer solubility by blending, copolymerizing or crosslinking the polyacrylonitrile membranes induced by chemical reactions. Another way of increasing the water selectivity was to treat the hydrophilic pendant groups with metallic hydroxides resulting in an incorporation of counter ions.¹¹⁻¹³ In this case there remains a problem of a long-term stability of the membrane because the counter ions on the membrane surface will eventually be wiped out during the transport operation. Maeda et al.¹³ circumvented this problem by using larger counter ions, so called polyions. They partially hydrolyzed the polyacrylonitrile hollow fiber to introduce carboxylic groups and then to make a complex with various polycations.

The objective of the present study is to manufacture in a laboratory scale a flat polyion complex membrane and to test this membrane for its pervaporation performances. The complex membrane is based on an asymmetric polyacrylonitrile membrane complexed with quarternized poly(4-vinyl pyridine) and membranes therefrom are used in the dehydration of ethanol-water mixtures. The

effect of hydrolysis degree in PAN, feed temperature and feed concentration on the pervaporation performance of the membrane were studied and discussed.

EXPERIMENTAL

Materials

Polyacrylonitrile(PAN) was obtained from Hanil Synthetic Fibers Co.(Seoul, Korea). It contains about 9 wt% polymethylmethacrylate with molecular weight of about 80,000($\rho=1.175\text{g/cm}^3$ and $[\eta]=0.14\text{-}0.19$).

Dimethyl formamide(DMF) used was from Jin Chemical Co. LTD. 4-Vinyl pyridine monomer was from Aldrich Chemical Company LTD., and methyl iodide was from Kokusan Co. LTD.

Characterization

For structural determination, an infrared spectrophotometer(FT-IR, Nicolet Model 5DX, USA) and a differential scanning calorimeter (DSC, DuPont Model 910) were used for hydrolyzed membranes. Scanning electron microscope (SEM, Jeol Model JSM-35 CF) was used for investigating the membrane morphology. For molecular weight determination, gel permeation chromatography(GPC, Shimadzu model Q94) was used.

Synthesis of Quarternized Poly(4-vinyl pyridine)

Quarternized poly(4-vinyl pyridine) was synthesized by the hydrogen transfer polymerization.¹⁴ Reaction of 4-vinyl pyridine(0.112 mol) with methyl iodide(0.112 mol) was carried out in 100 ml of DMF at -30°C for 1 hr in an open ampule, and a yellow product was precipitated at the end of the reaction. Then the product was separated and washed with ethyl acetate and vacuum-dried at 60°C for 6 hr. The yield was 69%. As the IR absorption band at $1,547\text{ cm}^{-1}$ in 4-vinyl pyridine shifted to a lower frequency of $1,517\text{ cm}^{-1}$, 4-vinyl pyridine was found to be quarternized. The bending vibration peak of methyl group at $2,934\text{ cm}^{-1}$ and the disappearance of two out of plane peaks of vinyl group at 991, and 926 cm^{-1} , respectively, show the formation of polymer. GPC analysis

showed that the molecular weight of quarternized poly(4-vinyl pyridine) was determined to be about 13,600.

Preparation of Polyion Complex Membranes

Figure 1 shows the scheme for the preparation of polyion complex membranes. A 20 wt% solution of PAN in DMF was cast on a glass plate and predried for 2 min under an IR lamp. Approximate temperature of the surface of the casting solution was about 60 °C. The casting solution and the plate were immersed into a water bath conditioned at 20 °C. An asymmetric PAN(APAN) membrane prepared was set on a specially designed surface reactor and reacted with 2.5 N aqueous sodium hydroxide solution in a water bath at 80 °C for 10-15 min. The hydrolysed PAN membrane(HPAN) was washed with water and dipped into an 10 wt% aqueous quarternized poly(4-vinyl pyridine) at 60 °C for 6 hrs. Finally the polyion complex membrane(CPAN) was washed with distilled water and then dried at room temperature. Reaction scheme of hydrolysis is shown in Fig. 2. Cyano group in PAN reacts with NaOH and finally becomes carboxylic group. This was visually confirmed by the change of color from brown to transparent. Also, the hydrolysis reaction was confirmed from the IR spectra where the stretching vibration band appeared at 2,250 cm^{-1} (cyano group) disappeared

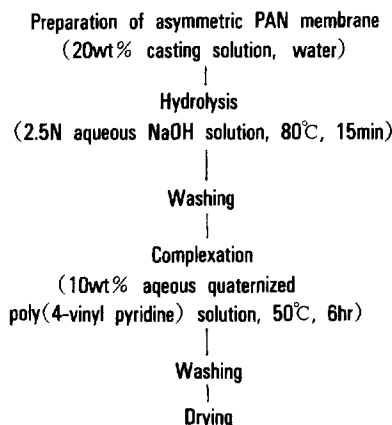


Fig. 1. Preparation of polyion complex membrane.

after hydrolysis.

Pervaporation Experiment

The pervaporation apparatus consisted of a permeation cell made of stainless steel, a constant temperature bath, and glass tubes for condensing and collecting the permeate vapor. The upstream compartment had a capacity of 500 cm^3 , and the membrane area in contact with liquid was about 25.98 cm^2 . The downstream pressure was maintained from 400 to 670 Pa(3-5 torr). Pervaporation experiments were carried out at constant temperature of 20, 50, 70, 90 °C, respectively. A detailed description of the apparatus is appeared elsewhere.¹

The separation analysis was carried out on a Shimadzu 6A gas chromatography equipped with a 3m long column packed with Porapak Q and

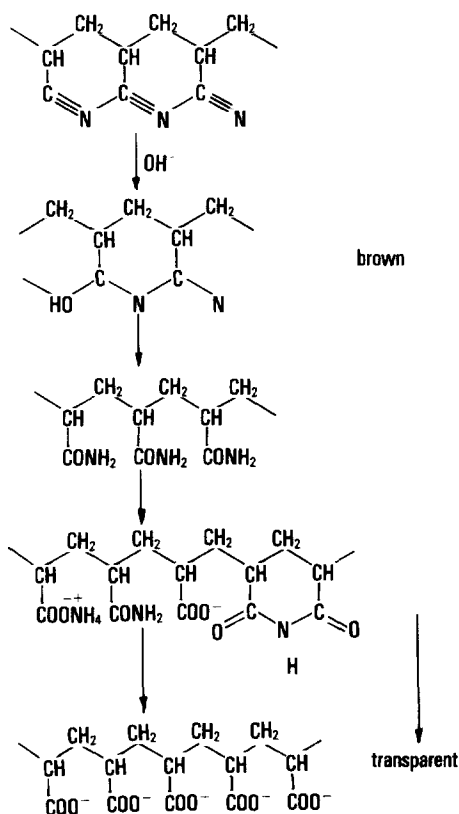


Fig. 2. Reaction scheme of hydrolysis.

with thermal conductivity detector.

The separation factor, $\alpha_{1/2}$, is defined as

$$\alpha_{1/2} = \frac{Y_1 / Y_2}{X_1 / X_2} \quad (1)$$

where Y_i 's are the weight fractions of permeates and X_i 's are those of the feeds, and 1 and 2 denote water and ethanol, respectively.

RESULTS AND DISCUSSION

B. Manjeet et al.¹⁵ reported the saponification reaction of PAN. The degree of hydrolysis of PAN was measured by Kjeldahl's method and by optical density of nitrile group in FTIR spectrum. In the present investigation simpler method was designed

to measure the degree of hydrolysis of PAN by utilizing DSC thermogram. DSC thermogram was measured for the asymmetric PAN membrane (Figure 3). It showed the exothermic peak at 327 °C resulting from the degradation of PAN. The intensity of endothermic peak appeared at 327 °C decreases as the hydrolysis is prolonged. As the cyano group in PAN is converted to carboxylic group, the number of cyano groups in PAN should decrease with the degree of hydrolysis. Therefore the area of the endothermic peak in DSC thermogram could be related to the degree of hydrolysis. Thus the degree of hydrolysis can be expressed with the following equation.

Degree of Hydrolysis :

$$H = \frac{\Delta H_i - \Delta H_f}{\Delta H_i} \times 100(\%) \quad (2)$$

where ΔH_i : Thermal decomposition energy of PAN determined by DSC thermogram appeared at around 327 °C.

ΔH_f : Thermal decomposition energy of PAN after hydrolysis determined by DSC thermogram appeared at around 280-300 °C.

From the above equation, the degree of hydrolysis was calculated to be 0%, 29% and 56% for the samples hydrolysing for 0 min, 10 min and 15 min, respectively. For these membranes we performed the pervaporation experiments and the results were also listed in Table 1. The flux decreased from 2.97 kg/m² · hr to 0.425 kg/m² · hr, but the

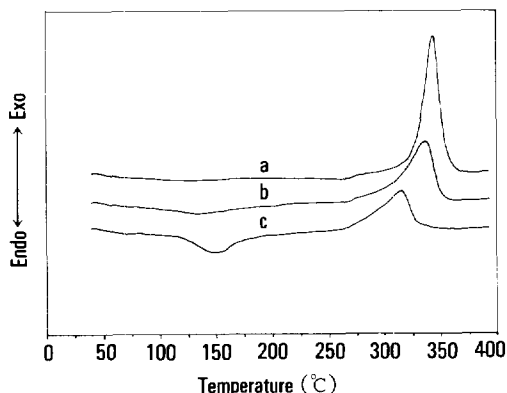


Fig. 3. DSC thermograms of (a) asymmetric PAN membrane, (b) PAN membrane hydrolysed for 10 min, and (c) PAN membrane hydrolysed for 15 min. Heating rate : 40 °C/min.

Table 1. Pervaporation Performance of Aqueous Ethanol through Hydrolysed and Complexed PAN Membranes

Sample	Hydrolysis Time (min)	ΔH (J/g)	H (%)	$C_f(\text{EtOH})^a$ (wt %)	Flux (kg/m ² · hr)	$C_p(\text{H}_2\text{O})^b$ (wt %)	$\alpha(\text{H}_2\text{O})$
HPAN-0	0	639.9	0	90.60	2.97	14.20	1.6
CPAN-29	10	452.0	29	90.83	0.38	86.42	63.0
CPAN-56	15	279.0	56	93.23	0.425	90.15	126.0

Operating condition : 30 °C.

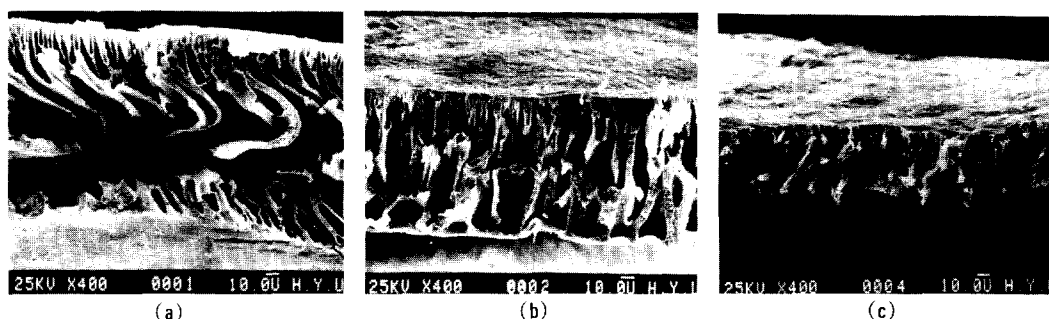
^a Ethanol concentration in feed in wt%.

^b Water concentration in permeate in wt%.

Table 2. Pervaporation Performance of Homogeneous, Asymmetric, Hydrolysed and Complexed PAN Membranes

Sample	$C_f(\text{EtOH})$ (wt %)	Flux ($\text{kg}/\text{m}^2 \cdot \text{hr}$)	$C_p(\text{H}_2\text{O})$ (wt %)	$\alpha(\text{H}_2\text{O})$	Thickness (μm)
PAN	88.90	0.02	99.92	10000	20
APAN ^a	90.60	2.97	14.22	1.6	160
HPAN-56 ^b	85.62	1.75	28.74	2.4	160
CPAN-56 ^c	93.23	0.425	90.15	126.0	120

Operating condition ; 30 °C.

^aAPAN ; Asymmetric polyacrylonitrile membrane.^bHPAN ; Hydrolysed polyacrylonitrile membrane.^cCPAN ; Complex polyacrylonitrile membrane complexed with poly(4-vinyl pyridine)**Fig. 4.** Scanning electron micrographs of (a) asymmetric PAN membrane (HPAN-0), (b) hydrolysed PAN membrane (HPAN-56) and (c) complex PAN membrane (CPAN-56).

separation factor increased from 1.6 to 126 as the degree of hydrolysis increased. In summary an increase of carboxylic group content in the base polymer contributed to an increase in the number of ion sites and thus the separation character.

The pervaporation performance of asymmetric, hydrolyzed and complexed PAN membranes is shown in Table 2. Polyion complex membrane exhibited an improved separation efficiency with a lower flux tested at 30 °C. Scanning electron microscopes reveal that the hydrolysis and complexation make membrane morphology become more dense (Fig. 4). The densification of the membrane is attributed not only to the annealing of the membrane during the hydrolysis reaction at 80 °C but also to the formation of carboxylic groups and the complexation of the membrane surface with poly(4-vinyl pyridine). Therefore the polyion complex

membrane showed a lower flux and higher separation factor than those of the hydrolysed membrane (HPAN-56). Note that the flux in polyion complex membrane is about 20 times to that of homogeneous and dense PAN membranes.²

Table 3 shows the effect of feed ethanol concentration on the pervaporation performance of poly-

Table 3. Effect of Ethanol Concentration on Polyion Complex Membrane CPAN-56 Performance

Ethanol Feed conc. (wt %)	Flux ($\text{kg}/\text{m}^2 \cdot \text{hr}$)	$C_p(\text{H}_2\text{O})$ (wt %)	$\alpha(\text{H}_2\text{O})$
93.23	0.425	90.15	126
80.00	0.705	93.40	57
58.08	1.290	92.03	16
28.98	3.828	96.08	10

Feed temperature ; 30 °C.

ion complex membrane (CPAN-56) when the feed temperature is about 30 °C. The flux decreases as the feed ethanol concentration increases. Separation factor, however, increases with the feed ethanol concentration.

The effect of feed ethanol temperature on the permeation flux and separation factor through the polyion complex membrane is shown in Table 4. The flux increases with temperature as expected. On the other hand, the separation factor is nearly constant throughout the temperature range tested. This observation is in contrast to a usual decrease of separation factor with temperature increase for PAN and non-crosslinked chitosan membranes.^{2,16} For non-ionic polymeric membranes, the flux generally increases and the separation factor decreases as the feed temperature increases. This phenomenon was resulted from the mobility of polymer chain due to temperature increase. For cross-linked and ion containing membranes, however, the separation factor was independent of the feed temperature.

According to Kesting,¹⁷ ions in solution affected the water structure. That is, there is a lineup of water dipoles within the hydration layer or layers of the various ions present. These water molecules tend to form a tightly bound, and oriented hydra-

tion layer around ions of either charge. He assumed that for cations the oxygen atoms of water are oriented into the ion and for anions the hydrogen atoms are so oriented. Ions can exert a net structure-making effect and a net structure-breaking effect of water. Ions having the latter effect break the water cluster and form a monomeric water. In that case the viscosity of solution decreases while the mobility of solution increases. Whereas, in the ions showing structure-making effect, the viscosity of solution increases and the mobility of solution decreases.

We have assumed that cation and anion in polyion complex are ordered in the membrane in such a way that water molecules in feed solution should be rearranged on and inside of the membrane. This ordered water is thought to be in a state that the water cluster is disrupted and the water structure is in a monomeric state. On these basis, it is reasonable to assume that the mobility of water in polyion complex membrane increases. If we compare the structure of water and ethanol, the capacity of association of water with ionic sites in the polyion complex membrane is greater than that of ethanol, and thus water is easy to move in the membrane. Therefore, in the polyion complex membrane, the selectivity of water does not decrease in comparison with the nonionic polymeric membrane.

Increasing the feed temperature induces the increase in flux. Ionic crosslinking in the polyion complex membrane enhances the chain immobilization and diffusional selectivity dominates the overall selectivity in the polyion complex membranes. In other words, temperature increases the free volumes in the polymer membrane. The sorption of water and ethanol in the polyion complex membrane was not much affected because of the macro-chain movement.

CONCLUSIONS

Polyion complexation of deliberately hydrolysed polyacrylonitrile membrane with quarternized poly

Table 4. Effect of Feed Temperature on the Permeation Flux and Separation Factor in PIC Membrane (CPAN-29)

Feed Temp. (°C)	Flux (kg/m ² · hr)	C _p (H ₂ O) (wt%)	α (H ₂ O)
30	0.380	86.42	63
40	0.550	86.14	62
50	0.824	86.55	64
60	1.008	88.29	75
70	1.250	87.36	68

Feed Conc. : 90.83 (wt%).

Membrane Thickness : 150 μm

Hydrolysis : 2.5N Aqueous NaOH solution at 80 °C
for 10 min

Complexation : 22wt% Aqueous polycation solution
at 80 °C for 2hr

(4-vinyl pyridine) enhances the pervaporation flux a total of 20 times to that of the homogeneous PAN membranes. Polyion complex membranes maintain temperature-independent separation factor while the flux increases with temperature. Also, the incorporation of polyion complex solves the problem of desorption of metal counter ions from the membrane surface after converting the metal ions to polycations.

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