

Separation of Liquid Mixtures by Using Polymer Membranes. III. Water–Alcohol Separation by Pervaporation through Modified PAN Membrane

CHUN-MIN HU and WEN-YEN CHIANG*

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Road, Third Sec., Taipei 10451, Taiwan, Republic of China

SYNOPSIS

The modification of polyacrylonitrile membrane with ethanolamine was carried out, and the permeation characteristics in pervaporation were examined using the aqueous alcohol solutions. In pervaporation of a water/alcohol solution, preferential permeation of water was observed for all these membranes because of the hydrogen-bonding interaction. The selectivity of the modified polyacrylonitrile (PAN) membrane depended on operating temperature, but was independent on the thickness of the membrane. Furthermore, it was found that the membrane with more ethanolamine content had a higher affinity to water. The effect of feed concentration and the molecular size of the permeating species on the separation factor and permeation flux was also investigated.

INTRODUCTION

The pervaporation process has been of much interest because of energy saving in the separation of azeotropic, close-boiling, or aqueous organic mixtures.

Polyacrylonitrile (PAN) is a good film-forming polymer with high mechanical strength. However, its use is limited to separation membranes because of its high hydrophobicity. Recent papers¹⁻⁷ have dealt with the pervaporation membrane separation of water/alcohol mixtures using the copolymer or graft copolymer of PAN with hydrophilic polymers.

This paper is a part of a series on the pervaporation separation of aqueous alcohol solution.^{8,9} Previous experiments concerned the introduction of hydrophobic monomers into water-soluble polyvinyl alcohol membrane. The present study attempts to incorporate a hydrophilic group into PAN that may cause an increase in the hydrogen-bonding interaction strengths between water and alcohol. The modification PAN membrane was obtained by the reaction of PAN with ethanolamine in dimethyl

sulfoxide (DMSO). The resultant structure and reaction mechanism were proposed in a previous paper.¹⁰ All synthetic membranes were applied to separate water/alcohol mixtures by the pervaporation technique.

EXPERIMENTAL

Materials

Dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), and ethanolamine (EA) of reagent grades were purchased from Wako Pure Chemical Industries. Acrylonitrile (AN) (Wako Pure Chemical Industries) purified as previously described.¹⁰ Azobisisobutyronitrile (AIBN) (Nakarai Chemical Co., Japan), recrystallized from methanol, was used as initiator.

Preparation of PAN

AN was polymerized¹¹ in DMF using AIBN as initiator for 10 h at 60°C. Polymers were precipitated in a large excess of methanol, and repeatedly washed with methanol. It was then ground to a fine powder and dried under vacuum at room temperature. The

* To whom correspondence should be addressed.

molecular weight of PAN was 91,000, which was determined by viscosity measurement.¹²

Reaction of PAN with Ethanolamine (EA)

The modified PAN were prepared by the reaction of PAN with ethanolamine. The general experimental procedure was as follows: PAN was dissolved in DMSO, then the appropriate amount of EA was added drop by drop and stirred. The reaction was allowed to proceed at the predetermined temperature for desired time. After the reaction, the product was precipitated when the solution was poured into a large amount of methanol. The product was washed with methanol several times, then dried at room temperature under reduced pressure. Modified PAN with different composition was obtained by controlling the mole ratio of amine to nitrile group.

Membrane Preparation

The membrane was obtained by casting from dimethyl sulfoxide (DMSO) solution. First, the product was dissolved in DMSO, then the solution poured into glass plates and the solvent allowed to evaporate at 60°C in a vacuum. The thickness of the membranes was 50–250 μm .

Pervaporation Experiment

Apparatus and procedure of the pervaporation was principally the same as described in the previous paper.¹³ Its upper compartment with a capacity of 250 cm^3 , containing the liquid mixture, was equipped with a stirrer, a thermometer, and a heating spiral connected to a circulation thermostatted bath. The membrane chosen for use was 5 cm in diameter and placed in a stainless steel pressure holder. A constant downstream pressure was maintained by a vacuum pump. The pervaporate was condensed in either of the two traps cooled in liquid nitrogen. The pervaporation experiments were usually carried out at 30°C, and made in the temperature range of -20–60°C to observe temperature dependence.

In order to keep the feed composition constant, the mass of pervaporate collected during a run was kept small compared with the mass of the feed. The separation analysis was carried out with Hitachi gas chromatography equipped with a 2-m long column packed with Porapak Q.

Two factors were used to evaluate the characteristic data of a pervaporation run: (1) the permeation flux is expressed in $\text{g}/\text{h}\cdot\text{m}^2$ and (2) the selectivity factor α , defined as

$$\alpha_{\text{water}} = \frac{y_{\text{water}}/y_{\text{alcohol}}}{x_{\text{water}}/x_{\text{alcohol}}}$$

where x and y denote the weight fraction of water and alcohol in the feed solution and in the pervaporate, respectively.

Swelling Ratio

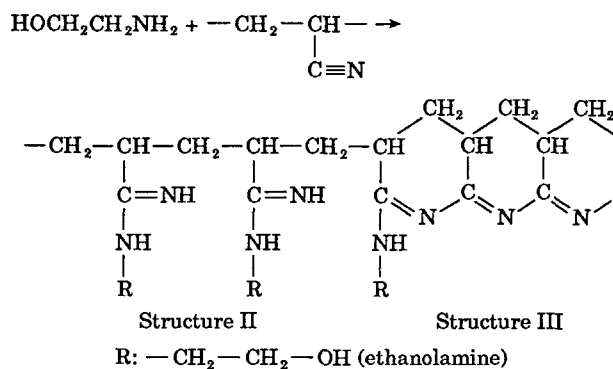
A piece of membrane was immersed in a water-alcohol mixture solvent at 30°C. After reaching equilibrium, the membrane was rapidly removed from the mixture solvent, wiped with tissue paper to remove adherent solvent, and weighed. The swelling ratio S is defined as

$$S = \frac{W_s - W_d}{W_d}$$

where W_d and W_s denote the weight of dry and solvent-swollen membranes, respectively.

RESULTS AND DISCUSSION

In a previous paper,¹⁰ it was found that a reaction occurred between PAN and ethanolamine (EA). Also, (1) an imine structure was obtained by nucleophilic attack of the amine group in ethanolamine on nitrile groups in PAN and (2) a further reaction between imine groups and nitrile groups could be proceeded to form a carbon-nitrogen conjugated structure.



Moreover, it was also found that the ratio of Structure I to Structure II in modified PAN increases with increasing the $\text{---NH}_2/\text{C}\equiv\text{N}$ feed concentration. The reason for such results was described in detail in previous study.

The IR spectrum of the product of PAN with EA (PAN-EA) was compared with PAN in Figure 1. It

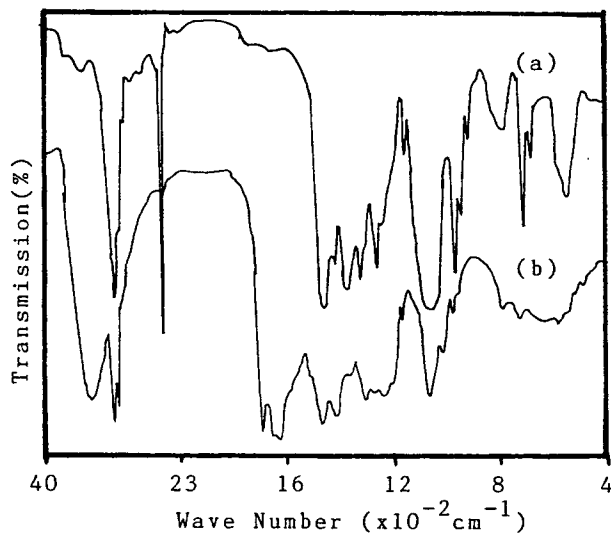


Figure 1 IR spectra of PAN membrane (a) and PAN-EA membrane (b).

shows that the PAN-EA had the new characteristic absorption bands at 1670 cm^{-1} and 1590 cm^{-1} which are due to $\text{C}=\text{N}$ (\uparrow) and conjugated $\text{C}=\text{N}$ (\downarrow). The band at 3480 cm^{-1} of PAN-EA is due to the hydroxy groups. It is expected that such hydrophilic groups in membrane might have a strong interaction with water in alcohol aqueous solution through hydrogen bonding.

The pervaporation of the membranes used in this experiment are shown in Table I. It indicates that the increase in the EA feed concentration tended to increase the oxygen content in PAN-EA, that is, increase the number of hydroxy groups.

Figure 2 shows the relation between the swelling ratio in alcohol-water mixtures at 30°C and the mole ratio of $\text{NH}_2/\text{C}\equiv\text{N}$. As shown in Table I, much more hydroxy groups were in membrane when the higher EA feed concentration was used. Therefore, the swelling ratio in aqueous alcohol solution increased

Table I Modified PAN Membranes Used in this Study

Membrane No.	Mole Ratio of $\text{NH}_2/\text{C}\equiv\text{N}$	Elemental Analysis			
		C	H	N	O ^a
1	0	67.91	5.63	26.36	0.10
2	1	59.36	7.13	25.28	8.23
3	0.5	62.21	5.92	25.67	6.20
4	0.25	64.75	5.34	26.10	3.81
5	0.125	66.71	5.88	26.22	1.19

^a O (%) = $100 - (\text{C} + \text{H} + \text{N})\%$.

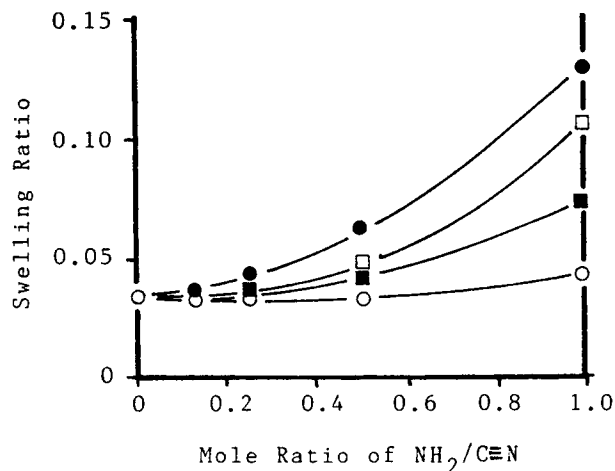


Figure 2 Dependence of swelling ratio on the mole ratio of $\text{NH}_2/\text{C}\equiv\text{N}$ in alcohol-water mixture. Water (\bullet); methanol (\circ); ethanol (\circ); 50% aqueous methanol solution (\blacksquare); 50% aqueous ethanol solution (\square).

monotonously with increasing the mole ratio of $\text{NH}_2/\text{C}\equiv\text{N}$. It could be also seen that the water caused swelling of the membranes to a far greater degree than does alcohol. From the above results, it is expected that this membrane has a stronger affinity to water than to alcohol in aqueous alcohol solution.

Figure 3 shows the dependencies of the permeation flux and separation factor on the EA feed concentration. It should be noted here that the membrane became water-soluble at the mole ratio of $\text{NH}_2/\text{C}\equiv\text{N}=2$. The value of the separation factor

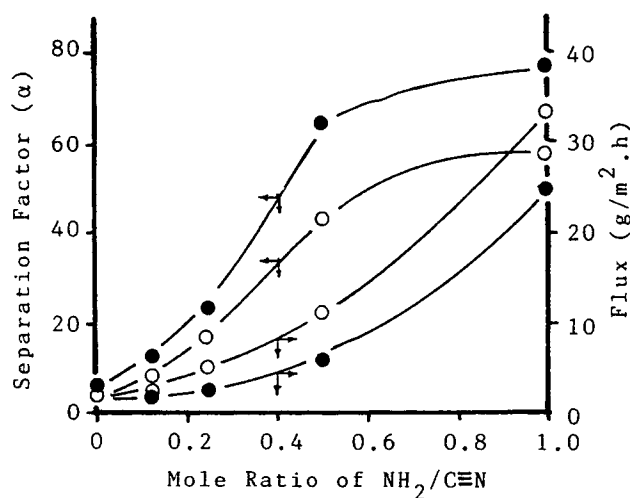


Figure 3 Dependence of separation factor α and permeation flux on the mole ratio of $\text{NH}_2/\text{C}\equiv\text{N}$. Methanol-water system (\circ); ethanol/water system (\bullet). Membrane thickness $117\ \mu\text{m}$; operating temperature 30°C .

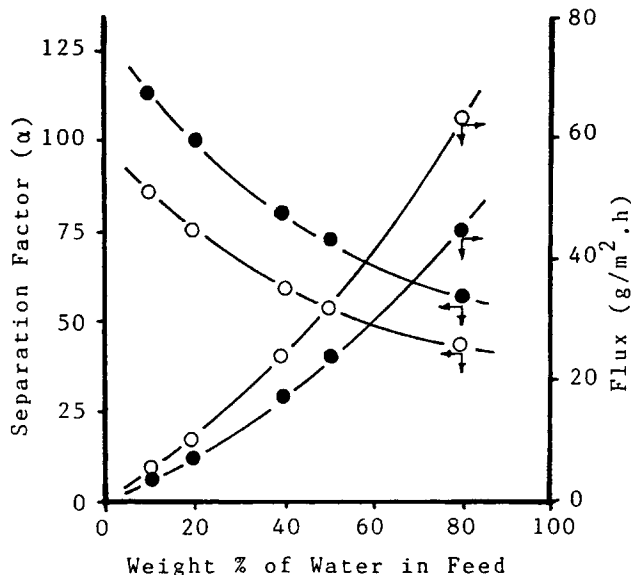


Figure 4 Dependence of separation factor α and permeation flux on the water concentration in the feed. Methanol-water system (O); ethanol/water system (●). Membrane thickness 117 μm ; operating temperature 30°C.

and permeation flux were generally greater in the modified PAN membrane than in the PAN membrane, although they were smaller when the mole ratio of $\text{NH}_2/\text{C}\equiv\text{N}$ was less than 0.2. As the EA feed concentration increased, both increased gradually to a maximum mole ratio of about $\text{NH}_2/$

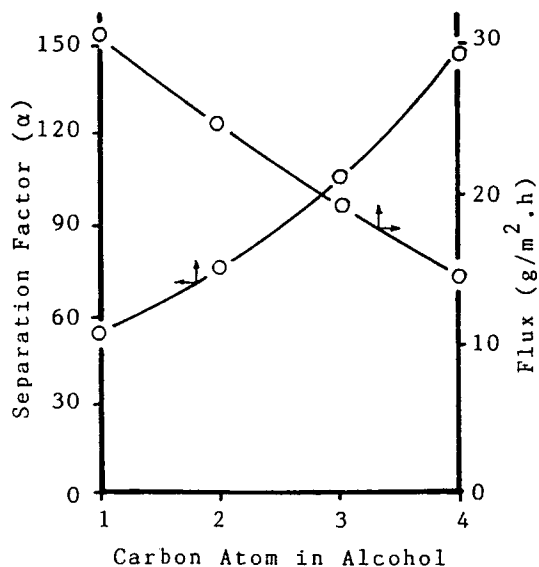


Figure 5 Dependence of separation factor α and permeation flux on the number of carbon atoms in *n*-alcohol of 50% aqueous ethanol solution through membrane no. 2. Membrane thickness 117 μm ; operating temperature 30°C.

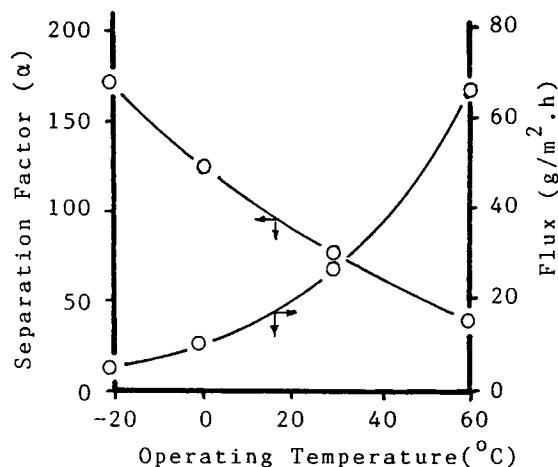


Figure 6 Dependence of separation factor α and permeation flux on the operating temperature of 50% aqueous ethanol solution through membrane no. 2. Membrane thickness 117 μm .

$\text{C}\equiv\text{N}=1.0$. This increase could be due to the enhancement of the membrane hydrophilicity by introducing greater EA content into membrane. The separation characteristics of the membrane for a water-methanol mixture were worse than for a water-ethanol mixture.

The relation between the pervaporation results and water concentration in the feed is shown in Figure 4. When the water concentration in the feed increased, the separation factor increased, whereas the flux decreased. This is the common behavior in

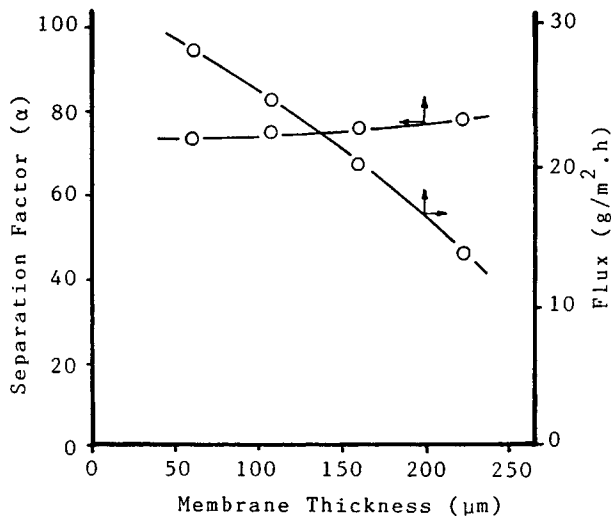


Figure 7 Dependence of separation factor α and permeation flux on the membrane thickness of 50% aqueous ethanol solution through membrane no. 2. Operating temperature 30°C.

the water-permselective membranes for separation alcohol/water solution.

According to solution-diffusion theory,¹⁴ permeation of liquids through polymer membranes involves a dissolution of the liquids in the upstream surface of the membranes and a diffusion within them. Apparently, the diffusion rate of a liquid decreases with increasing its molecular size. As could be seen in Figure 5, increase of the carbon atom in alcohol results in an increase of separation factor, but a decrease of permeation flux.

The effect of the operating temperature on the permeation through membrane no. 2 was investigated under conditions such as that the wt % of water in mixtures was fixed at 50%, and the operating temperatures were carried out at -20° , 0° , 30° , and 60°C (Fig. 6). If the hydrogen-bonding interaction is the major factor controlling the selectivity, it is expected that the selectivity might increase by lowering the operating temperature. As expected, the selectivity of the membrane toward water increased significantly by decreasing the operating temperature. The decrease of flux with lowering the temperature could be attributed to the decrease in diffusivity of permeating molecules through the membrane.

Figure 7 shows the effect of membrane thickness on permeation behaviors in 50% aqueous ethanol solution through membrane no. 2. It was found that the separation factor was independent of the thickness of the membrane, which was in the range of 50–250 μm . The permeation flux increased with decreasing thickness. Therefore, a membrane with high selectivity and flux could be obtained, if an ultrathin membrane can be prepared.

CONCLUSION

A membrane with a high separation factor and mechanical stability for aqueous alcohol solution separation, although the flux was low, could be obtained by the modification of PAN with ethanolamine. This separation was due to the hydrogen-bonding interaction for the incorporation of hydroxy groups into PAN membrane.

When EA component in the membrane increased, both the separation factor and permeation flux increased. Moreover, it was found that as carbon atoms in alcohol increased, the separation factor increased, whereas the flux decreased. Lowering the operating temperature also enhanced the selectivity toward water.

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REFERENCES

1. Y. Jin and R. Y. M. Huang, *Eur. Polym. Sci.*, **5**, 471 (1988).
2. M. Yoshikawa, M. Yokoi, K. Sanui, and N. Ogata, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 2159 (1984).
3. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 1585 (1986).
4. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *J. Appl. Polym. Sci.*, **33**, 2369 (1987).
5. T. Itoh, Y. Ohkawa, K. Ishihara, and I. Shinohara, *Polym. J.*, **11**, 827 (1983).
6. G. M. Hsiue and C. J. Hu, *J. Chinese Inst. Chem. Eng.*, **16**, 57 (1985).
7. G. M. Hsiue, Y. S. Yang, and J. F. Kuo, *J. Appl. Polym. Sci.*, **34**, 2187 (1987).
8. W. Y. Chiang and C. M. Hu, *J. Appl. Polym. Sci.*, 1988.
9. C. M. Hu and W. Y. Chiang, *Angew. Makromol. Chem.*, **179**, 157 (1990).
10. W. Y. Chiang and C. M. Hu, *J. Polym. Sci. Polym. Chem. Ed.*, **28**, 1623 (1990).
11. D. Braun, H. Cherdon, and W. Kem, *Techniques of Polymer Syntheses and Characterization*, Interscience, New York, p. 188.
12. H. Inagaki, K. Hayashi, and T. Matsuo, *Makromol. Chem.*, **84**, 80 (1965).
13. T. Itoh, H. Toya, K. Ishihara, and I. Shinohara, *J. Appl. Polym. Sci.*, **30**, 179 (1985).
14. E. Lacey and S. Loeb, *Industrial Processing with Membranes*, Wiley-Interscience, New York, 1972.

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