

Separation of Liquid Mixtures by Using Polymer Membranes. IV. Water-Alcohol Separation by Pervaporation through Modified Acrylonitrile Grafted Polyvinyl Alcohol Copolymer (PVA-G-AN) Membranes

WEN-YEN CHIANG and CHING-CHONG HUANG

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

SYNOPSIS

The acrylonitrile (AN) grafted onto polyvinyl alcohol (PVA) can improve the mechanical properties and water resistance of PVA; however, its hydrophilicity is decreased. Prepared PVA-g-AN membranes through modification with the NaOH and HCHO aqueous solutions can enhance its hydrophilicity. This modified PVA-g-AN membranes were used to separate alcohol/water solution with the pervaporation method. The flux was increased from 0.72 kg/m² h of the original membrane to 2.06 kg/m² h of the modified membrane. Moreover, adding a small quantity of CoSO₄ to the water-alcohol mixture can simultaneously increase the separation factor. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

There are two ways to separate the water/alcohol solution with the pervaporation technique. One is that water is selectively permeated through membranes.¹⁻⁴ Most publications on membrane separation of the aqueous alcohol solution deal with separation by selective permeation of water. Only a few reports have dealt with separation by selective permeation of alcohol.^{5,6} This research is based on the premise that the prepared PVA-g-AN membrane is a water permselective membrane. The pervaporation properties of the membranes were improved by the reaction of PVA-g-PAN with NaOH and HCHO aqueous solutions. On the other hand, a small quantity of metal salts added to the above liquid mixture resulted in increased permselectivity of the membrane.

EXPERIMENTAL

PVA BF-17, a product of Chang Chun Petrochemical Co., Taiwan, DP-1700, degree of saponification

of 98.5–99.2 mol %, and viscosity of 25–30 cp (4% aqueous solution, 20°C) was used. Acrylonitrile (AN) and dimethyl sulfoxide (DMSO) reagents were purchased from Wako Pure Chemical. The AN was successively washed with aqueous sodium hydroxide, aqueous phosphoric acid, and distilled water. It then was distilled after calcium hydride was used for dehydration. Potassium persulfate (KPS) (Kanto Chemical Co., Japan), recrystallized from methanol was used as an initiator.

Syntheses of PVA-g-AN

The reaction was carried out in a four-necked flask equipped with a stirrer, thermometer, condenser, and nitrogen inlet. The general experimental procedure and an example were as follows:

PVA 30.38 g (0.72 mole) and AN 30.38 g (0.57 mole) were dissolved in 300 mL DMSO after being stirred in an atmosphere of nitrogen. The temperature was adjusted at 60°C, and 0.05 g KPS was added as an initiator. Following the reaction time of 5 h, the products were precipitated in a large amount of water to dissolve the unreacted PVA. The PAN homopolymer in the product was extracted using dimethylformamide (DMF). After extraction,

PVA-g-AN was obtained and dried in a vacuum oven below 60°C.

Graft efficiency (%)

$$= \frac{\text{Weight of grafted branch}}{\text{Weight of PVA-g-AN formed}} \times 100\%$$

PVA-g-AN Membrane Preparation

PVA-g-AN 1.1 g was dissolved in 20 mL DMSO. The solution was poured onto plate glass, and the solvent was allowed to evaporate at 60°C in vacuo to form the membranes.

Modified of PVA-g-AN Membrane

PVA-g-AN Membrane was treated with aqueous NaOH and HCHO at 100°C for 6 h.

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, wiped with tissue paper to remove adsorbed 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.

Pervaporation Experiment

The apparatus and procedure of the pervaporation were principally the same as those described in the previous report.² Its upper compartment with a capacity of 250 cm³, 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 110 μm in thickness. After an overnight dip in the water-alcohol mixture, the membrane was removed, wiped dry with a tissue, 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 for 8 h. The pervaporation experiments were usually carried out at 30°C.

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 on a Hitachi gas chromatograph equipped with a column 2 m in length packed with Porapak Q.

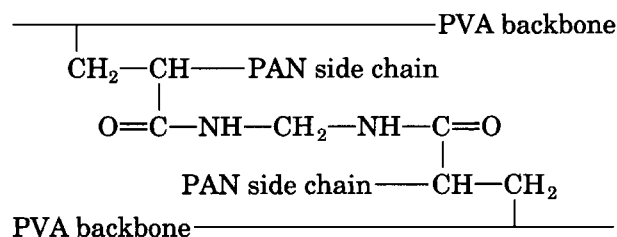
Two factors were used to evaluate the characteristic data of a pervaporation run: (1) The permeation flux is expressed in kg/m²h and (2) the selectivity factor α , defined as

$$\alpha = \frac{Y_{\text{water}}/Y_{\text{alcohol}}}{X_{\text{water}}/X_{\text{alcohol}}}$$

where *X* and *Y* denote the weight fraction of water and alcohol in the feed solution and in the pervaporate, respectively.

RESULTS AND DISCUSSION

In our previous study,⁷ a crosslinking structure was obtained within PVA-g-AN after the treatment of NaOH/HCHO aqueous solution. The resultant structure was proposed as follows:



Such crosslinking in PVA-g-AN was expected to have high mechanical strength and selectivity of water in an alcohol-water mixture.

Table I shows the composition of original PVA-g-AN membranes. These membranes were treated

Table I The Elemental Analysis of Products for Different PVA Feed Concentration

PVA/AN ^a	Elemental Analysis (%)			
	C	H	N	O ^b
1/4	60.62	7.62	14.49	17.27
1/2	60.08	7.90	13.22	18.80
3/4	58.32	8.13	10.62	22.93
1/1	57.48	8.42	8.66	25.44
4/3	57.09	8.65	7.92	26.34

^a Conditions: in DMSO at 60°C for 5 h.

^b O (%) = 100% (C + H + N %).

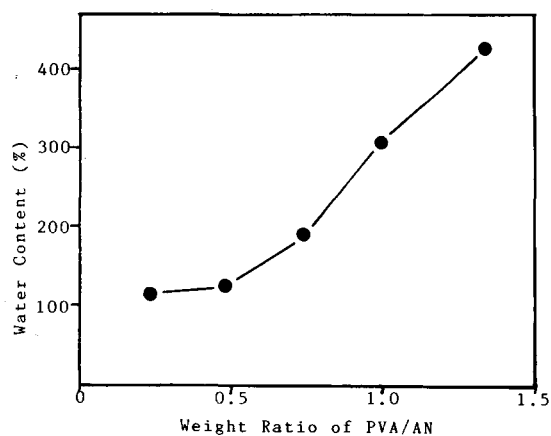


Figure 1 Effect of weight ratio of PVA/AN in feed on water content of PVA-g-AN membrane.

with NaOH and HCHO aqueous solution of different ratios.

In Figures 1, 2, and 3, the modified membranes had a higher water content than the original membranes. It means that the former should have a better selectivity of water in alcohol-water mixture than the latter as expected.

Figure 4 shows the relation between the swelling ratio in water-alcohol mixture at 30°C and the composition of graft copolymer membranes. Water causes swelling of the membrane to a greater degree than alcohol does. Moreover, the swelling ratio increases monotonously with the increasing composition of PVA in the membrane because of the increase of hydrophilicity. As the water concentration is increased, so is the swelling ratio. From the above results, it is expected that this membrane has a

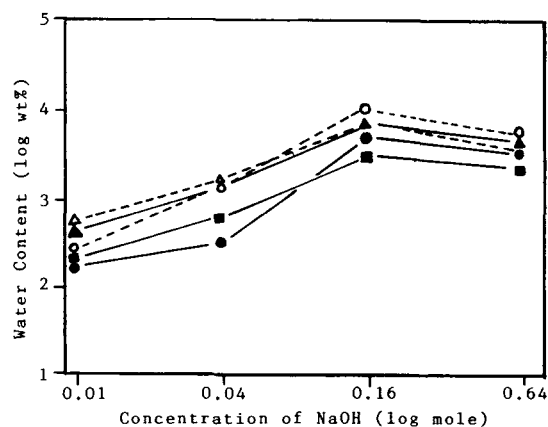


Figure 2 Dependence of water content on NaOH concentration of NaOH/HCHO modified PVA-g-AN membrane. Carried out at 100°C for 6 h. HCHO = 0.065 mole. (●) PVA/AN = 1/4; (○) PVA/AN = 1/2; (▲) PVA/AN = 3/4; (△) PVA/AN = 1/1; (■) PVA/AN = 4/3.

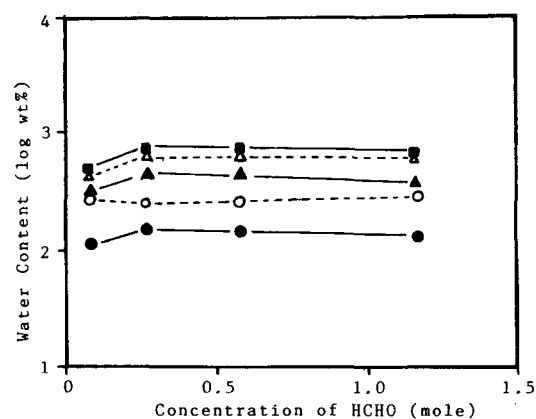


Figure 3 Dependence of water content on HCHO concentration of NaOH/HCHO modified PVA-g-AN membrane. Carried out at 100°C for 6 h. NaOH = 0.01 mole. (●) PVA/AN = 1/4; (○) PVA/AN = 1/2; (▲) PVA/AN = 3/4; (△) PVA/AN = 1/1; (■) PVA/AN = 4/3.

stronger affinity to water than to methanol in the aqueous methanol solution.

Figure 5 compares the permeation flux and the separation factor of the PVA-g-AN membrane before and after treatment with NaOH and HCHO aqueous solution. This figure reveals the modified membrane to have a better flux but a lower separation factor. However, this is not the result we expected. In order to improve this defect, we refer to the previous report,⁸ which describes a pattern of "holes" produced by the thermal motion of polymer chains in the membrane, and the diffusion of permeating molecules through the "holes." Therefore, addition of a small quantity of CoSO₄ metal salt to

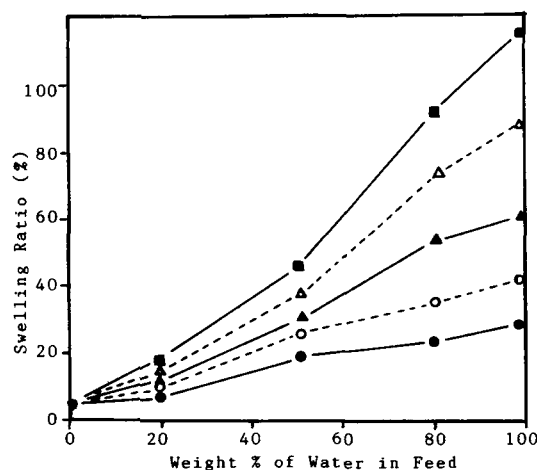


Figure 4 Effect of the weight of water/methanol on swelling ratio of modified PVA-g-AN membrane. (●) PVA/AN = 1/4; (○) PVA/AN = 1/2; (▲) PVA/AN = 3/4; (△) PVA/AN = 1/1; (■) PVA/AN = 4/3.

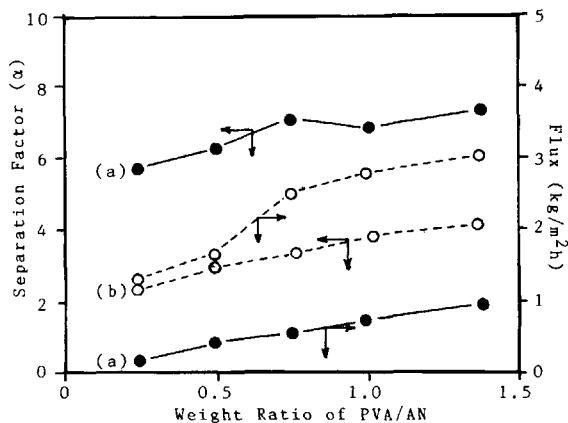


Figure 5 Dependence of permselectivity on the weight ratio of PVA-AN. Condition: Water/methanol = 80/20 at 30°C. (a) PVA-g-AN; (b) NaOH/HCHO modified PVA-g-AN.

the water-alcohol mixture could, via the property of the —OH groups on PVA-g-AN, induce chelation. This results in conformational changes in the PVA-g-AN molecules, thereby reducing the number of “holes” on the membrane. This contraction of the “holes” hardly affects the diffusivity of water molecules, but affects the diffusivity of larger alcohol molecules to a significant degree, after which only the small water molecules can pass through the membrane. Thus, the addition of salt to the water-alcohol mixture decreases the diffusivity of alcohol and increases the separation factor (Fig. 6). When 1.5×10^{-2} mol/kg CoSO_4 is added into the water-alcohol mixture, the separation factor reaches a maximum.

Dependence of the permeation flux of water and methanol on CoSO_4 concentration is shown in Fig-

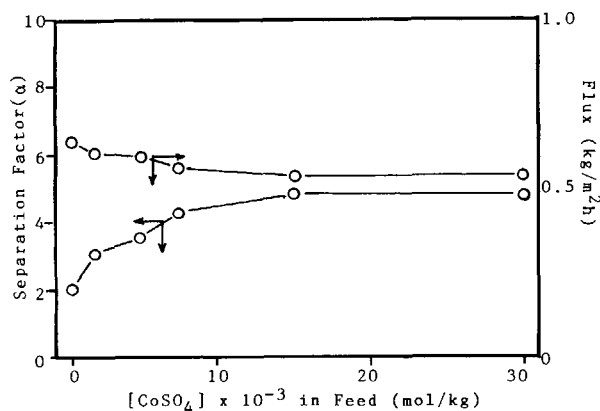


Figure 6 Dependence of permselectivity on cobalt salt of PVA-g-AN modified membrane. PVA/AN = 3/4, water/methanol = 50/50 (wt), operating temp. 30°C.

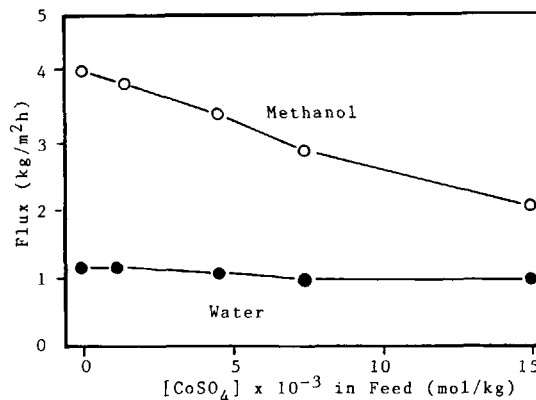


Figure 7 Dependence of permeation flux of water and methanol on various cobalt salt concentrations. (●) Water; (○) methanol; operating temp. 30°C. Membrane (PVA/AN = 1/2) was treated with 0.01 mole NaOH and 0.065 mole HCHO at 100°C for 6 h.

ure 7. The permeation flux of water is nearly constant irrespective of salt concentration, but the permeation flux of methanol decreases as the salt concentration increases. This result indicates that the increase in the separation factor could be due to the decreased rate of permeation in methanol.

According to the solution-diffusion theory,⁹ the diffusive cross-section is defined as the ratio of the molecule volume (V) and molecule length (L) [i.e., molecular shape (V/L)]. Table II shows calculated molecule length and shape of various alcohols. Apparently, the diffusion rate of a liquid decreases as its molecular size increases. As can be seen in Figure 8, an increase in the carbon atom in alcohol results in an increase in the separation factor, but a decrease in the permeation flux. In the presence of CoSO_4 , the contracted “hole” is small enough to hinder the diffusion of the larger alcohol molecules, and thus, the permeation rate of the alcohol decreases markedly with the increase in the bulkiness of the alcohol

Table II Calculated^a Molecule Length (L) and Molecule Shape (V/L) of Various Alcohols

Alcohol	$L(\text{Å})$	$V/L^b(\text{Å}^2)$
Methanol (CH_3OH)	2.9	23.2
Ethanol ($\text{C}_2\text{H}_5\text{OH}$)	4.2	23.1
<i>n</i> -Propanol (<i>n</i> -3) ($\text{C}_3\text{H}_7\text{OH}$)	5.4	23.3
<i>i</i> -Propanol (<i>i</i> -p) (<i>i</i> - $\text{C}_3\text{H}_7\text{OH}$)	4.3	29.6

^a L denotes the maximum zigzag calculated from Table of Interatomic Distances and Configuration in Molecules and Ions, Special Publication, No. 11, Chemical Society, London, 1958.

^b V was calculated by dividing the molecular weight by the density and the Avogadro number.

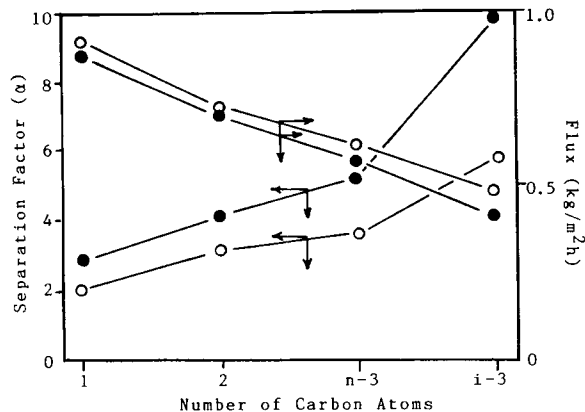


Figure 8 Effect of molecular length (L) and shape (V/L) on permselectivity of water/alcohol. (●) With the presence of 1.5×10^{-3} mol/kg CoSO_4 . (○) Without the presence of salt. Membrane (PVA/AN = 3/4) was treated with 0.01 mole NaOH and 0.065 mole HCHO at 100°C for 6 h.

molecule. The contraction is not small enough however to hinder the diffusion of the water molecule.

CONCLUSION

The permselective properties of PVA-g-AN modified by NaOH and HCHO aqueous solution were

studied. Although the separation factor and the permeation flux obtained in this experiment were not good enough, use of the chelating of cobalt on the PVA-g-AN membrane resulted in retention of its separation factor but enlarging its permeation factor.

REFERENCES

1. C. M. Hu and W. Y. Chiang, *J. Appl. Polym. Sci.*, **42**, 1829 (1991).
2. W. Y. Chiang and C. M. Hu, *J. Appl. Polym. Sci.*, **43**, 2005 (1991).
3. T. Hirotsu, *J. Appl. Polym. Sci.*, **34**, 1159 (1987).
4. S. Kimura and T. Nomura, *Membrane*, **8**, 177 (1982).
5. C. M. Hu and W. Y. Chiang, *Angew. Makromol. Chem.*, **179**, 157 (1990).
6. Y. M. Lee and K. Won, *Polym., J.*, **22**, 583 (1990).
7. W. Y. Chiang and C. C. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, in press.
8. A. Mochizuki, Y. Sato, H. Ogawara, and S. Yamashita, *J. Appl. Polym. Sci.*, **37**, 3357 (1989).
9. E. Lacey and S. Loeb, *Industrial Processing with Membranes*, Wiley-Interscience, New York, 1972.

Received May 22, 1992

Accepted July 2, 1992