

Separation of Water/Ethanol Mixture Through Poly(acrylonitrile-co-Acrylic Acid)/Poly(ethylene Oxide) Membranes by Pervaporation

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SYNOPSIS

The separation of water/ethanol mixtures was investigated by poly(acrylonitrile-co-acrylic acid) and by poly(acrylonitrile-co-acrylic acid)/poly(ethylene oxide) blend membranes. The flux increased with the content of acrylic acid in copolymers and the selectivity remained constant. The marked increase of the selectivity was observed for blend membranes of a certain blend ratio, suggesting that the two polymers are partially miscible. Poly(ethylene oxide) in blends was thought to act as a plasticizer as well as a preferentially water absorbing and diffusing component. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Pervaporation is a membrane separation process that can be used to separate liquid mixtures whose separation is very often difficult by conventional distillation. This membrane process, a liquid phase permeation in which the liquid feed mixture is in contact with the membrane in the upstream and the permeate is removed from the downstream as a vapor, was reported by Binning et al.¹ for the first time. After several decades it was realized that the process is the most efficient separation process for neutral substances such as organic liquid mixtures.

The separation process of pervaporation is based on a solution-diffusion mechanism, that is, the permeation rate is a function of solubility and diffusivity. Solubility is a thermodynamic property whereas diffusivity is a kinetic property. Both solubility and diffusivity also affect the selectivity of membranes. As for most of the membrane processes, pervaporation membranes are characterized by the transport rate through the membrane and the separation performance. For pervaporation, the transport rate is

usually represented by the flux J , the amount of liquid that is transported through the membrane per unit area and per unit of time. For the separation performance of pervaporation membranes the parameters are mathematically calculated from the concentrations of the components (A and B) in the feed (C_A^f and C_B^f) and in the permeate (C_A^p and C_B^p). The most commonly used parameter is the selectivity, defined as

$$\alpha_{A/B} = (C_A^p/C_B^p)/(C_A^f/C_B^f).$$

In recent years there has been increased work in the use of the pervaporation process for many organic liquid mixtures. Many efforts have been focused on the development of more effective membrane materials for the separation of water/ethanol mixtures. The selective separation of water from the water/ethanol mixture through membranes was carried out by incorporating a functional group into membranes that would have a strong interaction, preferentially with water molecules by hydrogen bonding. From this point of view, a great number of copolymer membranes were synthesized containing functional groups capable of a strong interaction with water through hydrogen bonding.²⁻⁵

Polymers containing ionic groups have been used

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for the separation of water/ethanol mixtures by the pervaporation process, in which the ion/dipole interaction between ionic groups and water molecules can be induced.⁶⁻⁹ The stronger the interaction of the ion with the water molecules, the more selectively these polymers will absorb and the easier water molecules will diffuse with respect to ethanol, provided that the polymer membrane does not swell too much.

Polymer blending could be an effective method to control the hydrophilic-hydrophobic balance of membrane for the pervaporation process. However, few workers¹⁰⁻¹³ have reported some results of polymer blending for the separation of water/ethanol mixtures by the pervaporation process.

The pervaporation performance of copolymer and copolymer blend membranes were investigated in this study. Polyacrylonitrile (PAN) was used as a base material, and the acrylic acid was incorporated into PAN as a hydrophilic component by copolymerization. Poly(ethylene oxide) was also blended with the copolymer as a hydrophilic component as well as a plasticizing material, and its pervaporation performance was analyzed in terms of copolymer composition and blend ratio.

EXPERIMENTAL

Materials

Poly(acrylonitrile-*co*-acrylic acid) was synthesized by emulsion polymerization at 40°C. Copolymer composition was determined by the acid titration

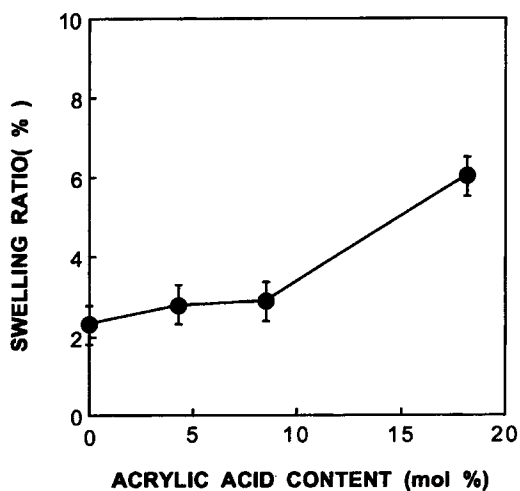


Figure 1 The effect of acrylic acid content in copolymers on the swelling ratio at 10 wt % water in the feed.

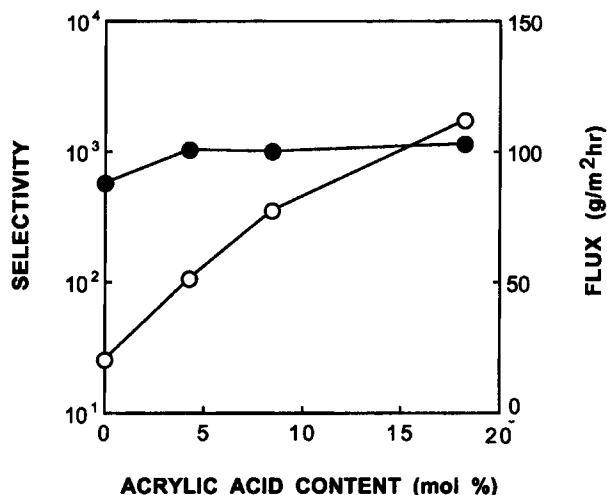


Figure 2 The effect of acrylic acid content in copolymers on the (○) flux and (●) selectivity at 10 wt % water in the feed.

method. Poly(ethylene oxide) used in this study was purchased from Aldrich Co. (reported $M_w = 100,000$ g/mol). *N,N*-Dimethyl formamide (DMF) and ethanol were reagent grade and used without further purification. Water was distilled before use.

Preparation of Membranes

Casting solutions were prepared by dissolving poly(acrylonitrile-*co*-acrylic acid) and poly(ethylene oxide) in DMF at a total concentration of 5 wt %. Clear and homogeneous solutions were obtained after stirring the solution at room temperature for

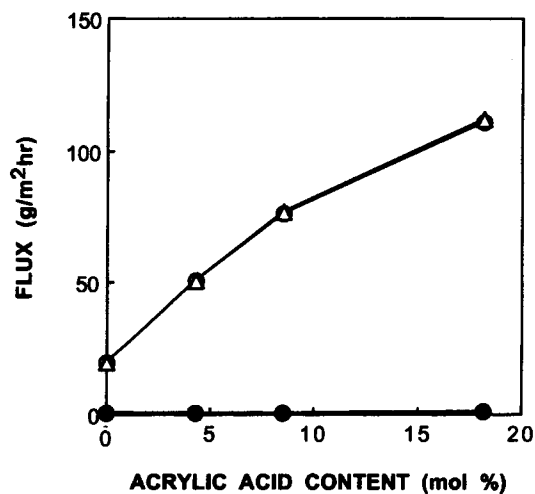


Figure 3 The effect of acrylic acid content in copolymers on the (Δ) total, (○) water, and (●) ethanol flux at 10 wt % water in the feed.

Table I Effect of Acrylic Acid Content on Flux and Selectivity

Acrylic Acid Content (mol %)	Water Flux (g/m ² h)	Ethanol Flux (g/m ² h)	Total Flux (g/m ² h)	Selectivity
0.0	19.68	0.320	20.00	560.98
4.3	50.46	0.440	50.90	1032.70
8.5	76.21	0.690	76.90	997.71
18.5	111.12	0.880	112.00	1140.40

Composition of feed solution: water/ethanol = 10/90.

1 h. No visible phase separation was observed. Then membranes were prepared by casting the solution on a glass plate. The solvent was removed by evaporation at 50°C for one day, and the membrane was dried at 60°C in a vacuum oven for another 2 days.

Sorption Experiment

Equilibrium sorption experiments were performed at 30°C using thick strips of membranes. Strips were dried in vacuum until no significant weight change was observed. The strips were immersed in water/ethanol mixture at 30°C. After equilibrium was reached, the membranes were blotted between tissue papers and weighed. From the difference of wet weight (after equilibrium sorption) and dry weight of the membranes, the total sorption was calculated. All experiments were performed at least three times, and the results were averaged.

Pervaporation Experiment

The pervaporation experiments were performed using two stainless cells. The effective area in each cell is 19.63 cm.² From the feed tank, which is kept at a constant temperature of 30°C, the feed is circulated through the cells to prevent concentration polarization of the feed solution in the vicinity of the membrane. The pressure at the downstream side was kept below 3 torr by a vacuum pump. The permeate was collected in a cold trap of liquid nitrogen. Flux was determined by the amount of the permeate collected per hour. The fluxes of the different membranes were normalized to a membrane thickness of 10 μm assuming the proportionality between the flux and the reciprocal membrane thickness. The compositions of the permeate were analyzed by gas chromatography.

RESULTS AND DISCUSSION

Poly(acrylonitrile-co-Acrylic Acid) Membranes

In Figure 1, the result of the sorption experiment for copolymer membranes is given at 10 wt % water in the feed. The swelling ratio is plotted against the acrylic acid content in copolymer. It shows that the swelling ratio of the membranes increases with an increase of the acrylic acid content in copolymer although the magnitude of swelling ratio is not large. Figure 2 shows the effect of the acrylic acid content in copolymers on the permeability and selectivity of the copolymer membrane: the flux increases with an increase of the acrylic acid content in copolymer whereas the selectivity remains constant. This result is compared with the work of Yoshikawa et al.¹⁴ This can be explained in relation to the result of the sorption experiment. As the acrylic acid content increases in copolymers, the membrane becomes more hydrophilic and its affinity to the feed solution increases. More liquid is absorbed in the membrane

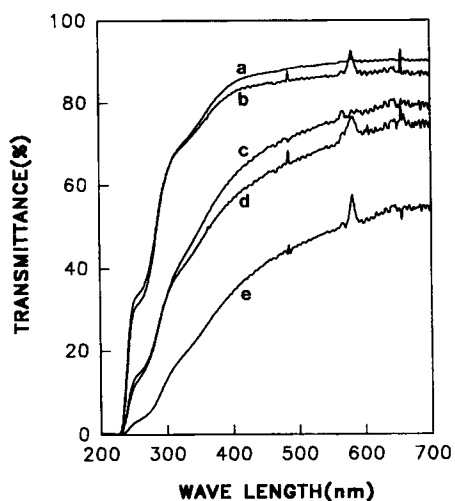


Figure 4 UV/visible spectra for poly(acrylonitrile-co-acrylic acid)/poly(ethylene oxide). The content of poly(ethylene oxide) in blend is (a) 0, (b) 1, (c) 2, (d) 4, and (e) 7 wt %.

as the acrylic acid content increases, and as a consequence the flux increases. On the other hand the selectivity is almost independent of acrylic acid content in copolymer. This means that the solubility and diffusivity of both permeants in the membrane increases with the increase of the acrylic acid content in the copolymers.

In order to analyze this pervaporation result, the flux was divided into each component. Figure 3 and Table I show the effect of acrylic acid content in copolymers on the total flux, water flux, and ethanol flux. These results indicate that water exclusively permeates through the membrane but the flux of both permeants increases with the acrylic acid content. The incorporation of acrylic acid into the membrane increases the sorption and permeation of water, resulting in the increase of the flux and selectivity as compared to PAN homopolymer membrane. However, the selectivity of copolymer membranes remains constant regardless of the acrylic acid content because the increase of the acrylic acid content in copolymers increases the diffusivity of both permeants as well as the solubility.

Poly(acrylonitrile-co-Acrylic Acid)/ Poly(ethylene Oxide) Blend Membranes

The blend membrane was prepared by mixing the copolymer containing 8.5 mol % acrylic acid and poly(ethylene oxide) (PEO). The membranes with 1 wt % PEO content were completely transparent but become increasingly less transparent with increasing PEO content indicating a phase separation.

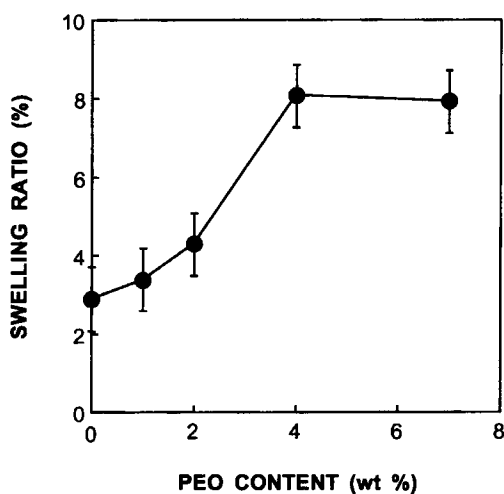


Figure 5 The effect of PEO content in blend on the swelling ratio at 10 wt % water in the feed. The acrylic acid content in copolymer is 8.5 mol %.

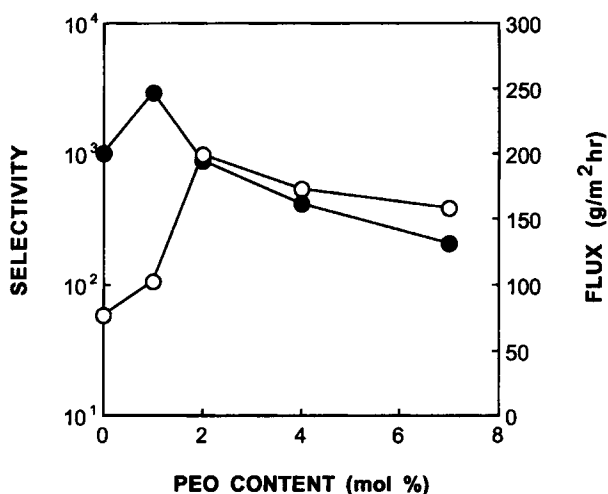


Figure 6 The effect of PEO content in blend on the (○) flux and (●) selectivity at 10 wt % water in the feed. The acrylic acid content in copolymer is 8.5 mol %.

This result was supported from a turbidity measurement of the membranes by use of a UV/visible spectrophotometer. Figure 4 shows that the transmittance of the blend membranes with 1 wt % PEO content hardly changes but decreases with an increase of PEO content indicating that a phase separation occurs. In other words, PEO is completely miscible with poly(acrylonitrile-co-acrylic acid) at molecular level up to 1 wt % PEO content. As the PEO content in the blend increases, the blend becomes less transparent and the transmittance de-

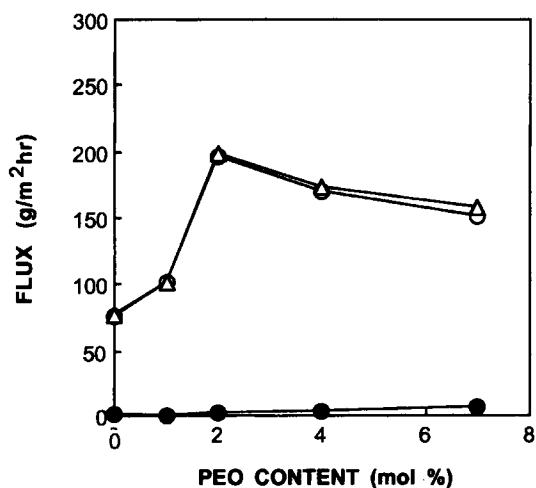


Figure 7 The effect of PEO content in blend on the (Δ) total, (○) water, and (●) ethanol flux at 10 wt % water in the feed. The acrylic acid content in copolymer is 8.5 mol %.

Table II Effect of Poly(ethylene Oxide) Content on Flux and Selectivity

PEO Content (wt %)	Water Flux (g/m ² h)	Ethanol Flux (g/m ² h)	Total Flux (g/m ² h)	Selectivity
0	76.21	0.690	76.90	-997.71
1	101.59	0.313	101.90	2921.10
2	196.59	2.010	198.60	880.54
4	169.51	3.690	173.20	413.54
7	151.35	6.550	157.90	207.92

Composition of feed solution: water/ethanol = 10.90.

creases markedly suggesting that the blend phase separates and PEO may exist as a dispersed phase. The dispersed phase of PEO may be a crystalline phase because the PEO is a crystallizable polymer.

Figure 5 shows that the swelling ratio increases with increasing PEO content in the blend. These results indicate that the addition of PEO into the copolymer increases the affinity of the membrane toward the feed solution and thus the membrane absorbs the feed solution more easily. Figure 6 illustrates that the selectivity has the maximum value at the 1 wt % PEO while the flux increases and then remains constant or slightly decreases as the PEO content increases further. These results seem to be closely related to the miscibility behavior of the two polymers. When the content of PEO is 1 wt %, two polymers are miscible at a molecular level. The PEO in this blend preferentially absorbs water and acts as a plasticizer for water to permeate. For the higher content of PEO, the blend phase separates and PEO

may exist as a crystalline phase through which no permeants could permeate, resulting in no change or a decrease in pervaporation performance.

Figure 7 shows the effect of blend ratio on the total flux, water flux, and ethanol flux. This result indicates that the total flux is almost the same as the water flux and that the ethanol flux is negligible. Particularly, the blend membrane shows a minimum ethanol flux for the blend of 1 wt % PEO content, resulting in a maximum selectivity (see Table II). Therefore the PEO increases the water flux while preventing the transport of ethanol through the membrane. Figure 8 shows a general behavior of pervaporation such that the flux increases with the increase of water in the feed whereas the selectivity decreases. By increasing water concentration in the feed the membrane is more swollen so that the flux increases and the selectivity decreases. Figure 9 compares the pervaporation performance of copol-

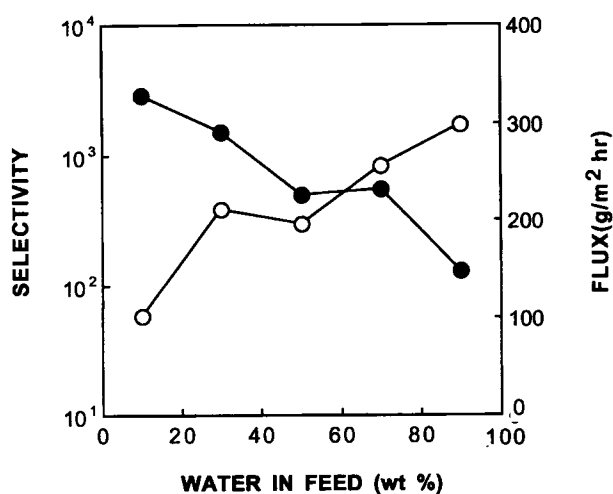


Figure 8 The effect of feed composition on the (○) flux and (●) selectivity. The PEO content in blend is 1 wt % and the acrylic acid content in copolymer is 8.5 mol %.

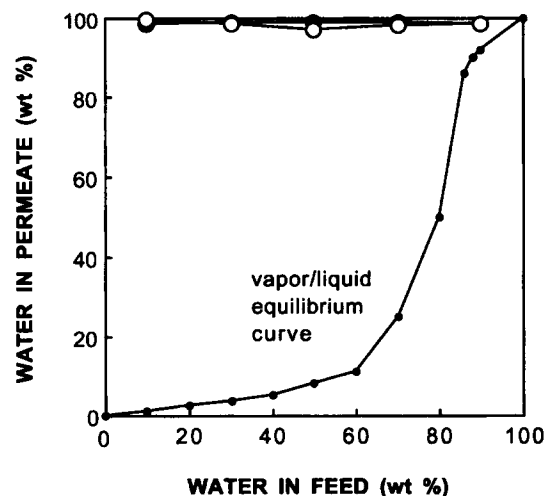


Figure 9 The effect of feed composition on permeate composition for (●) copolymer membrane and (○) copolymer blend membrane. The vapor-liquid equilibrium data were adapted from the literature.¹⁵

Table III Effect of Operating Temperature on Flux and Selectivity

Temperature (°C)	Water Flux (g/m ² h)	Ethanol Flux (g/m ² h)	Total Flux (g/m ² h)	Selectivity
20	95.11	0.250	95.36	3424.0
30	101.59	0.313	101.90	2921.1
40	121.43	0.420	121.85	2602.1
50	135.76	0.501	136.27	2438.8

Membrane: poly(acrylonitrile-co-acrylic acid)/poly(ethylene oxide) 99/1 wt %. Composition of feed solution: water/ethanol = 10/90.

omer membrane, copolymer blend membrane, and the vapor-liquid equilibrium curve for water/ethanol mixtures. As can be seen in Figure 9, both membranes have an excellent separation curve in all concentration ranges of water as compared with vapor-liquid equilibrium curve.

The effect of temperature on the flux was examined in order to infer the transport mechanism of each component through the membrane. As shown in Table III, the elevation in the feed temperature results in an increase of the flux and a decrease of selectivity. The apparent activation energy (E_{app}) for transport of each component could be calculated from the slope of the Arrhenius plot of the flux as shown in Figure 10. The apparent activation energies thus calculated for water and ethanol are 2.34 and 4.46 kcal/mol, respectively. This difference in the activation energy for water and ethanol allows us to speculate that ethanol permeates by a random

molecular diffusion within the amorphous matrix and water permeates by a selective transport through hydrophilic moiety in the copolymer and the PEO in the blend.¹⁴ The difference in E_{app} for each component may come from several material factors such as the molecular size, the affinity between permeates and membrane, etc. As a consequence, water molecules are preferentially absorbed and permeates more easily as compared with ethanol due to the smaller size as well as the higher affinity for the membrane containing the PEO that acts as a plasticizer for water transport.

CONCLUSIONS

An introduction of acid group into PAN enhances the pervaporation performance of the membranes. Transparent blend membranes can be prepared from poly(acrylonitrile-co-acrylic acid) and PEO. The equilibrium sorption experiments for blend membranes shows that the swelling ratio increases with the PEO content. At 1 wt % PEO content the flux and selectivity increased simultaneously, which could be explained by a combination of a plasticizing effect and increased preferential diffusion rates of the permeates through the membrane. Water was preferentially permeated through the copolymer and blend membranes over the entire range of feed composition. The transport mechanisms for water and ethanol seem to be different because the apparent activation energies for water and ethanol are different.

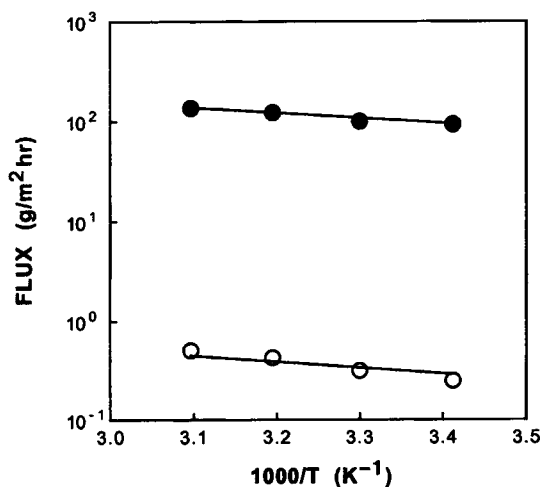


Figure 10 The effect of feed temperature on the (●) water and (○) ethanol flux. The acrylic acid content in copolymer is 8.5 mol %, the PEO content in the blend is 1 wt %, and the feed composition is 10/90 (water/ethanol) by weight.

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Received February 2, 1993

Accepted July 1, 1993