

Pervaporation Separation of Ethanol–Water Mixtures Using Ionically Crosslinked Blended Polyacrylic Acid (PAA)–Nylon 6 Membranes

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Synopsis

The pervaporation separation of ethanol–water mixtures was carried out through a series of ionically crosslinked polyacrylic acid (PAA)–Nylon 6-blended membranes crosslinked to varying degrees in aluminum nitrate solution. The polyacrylic acid (PAA)–Nylon 6 membranes were cast from homogeneous PAA–Nylon 6 mixtures to various thicknesses and then crosslinked. Optimum pervaporation results were obtained from crosslinked blends containing 75 wt% Nylon 6 and 25 wt% PAA. These membranes have separation factors (water/ethanol) of 35–40 at flux rates of 120–160 g/m² h. The optimum crosslinking time was found to be approximately 35 h to yield membranes with the best separation and flux rates at 25 wt% PAA content.

INTRODUCTION

There is a growing interest in the use of pervaporation separation processes for the separation of various organic liquid and organic aqueous mixtures, especially the ethanol–water system.^{2–7} In recent years, the research emphasis has been on the development of new polymer membranes,^{8–12} which have high separation factors, acceptable flux rates, with good stability in the various mixtures to be separated.

According to the solution–diffusion theory,¹³ the permeability of liquids through the polymer membrane can be considered as a composite form consisting of the product of the diffusivity and solubility coefficients, $P = P \times S$. Thus, criteria for selecting membranes for pervaporation separation based solely on solubility coefficients are not adequate because of increase of the diffusivity term. Thus the two parameters, diffusion (D) and solubility (S), must be considered jointly. Semiquantitative empirical equations to relate the separation factors and flux rates to the diffusion and solubility terms are currently under development in this laboratory and will be the subject of a separate report.

In order to adjust and control the hydrophilic–hydrophobic balance properties of a membrane, techniques such as blending and crosslinking,^{14,15} grafting,^{5,15} and copolymerization^{9–11} have been used by various investigators. Of these methods, blending and crosslinking have been successfully reported¹⁴

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for the separation of acetic acid–water mixtures. Recent studies in this laboratory have shown that ionically crosslinked polyacrylic acid (PAA)–Nylon 6-blended membranes with high separation factors and good flux rates can be prepared for the separation of acetic acid–water mixtures. It was thus thought appropriate to adapt and adjust the method used for preparing this type of polyacrylic acid (PAA)–Nylon 6 membrane for the separation of ethanol–water mixtures and this is the subject of this investigation.

EXPERIMENTAL

Apparatus and Experimental Procedure

The pervaporation apparatus consisted of an experimental cell made of aluminum, a constant temperature water bath, glass tubes for condensing and collecting the permeate vapor, and a vacuum pump. Details about the apparatus, particularly the permeation cell and the experimental procedures have been reported elsewhere.¹⁴

Materials

Nylon 6 was obtained from Polysciences Inc. and had an intrinsic viscosity of 1.4 determined in 90% by weight formic acid which corresponded to MW of approximately 42,000. The polyacrylic acid (PAA) used was obtained from Polysciences Inc. in a 25% by weight aqueous solution of molecular weight 150,000. The aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and dimethyl formamide used were all Baker analytical reagent grade obtained from Fisher Scientific.

Membrane Preparation

The blended PAA–Nylon 6 membranes were prepared by the wet technique previously developed in this laboratory.¹⁴ A 25 wt% aqueous PAA (MW 150,000) solution and a 10 wt% Nylon 6 solution in 88 wt% (or 90 wt%) formic acid were mixed together to form a homogeneous solution. The casting solution was cast onto a glass plate with the aid of a Gardner casting knife to appropriate thickness, predried at room temperature for 5 min, and then dried at 60°C for 50 min in a drying oven. It was then crosslinked in a 10 wt% aluminum nitrate crosslinking bath for different times. Following the crosslinking, it was immersed in deionized water for at least 10 h. The thicknesses of the resulting membranes ranged from 1 to 3.5 mils.

RESULTS AND DISCUSSION

Hydrophilic / Hydrophobic Balance of Blended Membranes

High separation cannot be obtained for the ethanol–water system using Nylon 6 membranes or the crosslinked polyacrylic acid membranes because while Nylon 6 is a comparatively hydrophobic polymer, the polyacrylic acid is too strongly hydrophilic. It was then decided to blend Nylon 6 with PAA to obtain a better balanced hydrophilic/hydrophobic structure of the modified membranes for the separation of ethanol–water mixtures. Preliminary tests showed that homogeneous blend solutions can be formed for a large range of

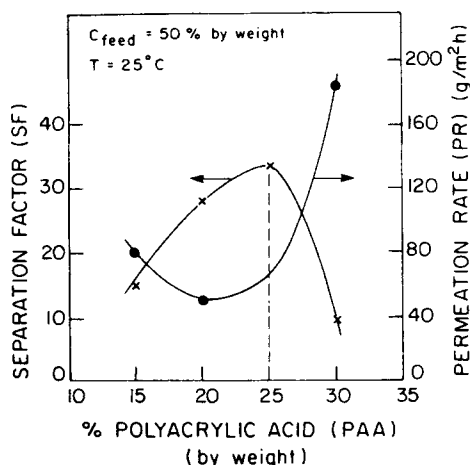


Fig. 1. Effect of polyacrylic acid (PAA) content in membrane (from composition 50% by weight ethanol temperature = 25°C).

PAA contents, from 15% to 50% by weight. The contents of two polymers in the casting solution and the crosslinking degree of PAA in the membranes play an important role in pervaporation performance. For the acetic acid-water system, the optimum composition of PAA in membranes was about 40 wt%, and the aluminum content calculated according to the ratio of Al/AA was 1/10.¹⁴ For the ethanol-water mixture, the optimum values would be different because of the difference in the systems to be separated.

Figure 1 shows the effect of PAA content in membranes on the separation factors and the permeation rates. All the pervaporation runs were carried out at 25°C with a 50 wt% concentration of ethanol-water mixture and the membranes used were crosslinked for about 40 h in 10 wt% Al(NO₃)₃ solution. One can see that the separation factors have a maximum at 25 wt% PAA content in the membranes, while the permeation rates show a minimum at 20 wt% PAA content. The parabolic permeation rate curve may be explained in terms of the solubility of liquid in membrane and the membrane density. Because PAA is a highly hydrophilic polymer, the increase of PAA in the membrane results in increased solubility of liquid in the membrane. As a result, the permeation rates increase when the PAA content is over 25 wt%. When PAA content is less than 20%, the membrane probably is not as dense as that with high PAA content membranes. One can also see that the maximum separation factor occurs at the 25 wt% PAA content in blended membrane while the minimum permeation rate corresponds to 20 wt% PAA content. Based on the selectivity of membrane the optimum hydrophilic/hydrophobic balance content of the blended PAA-Nylon 6 membranes for the 50 wt% ethanol-water mixture can be considered to be at 25 wt% PAA.

According to past studies conducted in this laboratory, the crosslinking of PAA can be achieved in two steps: diffusion of metal ions from crosslinking solution into membrane and crosslinking reaction.^{16,17} Because the rate of crosslinking reaction is very fast in the wet technique, the very thin top layer formed by crosslinking prevents the ions from the diffusion. In the case of

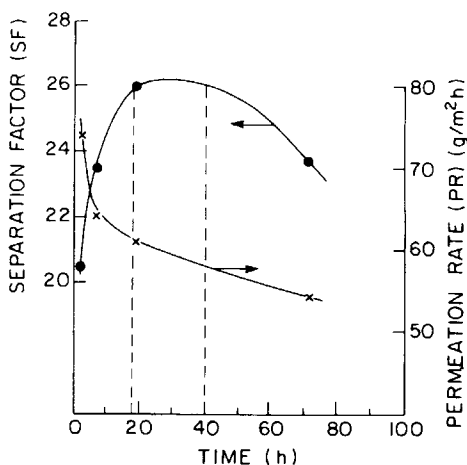


Fig. 2. Effect of crosslinking time (polyacrylic acid (PAA) content in membrane = 25%, concentration of feed = 50% by weight ethanol crosslinking temperature = 25°C, $\text{Al}(\text{NO}_3)_3$ = 10% by weight in H_2O).

blended membranes, because of the presence of Nylon 6 in the membrane the problem of diffusion is not as serious, and good quality membranes can be prepared by the wet technique.

It is convenient to indicate the effects of the crosslinking degree in terms of crosslinking time rather than Al^{3+} content in the membranes. Figure 2 shows the influence of crosslinking time on separation factors and permeation rates. All the pervaporation runs were conducted under the following conditions: Concentration of feed mixtures are 50 wt% of ethanol, pervaporation temperature is 25°C, composition of PAA in the casting solution is 25 wt%, and concentration of $\text{Al}(\text{NO}_3)_3$ in the crosslinking solution is 10 wt%. One can see that the separation factors have a maximum when the crosslinking time is approximately 35 h. The content of Al^{3+} in the membrane or the crosslinking degree increases with the crosslinking time, as a result the hydrophobic properties of the membrane¹³ are reduced while the membrane becomes denser. Thus, as can be seen from this figure, the permeation rate decreases with crosslinking time. The best crosslinking time of 25 wt% PAA-blended membranes for the separation of 50 wt% ethanol–water mixture is about 35 h for high membrane selectivity and permeability.

Selectivity of Blended Membrane for Ethanol–Water Mixtures

The effects of temperature and feed concentration on separation factors are shown in Figure 3. It can be seen that higher separation factors were obtained at low operation temperature than at high operation temperature regardless of the feed concentration. In pervaporation, diffusion is carried out by random oscillation of polymer chains in the amorphous regions of the membrane. When operating temperature increases, the frequency of oscillation increases, and the diffusion rates of two components consequently increase. A slight increase in the quantity of the component with low concentration in permeate results in an apparent decrease of the separation factor.

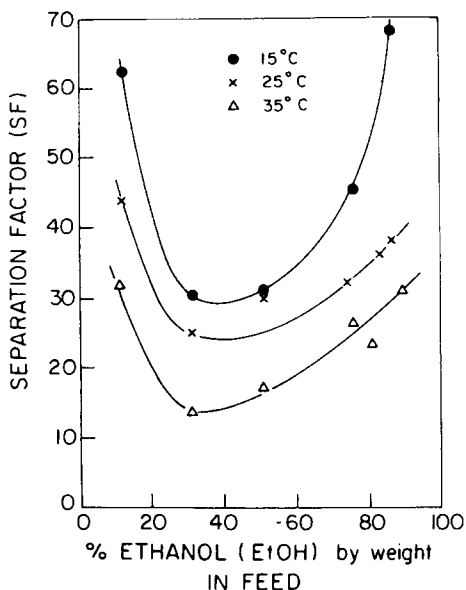


Fig. 3. Effects of temperature and concentration on feed on separation reactors. (●) 15°C; (×) 25°C; (Δ) 35°C.

It is also very interesting to note that the separation factors are minimum at all operation temperatures when the feed concentration is around 30 wt% of ethanol. At both extreme concentration ranges, the separation factors are also much higher. This phenomena was also observed in the separation of acetic acid mixture using blended PAA-Nylon 6 membranes at 25°C.¹⁴

The McCabe-Thiel diagram of Figure 4 shows how the concentration of permeate changes with feed concentration. The liquid-vapor equilibrium curve of ethanol-water is also given for comparison of pervaporation performance.

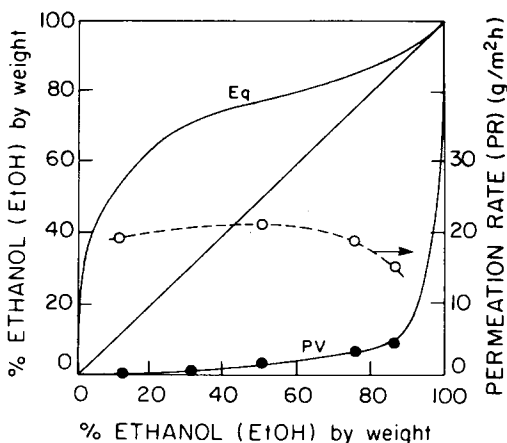


Fig. 4. Effect of feed composition on parameter composition and permeation rate.

It is difficult to quantitatively predict the separation factor because the pervaporation is a complex membrane separation process compared to other membrane separation techniques owing to the complicated interactions between the polymer and permeation components and the coupling of diffusion and solubility phenomena.¹⁸ Any interaction between two materials can influence other interactions between the two components, and the diffusion rate of one component, though membranes may change the diffusion characteristics of the other.

Permeation Rates of Blended Membranes for Ethanol–Water Mixtures

The effects of feed concentration on the permeation rates are shown in Figure 5. It is clear that the higher the operation temperature, the higher the permeation rate. This is a normal result in membrane separation processes. But the interesting phenomena is that the permeation rate shows a maximum at about 30 wt% ethanol concentration of feed mixture at any temperature. Generally speaking, the permeation rates always increase with the increase of water concentration of feed mixture. In the case of separation of the acetic acid–water system using the same PAA–Nylon 6 membranes where the only difference is the different PAA content in membranes, the permeation rates show normal characteristics, that is, they increase with water concentration in the feed mixture.¹⁴ The reason for their maximum values is not very clear. It may result from the plasticizing effect of ethanol on the membrane material, since at high concentration of ethanol it exerts a strong plasticizing effect on the polymer. When the concentration of ethanol is reduced to some extent, the plasticizing effect resulting from ethanol is reduced significantly. As a result, the soluble liquid in the membrane is reduced significantly, and the permeation rates decrease. The rise of the separation factors in this range provides complementary evidence for this interpretation.

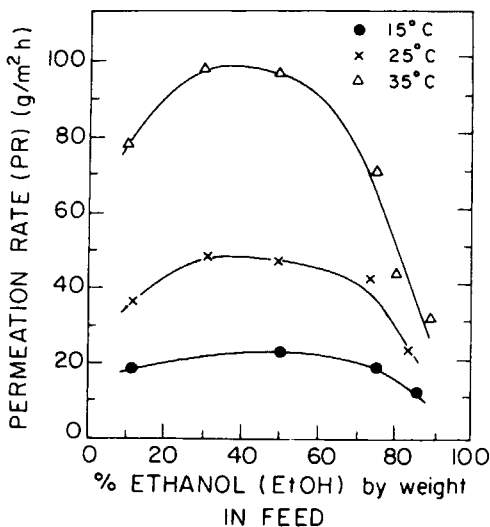


Fig. 5. Permeation rate vs. feed composition. (●) 15°C; (×) 25°C; (Δ) 35°C.

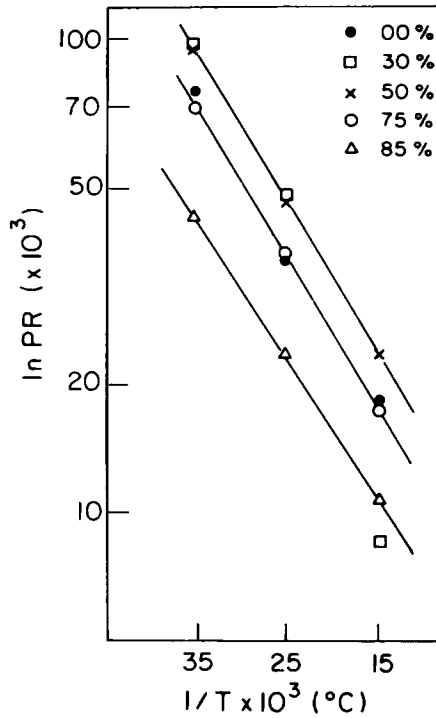


Fig. 6. Relationship between temperature and permeation rate. (●) 00%; (□) 30%; (×) 50%; (○) 75%; (Δ) 85%.

Figure 6 shows how closely the experimental data obey the Arrhenius equation. It is interesting to note that the line for 10 wt% ethanol and that for 75 wt% coincide with each other and so do the two lines for 30 wt% and 50 wt%. This indicates that the activation energies of permeation at these two concentrations are identical.

CONCLUSIONS

Several conclusions can be obtained from this study:

First, the selectivities of blended PAA-Nylon 6 membranes are high while the permeation rates are acceptable for the separation of ethanol-water mixtures. The separation factors have highest values at both high and low concentration ranges of ethanol. These blended membranes, due to their good pervaporation performance, simple preparation procedures, and facility in changing the ratio of polymer content to meet the hydrophilic/hydrophobic balance requirements, can be considered feasible candidates for the separation of ethanol-water mixtures and other aqueous solutions.

The best conditions for preparing blended PAA-Nylon 6 membranes for the separation of ethanol-water mixtures were found to be: PAA content in membrane 25 wt%, crosslinking time approximately 35 h at 25°C, while the Al(NO₃)₃ concentration in aqueous crosslinking solution was about 10 wt%. The polymer blending technique has again been demonstrated to be a simple and effective way to improve membrane pervaporation performance to meet

separation requirements for a given mixture. Other blended membranes obtained from different polymers are worthy of further investigations in order to produce membranes with good pervaporation properties.

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