

Pervaporation Separation of Acetic Acid-Water Mixtures Using Modified Membranes. I. Blended Polyacrylic Acid (PAA)-Nylon 6 Membranes*

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Synopsis

Membranes consisting of ionically crosslinked polyacrylic acid (PAA) and Nylon 6 were prepared and tested for the pervaporation separation of acetic acid-water mixtures. The polyacrylic acid (PAA) membranes were crosslinked in aluminum nitrate aqueous solution while the polyacrylic acid (PAA)-Nylon 6 blends were cast from homogeneous PAA-Nylon 6 mixtures to appropriate thicknesses and then crosslinked in aqueous aluminum nitrate solutions. Optimum pervaporation results were obtained from blends of Nylon 6 and PAA in the weight ratio of 60–75 wt% Nylon 6 and 25–40 wt% PAA which have separation factors (water/acetic acid) of over 60 and flux rates higher than 100 g/m² h at 15°C for the separation of acetic acid-water mixtures. The flux rates and separation factors could be altered by changing the blend composition of the membrane. The effects of the feed composition on the separation factors were investigated.

INTRODUCTION

Pervaporation is an emerging membrane separation process, where the feed mixture directly contacts with one side of a dense membrane under atmospheric pressure while a low partial pressure of the permeate species is maintained on the other side of the membrane by vacuum or a swept inert gas. The advantages of the simplicity, the low costs, the acceptable flux, and high selectivity have shown it to be a promising separation process.^{1–19,21}

In recent years there has been increased interest in the use of the pervaporation membrane separation process for separation of organic liquid mixtures. Many papers have focused on the separation of alcohol-water system, and small-scale plants for the separation of the ethanol-water system have been in operation for several years.^{22–26} Compared to the separation of ethanol-water mixtures, the separation of other mixtures has received relatively little attention. Acetic acid ranks among the top 20 organic intermediates in the chemical industry. The separation of acetic acid from water is an energy-expensive process. Because of the small differences in the volatilities of water and acetic acid in dilute aqueous solution, azeotropic distillation is used instead of binary distillation. The heat for evaporating 1 g of water is approximately 850 cal. It is thus desirable to develop a new separation process for saving energy and the pervaporation membrane separation technique is a

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potential candidate for this purpose. Yoshikawa et al.²⁰ have recently reported a study which deals with the separation of the acetic acid-water system by pervaporation. They achieved very high separation factors using poly(acrylic acid-co-acrylonitrile) membranes, but the permeation rates obtained were low. Contrary to other membrane processes, pervaporation requires the vaporization of a part of the liquid feed. Because a quantity of energy at least equal to that of evaporation is needed, it can be of practical use only when the selectivity is much higher than that obtained from ordinary techniques. The purpose of this paper is to develop new membranes which have high selectivity and acceptable flux rates for separating the acetic acid-water system and also to investigate the possibility of practical applications.

MATERIALS

For a binary pervaporation process, it is difficult to select a polymer which is suitable for a given mixture separation because of complex interactions between the membrane material and the two components to be separated. According to the "solution-diffusion" theory adopted by most investigators, there are three steps in the mass transfer process of pervaporation: the components of feed mixture dissolving in, diffusing through the membrane, and then evaporating from the other side of the membrane. If the partial pressure of components in the downstream side is low enough, the rate of evaporation is so rapid that there is practically no resistance against mass transfer. The diffusion depends on the gradient of permeate concentration across the membrane. The solubility of components in the membrane can be related to the interactions between the polymer and the two components to be separated and thus the solubility parameter is the logical choice to select and evaluate the membrane material for a given separation system.

Therefore, materials for dense membranes should be selected on the basis of maintaining a proper hydrophilic/hydrophobic balance criterion for a given separation system. An attempt to develop an empirical hydrophilic-hydrophobic balance criterion equation to estimate the permselectivity of the membrane based on solubility parameters, solubilities, and diffusivities of the liquids in the membrane is currently underway in this laboratory and will be the subject of a separate paper. Basically, a potential optimum material for each mixture to be separated exists, but usually a single polymer does not possess the required optimum structure. Several techniques of membrane preparation and modification may thus be useful for improving the membrane structure: crosslinking a reactive polymer, blending a hydrophilic polymer with a relatively hydrophobic polymer, grafting a selective species onto an inert film, and developing a new copolymer composed of both active and inert groups.

This study is concerned with using crosslinking and blending techniques to achieve highly selective membranes.

THEORY

According to the "solution-diffusion" theory, the permeation rate for pure liquid pervaporation in steady state can be described by Fick's law:

$$Q = -D(dC/dx) \quad (1)$$

where Q is the permeation rate, D is the diffusivity, and dC/dx is the concentration gradient across the membrane.

If a commonly used equation for D is introduced:

$$D = D_o e^{\tau C} \quad (2)$$

and the concentration on the downstream side of membrane is considered as zero (valid provided the pressure in the downstream side is low enough), Eq. (2) can then be simplified to

$$Q = (D_o/L)(e^{\tau C_s} - 1) \quad (3)$$

where τ is a constant at a given temperature, L is the thickness of membrane, and C_s is the solubility of liquid in polymer. Interactions between components can affect C_s for each component leading to nonlinearities for mixtures.

Equation (3) is valid for pure liquid permeation. For binary permeation, the pervaporation mechanism is more complex and an equation for total flux which is widely adopted and has been proven experimentally is a form of the Arrhenius relationship:

$$\text{Ln } Q = -E_p/RT + Q_o \quad (4)$$

where E_p is the activation energy of permeation, T is the operating temperature, and Q_o is a constant.

The selectivity of binary pervaporation can be generally expressed in terms of the separation factor:

$$\alpha_{B/A} = \frac{\alpha_{H_2O}}{\text{Acetic acid}} = \frac{\frac{Y_B}{Y_A}}{\frac{X_B}{X_A}} \quad (5)$$

here X is the feed composition, Y is the permeate composition, and component B is the preferentially permeating component.

For ideal binary liquid pervaporation the permeation rate of component i is proportional to the feed concentration:

$$q_i^o = x_i Q_i \quad (6)$$

where q_i^o is the ideal permeation rate of component i , x_i is the feed concentration of component, i , and Q_i is the permeation rate of pure component i . In fact, almost no ideal pervaporation exists because of the complex interactions between the polymer and permeating components. According to Huang and Lin,⁶ the real permeation rate (q_i) can be expressed by introducing a permeation ratio (θ_i) which is defined as the ratio of the real permeation rate to the ideal permeation rate:

$$q_i = \theta_i q_i^o \quad (7)$$

Then the composition of component B in permeate can be expressed by:

$$\begin{aligned}
 Y_B &= q_B / (q_B + q_A) = \theta_B q_B^o / [\theta_B q_B^o + \theta_A q_A^o] \quad (8) \\
 &= X_B / (X_B + KX_A) = \frac{Q_B X_B Q_B}{[\theta_B X_B Q_B + \theta_A X_A Q_A]} \\
 &= \frac{X_B}{X_B + \frac{\theta_A Q_A}{\theta_B Q_B} X_A} = \frac{X_B}{X_B + KX_A}
 \end{aligned}$$

where

$$K = (\theta_A Q_A) / (\theta_B Q_B) \quad (9)$$

EXPERIMENTAL

Apparatus and Experimental Procedure

The pervaporation apparatus consisted of a permeation cell made of aluminum, a constant temperature water bath, glass tubes for condensing and collecting the permeate vapor, a small McLeod gauge connected to the downstream vacuum line, and a two-stage Welch vacuum pump of 150 L/min.

To start an experimental run, the membrane was placed in the cell. To prevent breakage of the membrane, a filter paper was placed between the membrane and the porous sintered stainless steel plate of the permeation cell. After the liquid was poured into the permeation cell, the desired temperature of water in constant temperature bath was maintained. Liquid nitrogen was poured into the trap, the vacuum pump was turned on, and the pervaporation run was started. Every 30 min or 1 h the collected permeate sample was weighed to determine the permeation rate and analyzed using a Waters Associates differential refractometer Model R403 to determine the concentration of the sample. Approximately 2 to 3 hours were required to reach steady state.

Analysis of the permeate acetic acid mixture was determined using a Waters Associates differential refractometer Model R403 with an attached recorder. A calibration curve of refractive index vs. composition of acetic acid-water mixture was prepared using known quantities of the two components and a linear relationship was found in the range of 0–0.1% by weight. The analysis of permeate was carried out by simple dilution of the permeated sample in the concentrate ranges.

The necessary vacuum in the downstream was maintained by a two-stage Welch vacuum pump of 150 L/min capacity with a vented exhaust. The vacuum was measured by a small McLeod gauge in the vacuum line near the permeation cell and was kept below 0.5 mmHg.

Details about the permeation cell, the pervaporation apparatus, and the experimental procedure have been reported elsewhere.^{7,26}

Materials

Nylon 6 with molecular weight 42,000 and polyacrylic acid (PAA) with molecular weight 150,000 (in 25% aqueous solution) were obtained from Polysciences, Inc. Acrylic acid (AA) monomer was Baker grade from J. T. Baker Chemical Co. Acetic acid, aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), dimethyl formamide (DMF), and cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) used were all Baker analyzed reagent grade obtained from the J. T. Baker Chemical Co. Formic acid (88% and 90%) was obtained from Fisher Scientific.

Membrane Preparation

Preparation of Ionically Crosslinked Polyacrylic Acid (PAA) Membranes. A solution of PAA in water and a solution of aluminum nitrate in DMF were prepared separately. A predetermined amount of aluminum nitrate in DMF solution was added to the aqueous PAA solution and the agitation continued until a uniform solution was produced. The casting solution was cast onto a clean glass plate using a Gardner casting knife. The plate and the film were then heated in an oven for the desired time and temperature. Then they were immersed in an acetone bath at room temperature for various times. The membrane was removed from the glass plate and soaked in deionized water at room temperature for at least 24 h before further use.

Preparation of Blended PAA-Nylon 6 Membranes. A 25 wt% aqueous PAA solution and a 75 wt% Nylon 6 solution in formic acid were mixed together to form a homogeneous blended 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 about 5 min, and then dried at 60°C for 50 min in a drying oven. It was then crosslinked in a 10% aluminum nitrate crosslinking bath for about 30 h, then immersed in deionized water for a least 10 h before further use.

RESULTS AND DISCUSSION

Ionically Crosslinked PAA Membranes

The permeation rate and separation factors as a function of the mole ratio Al ions to AA are shown in Fig 1. As can be seen the permeation rate decreases while the separation factor increases with the increasing aluminum content. This can be easily explained by the fact that as aluminum ions are introduced into the membrane, a higher degree of crosslinking is obtained, resulting in a better hydrophilic/hydrophobic balance in the membrane for the acetic acid-water system. The results indicate that more aluminum ions should be introduced into the membrane to obtain higher separation factors. Unfortunately, if the ratio of aluminum ions to AA is over 1/6, the membranes become brittle.

Table I shows the effect of overnight acetone treatment on both permeation rate and separation factor. It is clear that the membranes with acetone treatment possess higher separation factors and lower permeation rates compared to those membranes without acetone treatment.

The selectivities for separation of acetic acid-water mixture using ionically crosslinked PAA membranes are quite low, thus the use of the blending

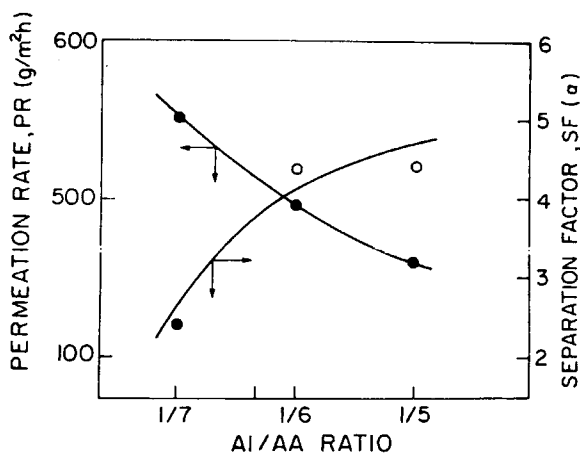


Fig. 1. Effect of mole ratio Al/AA on permeability and separation factor for ionically crosslinked PAA membranes. Permeation rate is the total of permeate (acetic acid + water), separation factor is $\alpha = (\text{H}_2\text{O}/\text{acetic acid})$.

TABLE I
Effects of Acetone Treatment for Ionically Crosslinked PAA Membranes

Acetone treatment*	ratio of Al to AA	Permeation rate (g/m ² h)	Feed concentration (wt% HAc)	Separation factor α (H ₂ O/HAc)	Operating temperature (°C)
No	1:6	457	45.6	4.7	15
Yes	1:6	352	48.5	5.8	15
No	1:7.4	551	49.4	2.4	15
Yes	1:7.4	393	47.1	7.6	15

*Duration of acetone treatment 12 hours (overnight)

technique to obtain the required hydrophilic/hydrophobic balance of the membrane to achieve high separation factors for the separation of the acetic acid-water system.

Blended PAA-Nylon 6 Membranes

Polyacrylic acid has very strong affinity with and can be dissolved easily in water. Through crosslinking, its hydrophilicity is reduced. Because of mechanical properties, the hydrophilic/hydrophobic balance for acetic acid-water system cannot be approached by increasing the crosslinking content in the membranes. The simplest way is thus to blend the PAA with a relatively inert polymer. It was found that a homogeneous PAA blended solution with Nylon 6 can be formed using formic acid as solvent in the 25–45% PAA range of composition. The blended solutions in this range were optically clear and checked by UV spectrometry.

As reported previously,²⁶ the best proportion of polyacrylic acid (PAA) in blended membranes with Nylon 6 for separation of acetic acid from water is about 40% by weight of PAA. Figure 2 shows the relationship between permeation rate and temperature. As can be seen, the experimental results agree very well with the Arrhenius relationship.⁴ Figure 3 shows how the

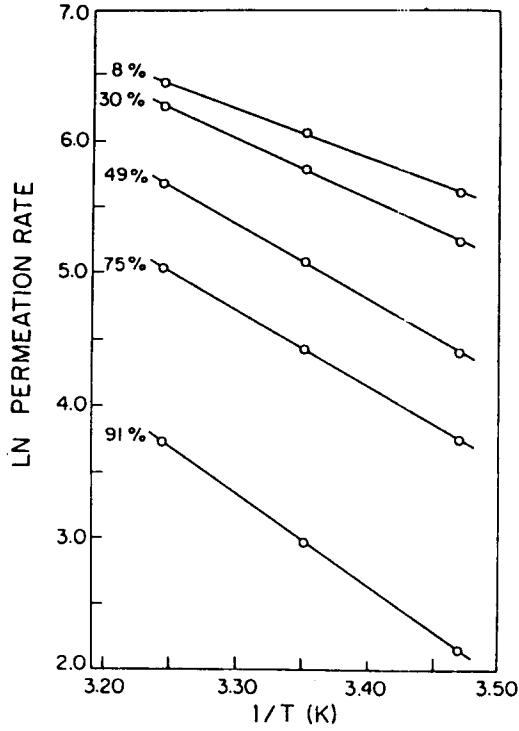


Fig. 2. The effect of temperature on permeation rate for blended PAA-Nylon 6 membranes for different acetic acid-water compositions (in wt%). Permeation rate is the total of permeate (acetic acid + water).

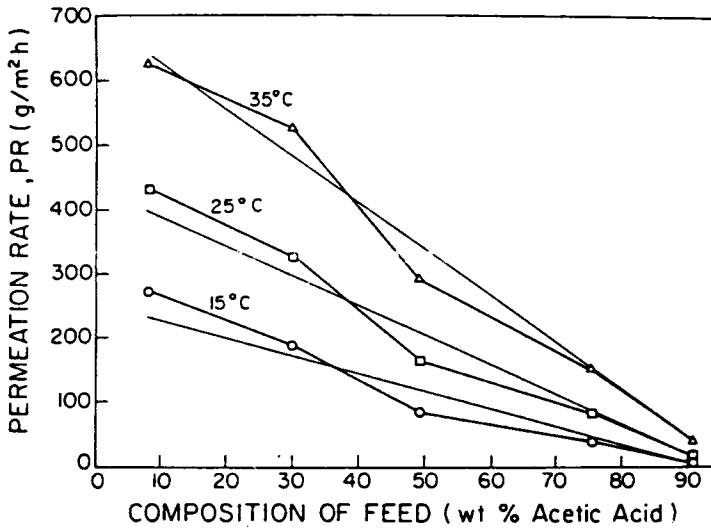


Fig. 3. The effect of feed concentration on permeation rate. (Refers to total of permeate acetic acid + water.)

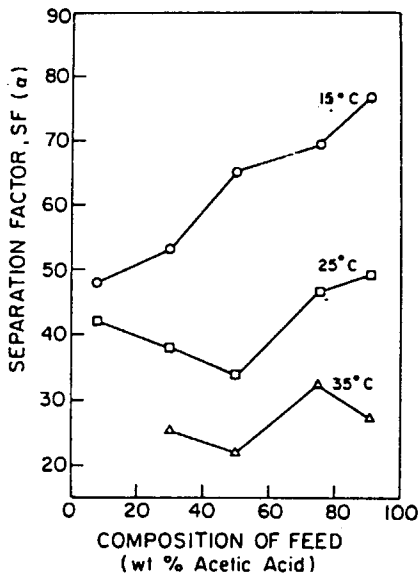


Fig. 4. Effects of feed concentration on separation factors. ($\alpha = \text{H}_2\text{O}/\text{Acetic acid}$).

permeation rate changes with feed composition. For the whole range of feed concentrations, the permeation rate may be expressed in terms of straight lines which have different slopes for different temperatures.

The effects of feed concentration for different operating temperatures on separation factors are shown in Figure 4. It can be seen that the separation factors obtained at lower temperature are always higher than those obtained at higher operating temperatures, and they increase steadily with increase in acetic acid content of feed at 15°C. At 25°C and 30°C, a minimum in the separation factor in the middle concentration range of feed is observed.

Table II shows the experimental values of feed and permeate concentration and separation factor $\alpha = (\text{H}_2\text{O}/\text{Acetic acid})$ for a 40% PAA-Nylon 6-blended membrane at various temperatures determined analytically by differential refractometry.

CONCLUSIONS

Blended PAA-Nylon 6 membranes were found to possess high selectivities for the separation of acetic acid-water system.

The experimental results reported indicated that blending a hydrophilic polymer with a relatively hydrophobic polymer can be a useful technique for producing improved perselective membranes.

The membranes used in this report were found to be stable for the period of the experiments. However, it would be necessary to conduct long-term durability studies for future practical applications. Research on the membranes obtained from the blending and grafting techniques for the dehydration of alcohol will be reported in separate papers.^{27,28}

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TABLE II

Experimental Values of Feed and Permeate Concentration and Separation Factors ($\alpha = \text{H}_2\text{O}/\text{Acetic Acid}$) at Various Temperatures (40% PAA-nylon 6-blended membrane ionically crosslinked in aluminum trinitrite solution)

T (°C)	Feed concentration* (mol% H ₂ O)	Permeate concentration* (mol% H ₂ O)	Separation factor (α) H ₂ O Acetic Acid
15	97.43	99.95	48.4
	88.53	99.76	53.3
	77.37	99.56	65.7
	51.92	98.69	69.5
	24.18	96.33	82.3
25	97.43	99.94	42.2
	88.53	99.66	38.1
	77.37	99.14	33.8
	51.92	98.07	47.0
	24.18	93.99	49.1
35	97.43	99.95	54.5
	88.53	99.49	30.3
	77.37	98.68	21.9
	51.92	97.27	33.0
	24.18	89.72	27.4

* Determined using Differential Refractometry

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