

Pervaporation Separation of Ethanol–Water Mixtures Using Crosslinked Blended Polyacrylic Acid (PAA)–Nylon 66 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 66 blended membranes crosslinked to varying degrees in aluminum nitrate solution. Optimum pervaporation results were obtained from crosslinked blends containing 75 wt % nylon 66 and 25 wt % PAA. The optimum crosslinking time was found to be between 30 and 40 h. The optimum operating temperatures of the pervaporation runs were found to be 2–3°C below the boiling points when the highest permeation flux reached 857.6 (g/m² h) and the best separation factors (water/ethanol) were 10.1.

INTRODUCTION

There is a growing interest in the use of pervaporation separation processes for separation of the ethanol–water system.^{1–6} Recently the use of ionically crosslinked blended polyacrylic acid (PAA)–nylon 6 membranes to separate ethanol–water mixtures has been reported from this laboratory.⁷

According to the solution diffusion theory,⁸ there are two parameters, diffusion and solubility, that affect the permeability of liquids through the polymer membrane. They can be adjusted and controlled by changing hydrophilic–hydrophobic balance properties of a membrane. Therefore, it is one of the important goals of pervaporation separation research to keep developing new membrane materials.

Compared with nylon 6, nylon 66 is a little bit more hydrophobic.^{9,10} For some mechanical properties, nylon 66 is a little better than nylon 6.¹⁰ A recent study in this laboratory found that nylon 6 is still too hydrophilic for PAA–nylon blended membranes and suggested the use of nylon 66 instead of nylon 6.¹¹ The subject of this investigation is to develop this new material of crosslinked PAA–nylon 66 blended membranes, test its pervaporation properties, and optimize its preparation and operating conditions over a wide range of temperatures and feed concentrations.

EXPERIMENTAL

Materials

The nylon 66 used was obtained from Polysciences, Inc. The polyacrylic acid (PAA) was obtained from Polysciences in a 25% by weight aqueous solution

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of molecular weight 90,000. The aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was Baker analytical reagent grade and was obtained from the J. T. Baker Chemical Co. The formic acid was obtained from BDH Chemicals. The ethanol and methanol were commercial grade products.

Membrane Preparation

The blended PAA-nylon 66 membranes were prepared by the wet technique.^{7,14,17} The nylon 66 was dissolved in 88 wt % formic acid at room temperature to form a 10 wt % nylon 66 solution. The nylon 66 solution and the 25 wt % PAA (MW 90,000) aqueous solution were mixed together and blended for 24 h to form a homogeneous solution. The casting solution was cast onto a glass plate with the aid of a Gardner casting knife adjusted to an appropriate thickness. The membrane was then predried at room temperature for 10 min before drying in an oven at 55–60°C for 50 min. This was followed by cross-linking in a 10 wt % $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ aqueous solution at room temperature for different times. It was subsequently removed from the crosslinking bath, rinsed, and immersed in deionized water for at least 30 h. Then it was put into methanol for 24 h before being put again into deionized water ready for using. The thickness of the films was measured with a digital micrometer and was in the range of 42–81 μm (1.65–3.20 mils).

Apparatus and Experimental Procedure

The pervaporation apparatus consisted of an experimental cell, made of stainless steel, which held the membrane and the liquid to be permeated, a thermostatic regulator, a Haake circulator to maintain the feed temperature, an agitator for eliminating concentration and temperature gradients of the liquid feed, glass tubes for condensing the permeate vapour and collecting the condensed liquid of the permeate vapour, and a vacuum pump. The vacuum degree of the system was kept below –750 mm Hg. Liquid nitrogen was used as the condensing agent. The analysis of the permeate was done using an Anton-Paar DMA60 digital density meter. Details about the apparatus and procedures have been previously reported from this laboratory.¹¹

Swelling Measurements

The sorption capacity of membranes was measured by immersing the membrane samples in water and 50 wt % water-ethanol solution respectively at room temperature for 80 h. After wiping up the excess liquid with Kimwipe, the membranes were weighed as quickly as possible. The procedure was repeated several times to get reproducible data. The samples were then dried in a vacuum oven at room temperature for 80 h to a constant weight.

RESULTS AND DISCUSSION

Compatibility of PAA with Nylon 66

The experiments showed that polyacrylic acid is compatible with nylon 66 only in a certain range of concentration. Beyond this range, the membranes

TABLE I
Compatibility of PAA and Nylon 66

Experiment number	1	2	3	4	5
10 wt % nylon 66 solution (g)	50	50	60	40	50
Pure nylon 66 (g)	5	5	6	4	5
25 wt % PAA solution (g)	3.5	5	8	6.9	10.8
Pure PAA (g)	0.875	1.25	2	1.7	2.7
Ratio of PAA/nylon 66	15/85	20/80	25/75	30/70	35/65
Compatibility coagulation	Phase separation	OK	OK	OK	Cloudy

cannot be prepared by the wet technique. Table I gives the experimental results of the compatibility. It can be seen from Table I that the 10 wt % nylon 66 solution of formic acid and 25 wt % PAA aqueous solution are compatible only when the ratio of PAA/nylon 66 is between 15/85–35/65 by weight. That is, the content of PAA is between 15 and 35 wt %. The reasons why PAA and nylon 66 are not very compatible may be due to the fact that they have such different molecular structures in terms of hydrophilic and hydrophobic properties.

Hydrophilic/Hydrophobic Balance of Blended Membranes

High separation cannot be obtained for the ethanol–water system using nylon 66 membranes or the ionically crosslinked polyacrylic acid membranes, because, while nylon 66 is a comparatively hydrophobic polymer, the crosslinked polyacrylic acid is too strongly hydrophilic. It was then decided to blend nylon 66 with PAA to obtain a better balanced hydrophilic/hydrophobic structure of the modified membranes for the separation of ethanol–water mixtures. The contents of the two polymers in the casting solution and the crosslinking degree of PAA in the membrane play important roles in pervaporation performance.

Figures 1 and 2 show the effects of PAA content in membranes on permeation flux and separation factor. All the pervaporation runs were carried out at 35°C with a 50 wt % concentration of ethanol–water mixture and the membranes used were crosslinked for 30 h in 10 wt % $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution. It can be seen that the separation factors have a maximum at 25 wt % PAA content in the membranes, while the permeation flux increases with increase of the PAA

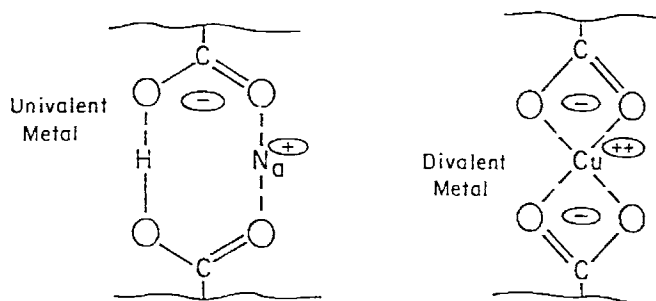


Fig. 1. Nature of crosslinkages.

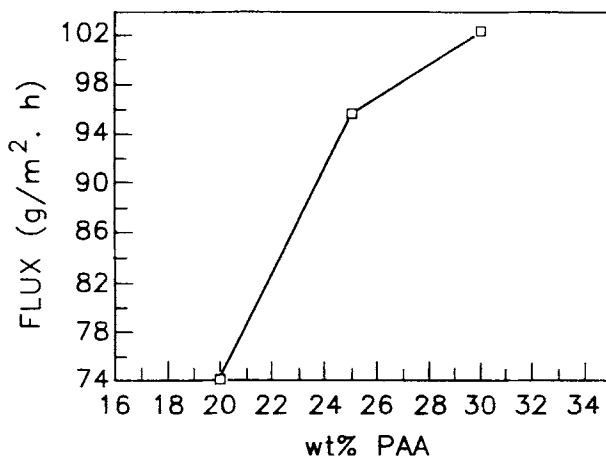


Fig. 2. Effect of PAA content in membrane on permeation flux (feed concentration: 50 wt % ethanol; temperature: 35°C).

content. The permeation flux curve may be explained in terms of the solubility of liquid in membranes. That is, the permeation rates increase when the PAA content increases.

The term ionic crosslinking might be initially used to explain the role of metal oxides, such as ZnO, in the vulcanization of carboxylated rubber. Later it was realized that the introduction of charged groups in polymers and, therefore, the potential to form ionic bonds would give the polymers new properties. The ionic intermolecular bonds result from partial or complete neutralization of pendant carboxylic acid groups (Fig. 14). It is believed that lower valence counterions (like Na and K) are generally surrounded by the field created by charged polymer molecule, while for higher valence (Cu, Ca, Mg), they would be located more specifically at the carboxylic sites.¹⁸ Unlike typical covalent crosslinks found in other organic polymers, the ionic forces are diffuse and nondirectional, and they act at great distances. The exact nature of the ion bonding is not clear but it has been found that the amount of bonding increases with extent of neutralization and with the valence of the cation. Research on polycarboxylic acid has shown that addition of multivalent cations causes the formation of clusters, and eventually the clusters may become sufficiently large to precipitate. Work previously done in this laboratory has shown that using $\text{Al}(\text{NO}_3)_3$ aqueous solution to treat nylon 6 and poly(acrylic acid) membranes caused the T_g of the membranes to increase by 40°C. This proves that ionic crosslinking truly occurred.

There are several functions for using $\text{Al}(\text{NO}_3)_3$ to crosslink the blended membrane, such as preventing the PAA from dissolving in water, making water molecules fairly clustered,¹³ substantially increasing T_g of the membranes,^{11,12} etc. The Al^{3+} content in the membranes influences the transport property of the membranes. According to past studies conducted in this laboratory the crosslinking of PAA is achieved in two steps: diffusion of metal ions from crosslinking solution into the membrane and the crosslinking reaction,^{14,15} and diffusion is the controlling step. Therefore, the temperature, time, concentration, and concentration gradients of the crosslinking bath of crosslinking reaction

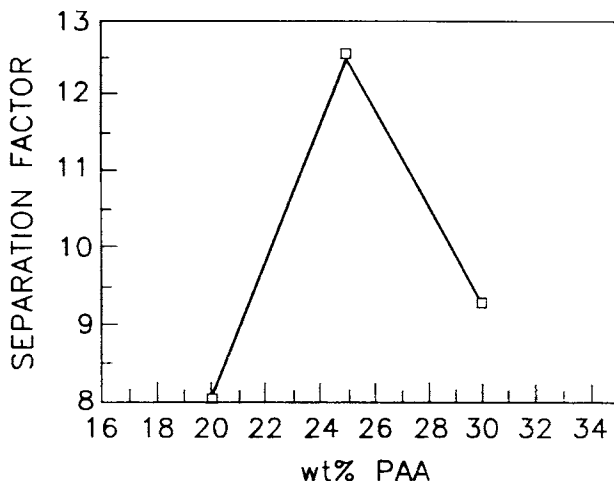


Fig. 3. Effect of PAA content in membrane on separation factor (feed concentration: 50 wt % ethanol; temperature: 35°C).

affect the crosslinking degree. Obviously, it is convenient to indicate the crosslinking degree of the Al^{3+} content in the membranes in terms of crosslinking reaction time rather than crosslinking temperature and crosslinking bath concentration. Figures 3 and 4 show the influence of crosslinking time on permeation fluxes and separation factors. For these figures all the pervaporation runs were conducted under the following conditions: concentration of feed mixture is 50 wt % of ethanol, pervaporation temperature is 35°C, composition of PAA in the membrane is 25 wt %, and concentration of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in the crosslinking solution is 10 wt %. It can be seen from Figures 3 and 4 that permeation fluxes and separation factors both have a maximum when the crosslinking time is between 30 and 40 h. The content of Al^{3+} in the membrane or the crosslinking degree increases with crosslinking time; as a result, the

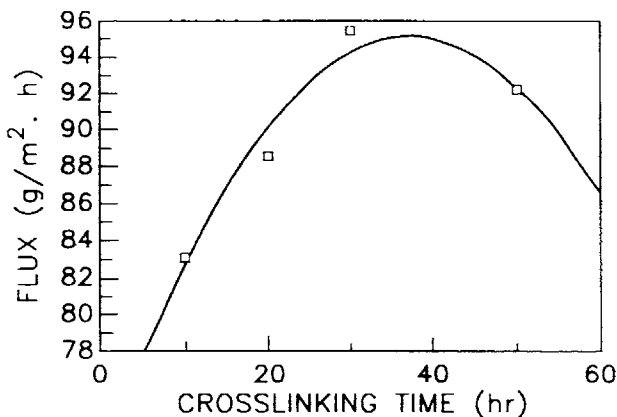


Fig. 4. Influence of crosslinking time on permeation flux (feed concentration: 50 wt % ethanol; temperature: 35°C).

TABLE II
Operating Temperatures 2–3°C below the Boiling Points

Feed concentration (wt % ethanol)	Boiling point (°C)	Operating temperature (°C)
10	92	90
30	87.5	85
50	82	80
70	80.2	78
90	78.3	75
95	78.2	75

hydrophobic properties of the membranes are reduced while the membranes become denser.⁷ Therefore, Figure 3 may be explained in this way: when crosslinking time is less than 30 h, the hydrophilic/hydrophobic properties of the membranes play a main role, but when crosslinking time is more than 40 h, the densities and morphology of the membranes play the main role. The best crosslinking time for 25 wt % PAA blended membranes for the separation of 50 wt % ethanol–water mixture is about 30–40 h for obtaining high membrane selectivity and permeability.

Sorption Capacity

It is well-known that mass transfer through a membrane by pervaporation occurs by a three-step mechanism. The permeant first sorbs into the membrane, then diffuses through to the downstream side, where it desorbs. Of the three steps, desorption of the permeant does not have a major influence on the overall process, because, as long as the partial pressure of component in the downstream side is less than the saturation vapor pressure, the rate of evaporation is very fast. The permeability of a component through a membrane depends on both the sorption and diffusion steps:

$$P = D * S$$

TABLE III
Relationship Between Membrane Composition and Water or Solution Sorption Capacity

Membrane composition ^a (wt % PAA)	Uptake onto dry membrane (wt %)		Solubility in wet membrane (wt %)	
	Water	Solution ^b	Water	Solution ^b
20	25.7	16.6	20.4	14.2
25	41.8	17.8	29.5	15.1
30	44.4	18.3	30.8	15.5

^a Crosslinking time = 30 h.

^b 50 wt % ethanol–water solution.

where P , D , and S are the permeability, diffusivity, and solubility respectively. The methods to calculate the diffusion coefficients, and thus to predict the permeability and selectivity, are currently important subjects in membrane transfer research. The solubility and components uptake can be obtained directly from swelling or sorption capacity experiments.

Table III shows the relationship between membrane composition and water or solution sorption capacity. It can be seen that the sorption capacity rises with increasing PAA content in the membrane. This agrees with the effect of PAA content in the membrane on permeation flux. The fact that pure water sorption capacity is much larger than the solution (50% wt ethanol) sorption capacity also agrees with the selectivity of the membrane to the two components. From Table IV, similar conclusions can be obtained about the crosslinking time and amount of crosslinking.

Permeation Flux of Blended Membrane for Ethanol-Water Mixtures

The effects of temperature and feed concentration on the permeation flux are shown in Figure 5. All the pervaporation runs were conducted under the following conditions: composition of PAA in the membrane is 25 wt %, concentration of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in the crosslinking solution is 10 wt % and, crosslinking time is 30 h. It is apparent that the higher the operation temperature, the higher the permeation rate. This is a normal result in membrane separation processes, but the interesting phenomenon is that the permeation fluxes show a maximum at about 50 wt % ethanol concentration of feed mixture at any temperature. It has been observed¹⁷ that permeation fluxes always increase with the increase of water concentration. Xu and Huang⁷ attributed this to the plasticizing effect of ethanol on the membrane material. According to their viewpoint, when ethanol concentration is less than 50 wt %, it exerts a strong plasticizing effect on the material, that is, the plasticity of the material increases significantly with the increase of ethanol concentration and plasticization play a main part.

Selectivity of Blended Membrane for Ethanol-Water Mixtures

The effects of temperature and feed concentration on separation factors are shown in Figure 6. All the pervaporation runs were conducted under the fol-

TABLE IV
Relationship Between Crosslinking Time and Water or Solution Sorption Capacity

Crosslinking time ^a (h)	Uptake onto dry membrane (wt %)		Solubility in wet membrane (wt %)	
	Water	Solution ^b	Water	Solution ^b
10	38.8	16.1	28.0	13.9
20	40.5	16.9	28.8	14.5
30	44.4	18.3	30.8	15.5
50	38.3	17.0	27.7	14.6
60	25.6	16.2	27.5	13.9

^a Membrane composition: 300 wt % PAA.

^b 50 wt % ethanol-water solution.

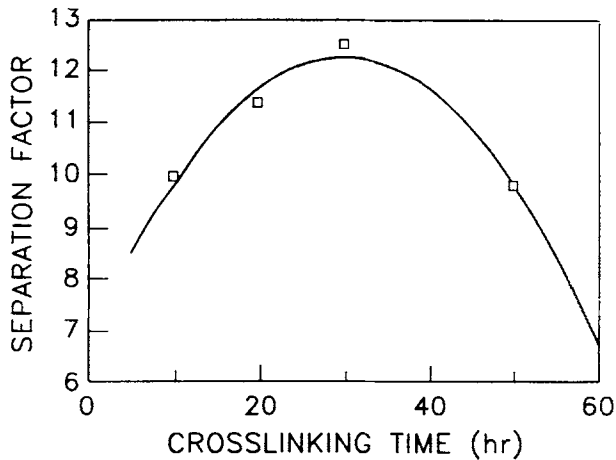


Fig. 5. Influence of crosslinking time on separation factor (feed concentration: 50 wt % ethanol; temperature: 35°C).

lowing conditions: composition of PAA in the membrane is 25 wt %, concentration of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in the crosslinking solution is 10 wt %, and crosslinking time is 30 h. As can be seen, the higher separation factors were obtained at low operating temperatures than at high operation temperatures regardless of the feed concentration. In pervaporation, diffusion is carried out by random oscillation of polymer chains in the amorphous regions of membrane. When operation temperature increases, the frequency of oscillation increases, and the diffusion rate of two components consequently increase. A slight increase in the quantity of the component with low concentration in permeate results in a decrease of separation factor. It is also very interesting to note that the separation factors are low at all operating temperatures when feed concentration is between 30–50 wt % of ethanol. At both extreme concentration ranges, the separation factors are higher.

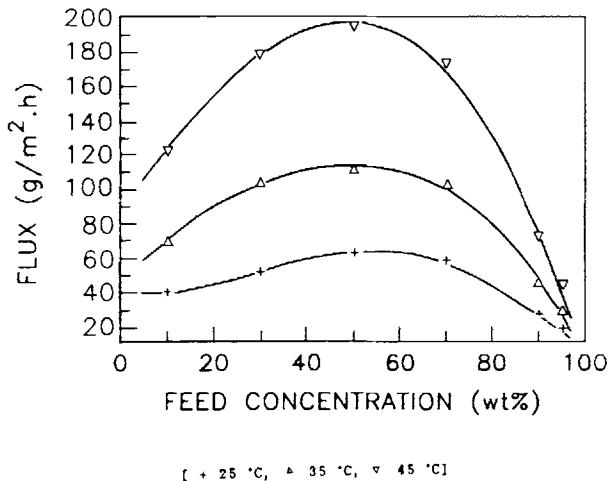


Fig. 6. Effects of temperature and feed concentration on permeation flux.

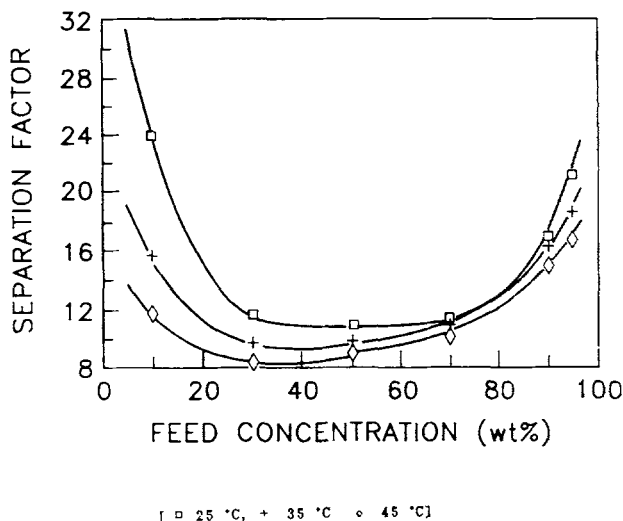


Fig. 7. Effects of temperature and feed concentration on separation factor.

Optimization of Pervaporation Runs

As can be seen from Figures 5 and 6, when operating temperature increases from 25°C to 45°C, the permeation fluxes increase about by two times, while the separation factors are reduced by a factor of 3-4. As a result, raising operating temperature should favour the pervaporation runs. From this point of view, pervaporation runs at 75°C were carried out and the results are shown in Figures 7 and 8. As can be seen from these figures, the permeation fluxes have increased substantially. The graph of separation factor has also changed shape. For low ethanol concentration (10-30 wt %), the separation factors are reduced; for middle ethanol concentration (50-70 wt %), the separation factors have no apparent changes; while for high ethanol concentration (90-95 wt %), the separation factors even increased slightly. These indicate that for separation

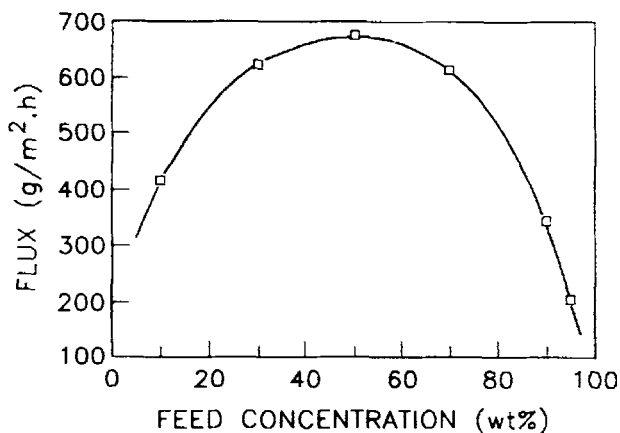


Fig. 8. Permeation flux vs. feed concentration at 75°C.

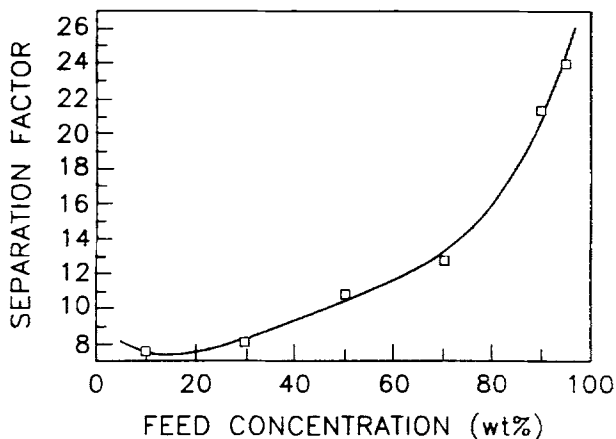


Fig. 9. Separation factor vs. feed concentration at 75°C.

factors, the lower ethanol feed concentration are more sensitive to temperature than higher ethanol feed concentration. Thus it is shown that high operating temperature favours the pervaporation process, and the operating temperature may be raised further to near the boiling point. From this point of view, according to the distillation equilibrium data of the ethanol-water system¹⁶ through calculations, a set of tests have been designed whose operating temperatures are 2–3°C below the boiling points. Table II shows different feed concentrations, the calculated different boiling points, and the different operating temperatures. The results are shown in Figures 9 and 10. It can be seen that the maximum flux has reached 857.6 g/m² h while separation factors did not change much. Comparing Figure 9 with Figure 7, it can be seen that the shape of the curve has changed, since Figure 9 is at a different operating temperature.

Figure 11 shows how the concentration of permeate changes with feed concentration when the operating temperatures are below the boiling points by 2–3°C. The liquid-vapour equilibrium curve of ethanol-water (under 95 wt %) is

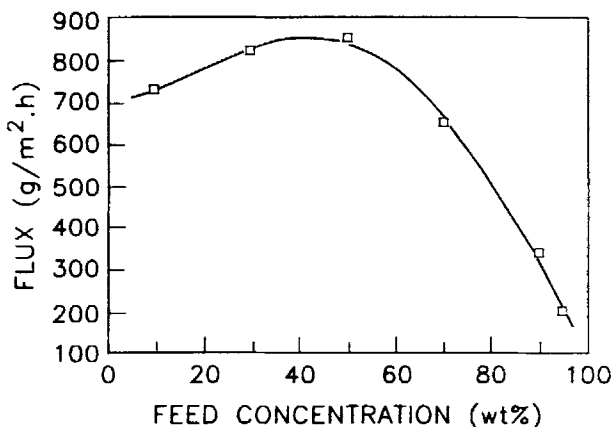


Fig. 10. Permeation flux vs. feed concentration at temperatures 2–3°C below the boiling points.

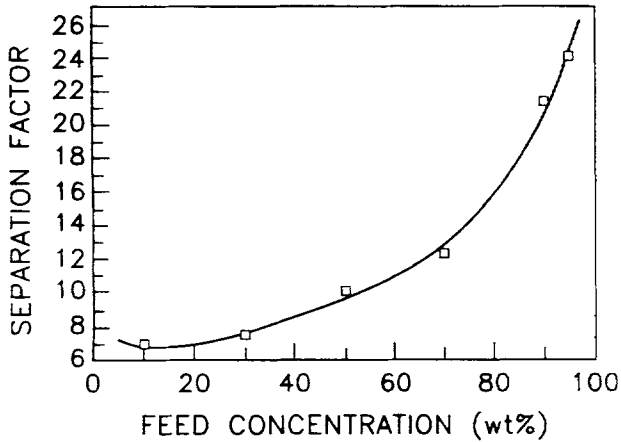
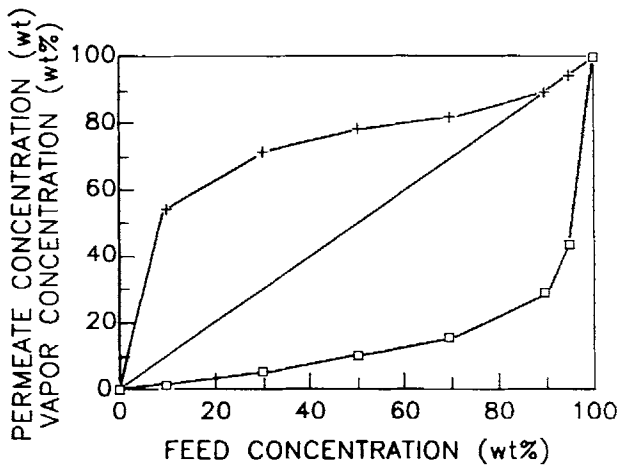


Fig. 11. Separation factor vs. feed concentration at temperatures 2–3°C below the boiling points.

also given for comparison. Figures 13 and 14 show that over a wide temperature region, the experimental data closely obey the Arrhenius equation. If the experiment cell is improved so that it can work under pressure and as a result the operating temperatures of 90 and 95 wt % feed concentrations can be raised to 90°C, then, according to Figure 13, permeation fluxes will reach 621.5 ($\text{g}/\text{m}^2 \text{h}$) and 354.6 ($\text{g}/\text{m}^2 \text{h}$) respectively for 90 and 95 wt % feed concentrations, while, according to Figures 6, 8, and 10, the separation factors should not change much.



(□ pervaporation curve, + distillation curve)

Fig. 12. Permeate concentration vs. feed concentration at temperatures 2–3°C below the boiling points.

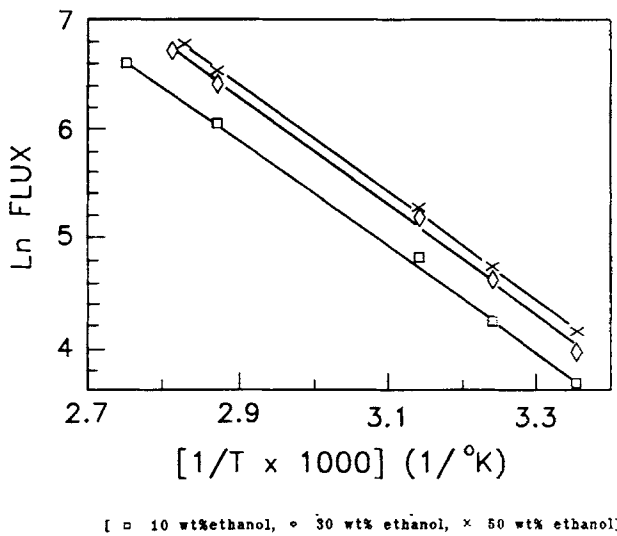


Fig. 13. Arrhenius relationship between permeation flux and temperature.

CONCLUSIONS

From this study it may be concluded that:

1. The best conditions for preparing PAA-nylon 66 membranes for separation of ethanol-water mixtures were found to be: PAA content in the membrane 25 wt %, crosslinking time 30-40 h at room temperature, while the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ concentration in crosslinking solution was 10 wt %.

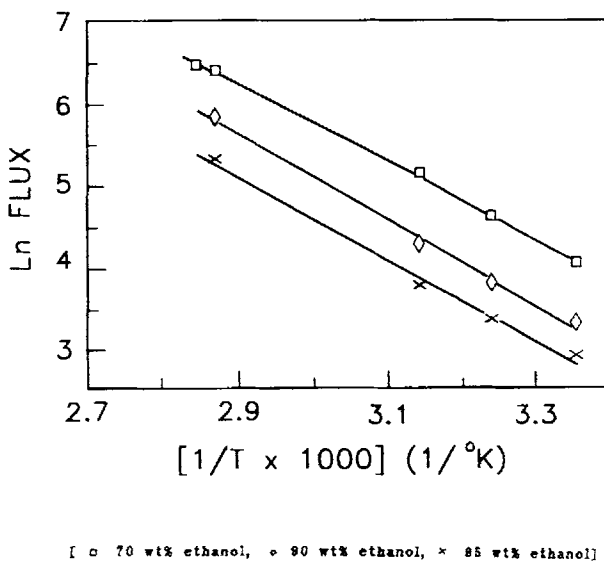


Fig. 14. Arrhenius relationship between permeation flux and temperature.

- Higher operating temperatures favor pervaporation runs. At higher temperatures, in the middle concentration range of feed, ethanol-water mixtures can yield highest permeation fluxes while separation factors were not very low. At high concentration ranges of ethanol-water feed mixture relatively high separation factors were obtained with good permeation fluxes.

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