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Pervaporation Separation of Ethanol–Water Mixtures Using Crosslinked Blend Membranes

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ABSTRACT

Blend membranes prepared from polyacrylic acid/*N*-methylol nylon-6 and polyvinyl alcohol/*N*-methylol nylon-6 are crosslinked with multivalent cation (Al^{3+}) and maleic acid, respectively. The resultant membranes exhibit strong plasticization phenomenon for the pervaporation separation of ethanol–water mixtures. Interesting "permeation enhancement" is observed for both crosslinked blend membranes. From the comparison between pervaporation and sorption data, it is suggested that, for hydrophilic membranes, sorption property dominates the membrane performance at feed solutions of higher water content, while diffusion property governs the membrane performance at feed solutions of higher ethanol content.

Key Words. Crosslinked blend membrane; *N*-Methylol nylon-6; Polyacrylic acid; Polyvinyl alcohol, Pervaporation; Ethanol–water mixtures

INTRODUCTION

For a practical application, a membrane with both high selectivity and permeability is an indispensable prerequisite. In order to establish pervaporation as a competitive separation process, research has been concentrated on the development and optimization of new membrane materials.

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According to the solution-diffusion model, the differences in diffusivities and solubilities of permeants in nonporous polymer membranes enable the separation of liquid mixtures and determine the permeabilities of liquids through the membrane. The hydrophobic–hydrophilic property of the membrane, which affects the diffusivities and solubilities of permeants in membrane, can be adjusted and controlled via various techniques such as blending, crosslinking, and copolymerization (1) to achieve a better membrane performance.

N-Methylol nylon-6 membranes show a high affinity to ethanol (2). Its membranes exhibit high permeability, especially in feed solutions of high ethanol concentration, but with a loss in its separation performance. Therefore, an approach of blending this slightly hydrophobic material with hydrophilic polymers such as polyacrylic acid (PAA) and polyvinyl alcohol (PVA), and further crosslinking this blend system to prevent extensive membrane swelling in alcoholic aqueous solutions, to improve membrane performance is attractive.

PAA is a strongly hydrophilic polymer, and the hydrogen atoms at the carboxyl groups can dissociate to give a charged character. Ionic crosslinking by use of multivalent metal cations such as Ca^{2+}, Mg^{2+}, and Al^{3+} has been successfully employed to form ionic crosslinks in PAA-containing membrane systems (3–5). Factors such as the concentration of the ionization sites, nature of the cation, and cation concentration are believed to have an effect on the crosslinking reaction. In the ionically crosslinked PAA, the main chain $(CH_2\text{-}CH)_n$ is hydrophobic and stable, while the crosslinking sites have the function of attracting water molecules, which makes the membrane preferentially permeate water (6). Furthermore, ionically crosslinked PAA possesses many improved properties such as higher mechanical strength, better thermal stability, insolubility in water, and resistance to many chemicals. Several ionically crosslinked blend membranes of various nylons and PAA have been applied to the pervaporation separation of water–ethanol mixtures (7–9). These modified membranes show an improved pervaporation performance compared to the original nylons.

PVA is the primary material from which the commercial GFT membranes are fabricated and has been studied intensively in pervaporation because of its excellent film-forming, highly hydrophilic, and good chemical resistant properties (10–12). However, PVA has poor stability in aqueous solutions. Maleic acid, a dicarboxylic acid, is often used as a crosslinking agent for PVA (13, 14). For example, the GFT membrane is prepared by casting an aqueous solution of PVA and maleic acid in an ultrathin film on a microporous polyacrylonitrile supporting membrane, evaporating the solvent, and heat-curing. The resultant crosslinked PVA membranes show excellent permselectivity for the separation of ethanol–water mixtures (15). It has also been reported that the *N*-methoxymethyl nylons react readily with maleic acid to form the crosslinked structure (16).

In a previous study (2), *N*-methylol nylon-6 was prepared and its membrane was utilized to separate water–ethanol mixtures by pervaporation. The results showed that these membranes had a much higher permeability than the nylon-6 membrane with an equivalent selectivity. In this work, *N*-methylol nylon-6 of 33% substitution is blended with PAA and PVA, then crosslinked by a multivalent cation (Al^{3+}) and maleic acid, respectively. The pervaporation performance of these crosslinked blend membranes for the separation of ethanol–water mixtures is investigated.

EXPERIMENTAL

Materials

The preparation of *N*-methylol nylon-6 of 33% substitution has been described previously (2). Poly(acrylic acid) with molecular weight 450,000 and polyvinyl alcohol with molecular weight 133,000 and 99 mol% hydrolyzed were obtained from Polysciences, Inc. The aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$ is of analytical reagent grade (J. T. Baker Chemical Co). Reagent grade maleic acid was purchased from Fisher Scientific Co. The 88% formic acid solution was obtained from BDH Chemicals.

Membrane Preparation

A 10 wt% PAA or a 5 wt% PVA solution in 88 wt% formic acid was mixed with a 10 wt% *N*-methylol nylon-6 solution in 88 wt% formic acid to form homogeneous solutions.

N-Methylol Nylon-6 and PAA Blend Membranes

The blend solutions were cast onto a clean glass plate with the aid of a Gardner casting knife to appropriate thicknesses. The casting films were air dried at room temperature for 24 hours in a dust-free, environmentally controlled chamber, then vacuum dried at room temperature for 6 hours. The dried membrane was peeled off from glass plate for further modification. Ionic crosslinking of the *N*-methylol nylon-6 and PAA blend membranes was performed by submerging them into a 10 wt% aluminum nitrate solution bath for 24 hours at room temperature. Twenty-four hours was chosen for the crosslinking time, since, in the study of ionically blended nylon-PAA membranes (8, 9), it was found that 20–30 hours is the optimal crosslinking time. After the desired crosslinking time, the membrane was removed from the crosslinking bath and rinsed with water. It was then stored in deionized water for 24 hours before usage to allow the free ions to diffuse out of the membrane.

N-*Methylol Nylon-6 and PVA Blend Membranes*

Maleic acid was added directly into the solutions and continuously stirred for 6 hours to completely dissolve the maleic acid. The resultant solutions was filtered to removed any solid residual. The casting and drying procedures followed the above. The maleic acid-containing blend membranes were heated at 180°C for 10 minutes, then stored in deionized water for further use.

Pervaporation

Pervaporation was conducted for these modified blended membranes over the entire concentration range of water–ethanol mixtures at 30°C. Pervaporation was carried out in the same way as described previously (2). The permeability, separation factor, and pervaporation separation index (PSI) are calculated as follow:

$$\text{Permeability} = Q/Adt$$

$$\text{Separation factor} = (y_w/y_e)/(x_w/x_e)$$

$$\text{PSI} = (\text{permeability})(\text{separation factor})$$

where Q is the collected amount of permeate at time interval of t, A is the effective membrane area, d is the membrane thickness, x_w and x_e are the concentrations of water and ethanol, respectively, in the feed solution, and y_w and y_e are the concentrations of water and ethanol, respectively, in the permeate.

Sorption Measurement

The dried membrane sample was immersed in ethanol–water mixtures of different concentrations to equilibrate at 30°C for at least 24 hours. Subsequently, the membrane was taken out of the solution, blotted, and placed in a clean dry container that was connected to a cold trap followed by a vacuum pump. The liquid absorbed by the membrane was thus desorbed and collected in the cold trap, and then weighed and analyzed for the composition. The same vacuum and trapping system as used in pervaporation was used for the desorption process. The vacuum-dried membrane sample was also weighed for the calculation of sorption capacity.

RESULTS AND DISCUSSION

Crosslinked PAA/*N*-Methylol Nylon-6 Blend Membranes

It has been reported that PAA solutions are partially compatible with nylon solutions. In the nylon-6/PAA system (8) a homogeneous blend solution can be formed for a PAA content up to 50 wt%, while in the nylon-66/PAA system (9) a homogeneous solution can only be formed for a PAA content up to 35 wt%. In their experimental procedure, a 25 wt% PAA aqueous solution was used for blending. Since water is a nonsolvent for nylons, increasing the amount of added PAA aqueous solution will increase the amount of water in the blend solution, thus causing the precipitation of nylons from solution. In this study we used 88% formic acid to prepare *N*-methylol nylon-6 and PAA solutions. It was found that an optically clear blend solution can now be formed over the entire range of blend ratios.

The sorption capacities of water and ethanol are listed in Table 1 or the ionically crosslinked membranes with different PAA contents. The sorption amount of water increases, while the sorption amount of ethanol decreases with increasing PAA content. This indicates that the hydrophilicity of the blend membrane increases with an increase of PAA content.

It has been reported that both the permeability and separation factor of a PAA membrane can be significantly improved by ionization with alkali metal cations (17). This phenomenon can be accounted for by the fact that ionized groups hydrate strongly and exclude organic solvents (salting-out effect). But these membranes suffer from the problem of long-term stability by eluting out of the alkali metal ion from the membranes during the pervaporation operation. In order to avoid the regeneration of

TABLE 1
Sorption Amount of Water and Ethanol in Crosslinked PAA/*N*-Methylol Nylon-6 Blend Membranes

PAA content in membrane	Water sorption amount, g/g polymer	Ethanol sorption amount, g/g polymer
0	0.18	1.87
0.1	0.25	1.05
0.3	0.40	0.81
0.5	0.55	0.40
0.7	0.81	0.30

the acid form, we used the multivalent cation, Al^{3+}, to prevent dissociation through ionic crosslinking. Past studies showed that the crosslinking rate of PAA is so fast that further diffusion of cation into the membrane will be prevented due to the first formed surface layer (18, 19). For the blend membranes studied here, the presence of *N*-methylol nylon-6 in the membrane gives more channels for cation diffusion, thus a uniform crosslinked blend membrane can be achieved.

The pervaporation performances of the ionically crosslinked PAA/*N*-methyl nylon-6 blend membranes are shown in Figs. 1 and 2. An interesting "permeation enhancement," in which the permeation rate of individual permeants in mixtures is higher than that of a pure component, was observed. The total, water, and ethanol permeabilities show a maximum value at ethanol concentrations between 50 and 70 wt%. This phenomena can be explained in terms of plasticizing effects of water and ethanol on the membranes. As discussed previously (2), although the permeability of one component is also enhanced by its own plasticization effect, a maximum permeability of one component results essentially from the strong plasticizing effect of the other component on the membrane. In this pervaporation system, both the water and ethanol exhibit strong plasticizing effects which cause the observed maximum permeabilities.

Since the blend membrane consists of *N*-methylol nylon-6 and PAA, it is possible that both hydrophobic domains and hydrophilic domains exist. The hydrophobic domain, mainly attributed to *N*-methylol nylon-6, has a strong affinity to ethanol. The maximum in water permeability curves probably results from the membrane plasticization induced by ethanol in this domain. The maximum in ethanol permeability curves can be explained by the fact that the ionic crosslinking linkage in membrane (hydrophilic domain) becomes somewhat loose due to the sorption of water, therefore enhancing the ethanol permeability. It can also be observed that the relative permeability enhancement for ethanol is greater than that for water, suggesting that water has a stronger plasticizing effect on ethanol permeation for the ionically crosslinked membranes.

The effect of ethanol concentration in feed on the separation factor for the ionically crosslinked blend membranes is shown in Fig. 1. It can be seen that higher separation factors are obtained at both extreme concentration ranges. This phenomenon was also observed in the separation of ethanol–water mixtures using blended PAA/nylon-6 and PAA/nylon-66 membranes (8, 9).

High separation can be obtained by adjusting the hydrophobic/hydrophilic balance of a membrane. Since *N*-methylol nylon-6 is a comparatively hydrophobic polymer, while PAA is a strongly hydrophilic one, control of the ratio of the two polymers in blends might result in better

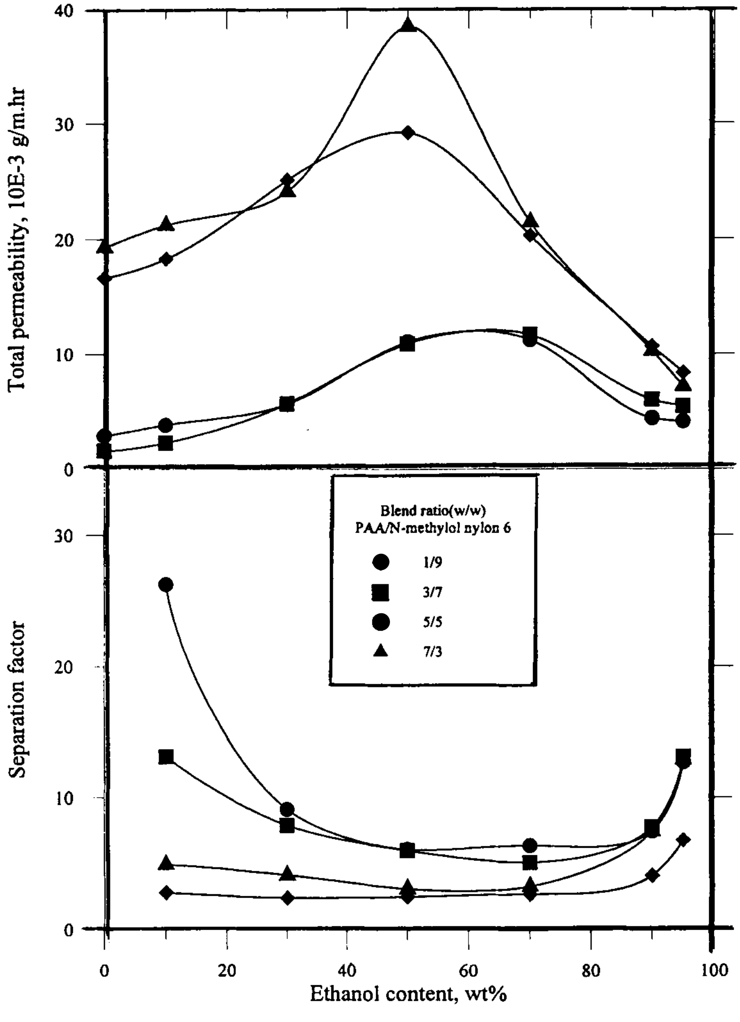

FIG. 1 Overall pervaporation performance versus feed concentration for crosslinked PAA/N-methylol blend membranes with different blend ratios.

membrane performance. Figure 3 shows the effect of PAA content in the blend membrane on total permeability, separation factor, and PSI for feed solutions of 50 and 95 wt% ethanol, respectively. All the pervaporation runs were carried out at 30°C, and the membranes used were crosslinked for 24 hours in 10 wt% aluminum nitrate solution. The permeabilities have

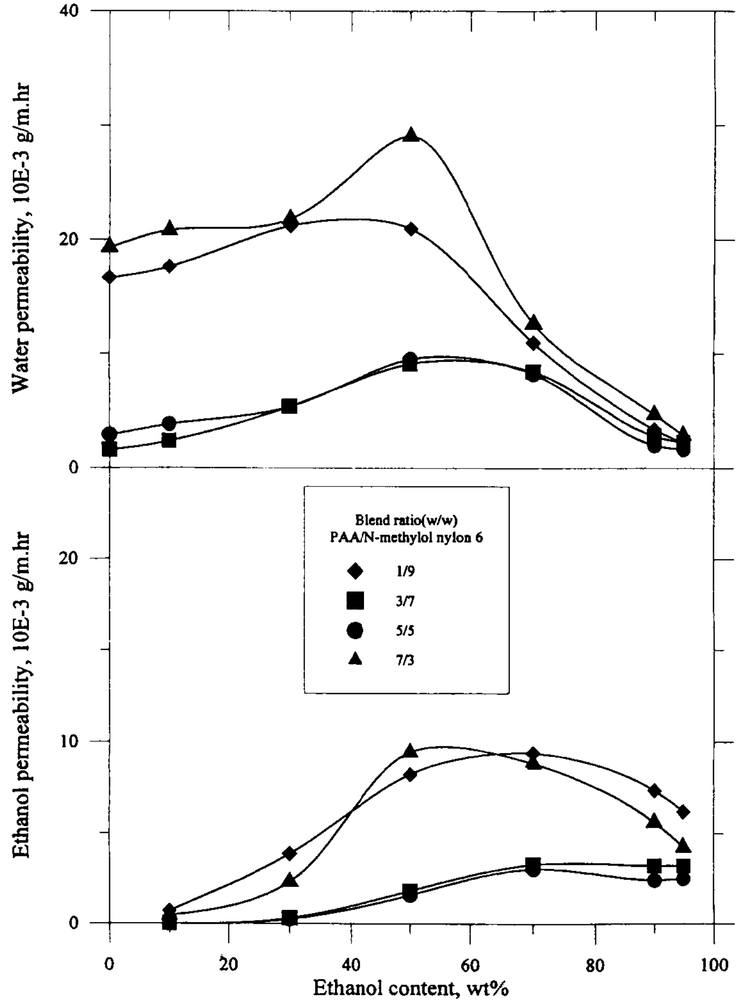

FIG. 2 Individual permeability versus feed concentration for crosslinked PAA/*N*-methylol nylon-6 blend membranes with different blend ratios.

a minimum at 50 wt% PAA content in a membrane, which is particularly pronounced for a feed solution with a high water content, i.e., 50 wt% water compared to 5 wt% water, while the separation factors also show a maximum about 50 wt% PAA. The parabolic permeability curve may be explained in terms of the solubility of the feed components in the mem-

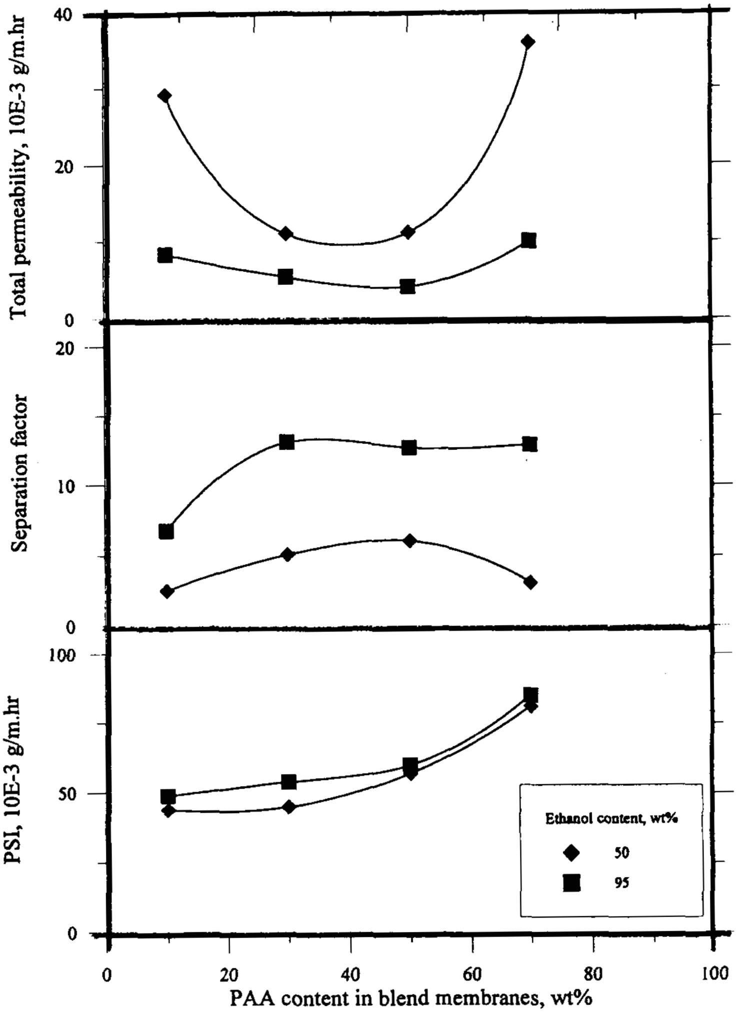

FIG. 3 Effect of PAA content on the pervaporation performance.

brane and the membrane density. Since PAA is a highly hydrophilic polymer, the increase of PAA content in blend membranes improves the water solubility in the membrane, as shown in Table 1, which is more significant for feed solutions of higher water content. When the PAA content exceeds 50 wt%, the sorption property of the membrane is the dominant factor for the permeation, thus the permeability increases with an increase of PAA content. On the other hand, the membrane structure becomes more compact with increasing the PAA content as a result of ionic crosslinking. When the PAA content is less than 50 wt%, the diffusion property plays a more important role than the sorption property, and the permeability decreases with an increase of PAA content due to the difficulty through a compact membrane structure.

The pervaporation separation index (PSI) is used as a measure of pervaporation performance (2). As shown in Fig. 3, the PSI value increases with increasing PAA content for feed solutions of both 50 and 95 wt% ethanol. It can be seen that the addition of hydrophilic PAA into the blend membranes increases the hydrophilicity of the original hydrophobic *N*-methylol nylon-6, thus improving the pervaporation performance of membranes for the separation of ethanol–water mixtures.

Crosslinked PVA/*N*-Methylol Nylon-6 Blend Membranes

Maleic acid is an effective crosslinking agent which can react with the pendant hydroxy groups in polyvinyl alcohol (20) and *N*-methoxymethyl nylons (16) and improve the pervaporation performance. In the blend system studied here, it is believed that crosslinking will occur among maleic acid, *N*-methylol nylon-6, and PVA.

The pervaporation performance of PVA/N-methylol nylon-6 membranes of blend ratio 50/50 by weight crosslinked with different maleic acid contents are shown in Figs. 4 and 5. The water permeability is about one order higher than ethanol permeability, and maximum values can be found for all total, water, and ethanol permeabilities at a feed ethanol content between 60 and 70 wt%. As discussed above, these crosslinked blend membranes are water-selective, and their permeability is enhanced notably by the strong plasticizing effects of both water and ethanol. The water permeability at a feed solution of 95 wt% ethanol (5 wt% water) is still about 3–4 times higher than that of pure water. Poly(vinyl alcohol) is a highly hydrophilic polymer material, and the pervaporation flux of its crosslinked membrane decreases with increasing ethanol content in the feed (21). However, when blended with the more hydrophobic *N*-methylol nylon-6, the membrane performance is totally different. The presence of the more hydrophobic component in blend membranes raises the water permeability at feed solutions of higher organic content due to the plasticization of ethanol, while still maintaining good separation properties. Figure 1 also gives a plot of separation factor versus ethanol content in feed for the various crosslinked blend membranes. The separation factor has the highest value (100–200) at 95 wt% ethanol, which contributes to the

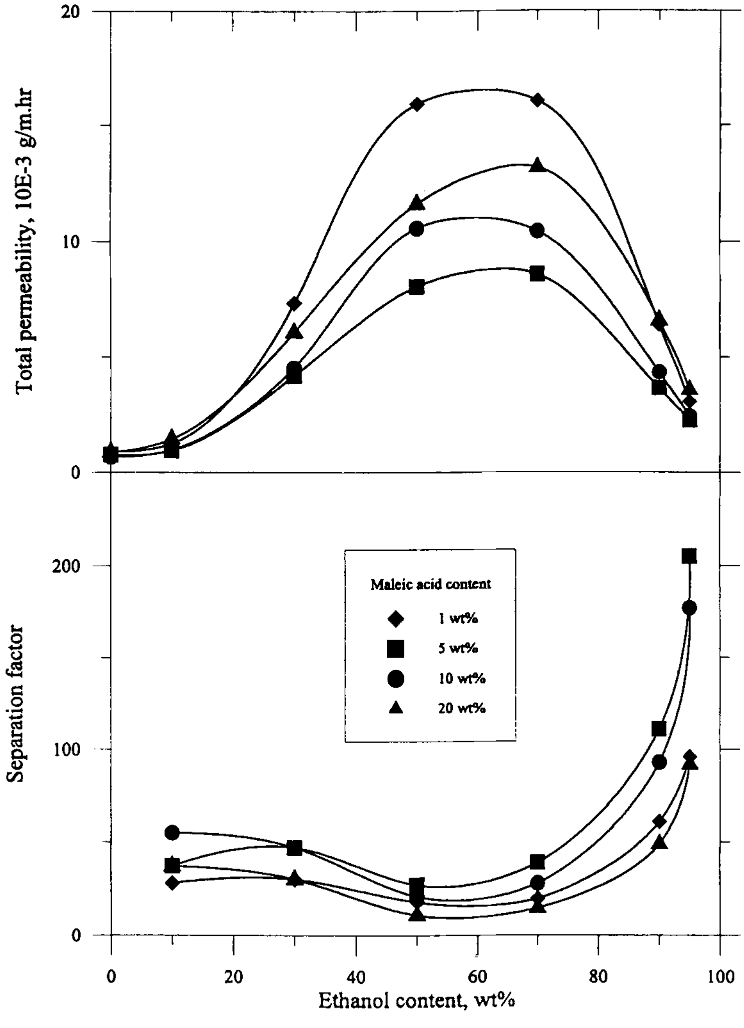

FIG. 4 Overall pervaporation performance versus feed concentration for crosslinked PVA/*N*-methylol nylon-6 blend membranes with different maleic acid contents. Blend ratio: 50/50 by weight.

highly enhanced water permeability by the plasticizing effect of ethanol on the membrane at feed solutions of high ethanol content.

The effect of maleic acid content on membrane performance at a feed solution of 95 wt% ethanol is shown in Fig. 6 as replotted from Fig. 4.

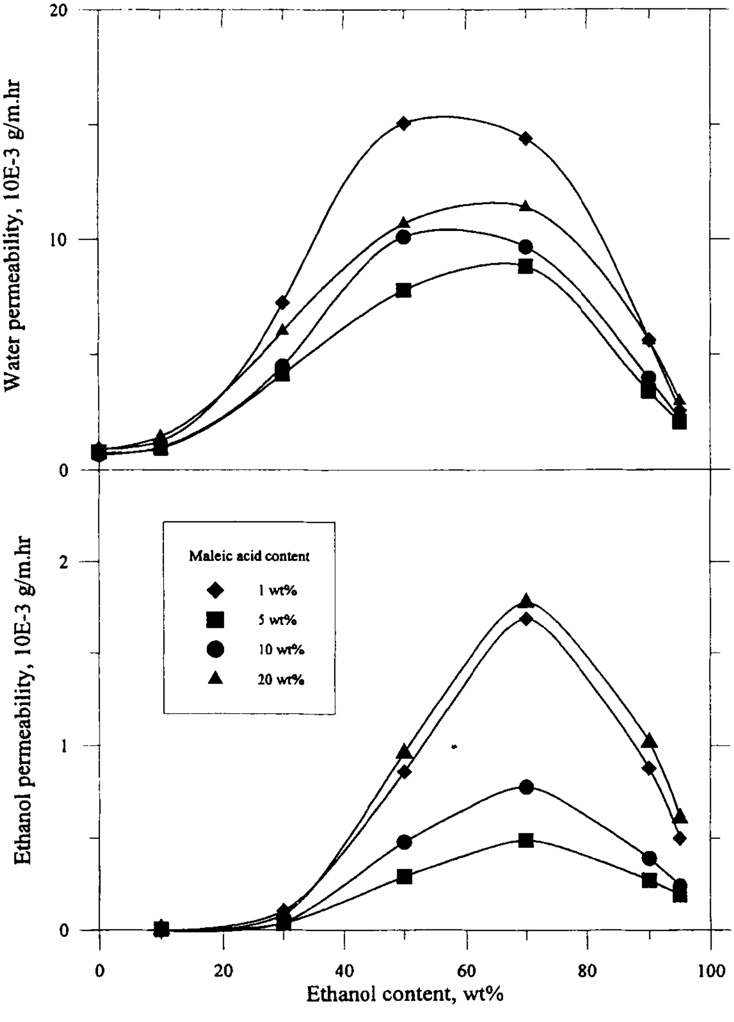

FIG. 5 Individual permeability versus feed concentration for crosslinked PVA/*N*-methylol nylon-6 blend membranes with different maleic acid contents. Blend ratio: 50/50 by weight.

Maximum separation factor and minimum permeability are observed at 5 wt% maleic acid. Generally speaking, as the crosslinking density in the polymer increases, the resultant membrane has a more compact network structure with less chain mobility. Therefore, the free volume in the polymer decreases, leading to a decrease in both solubility and diffusivity,

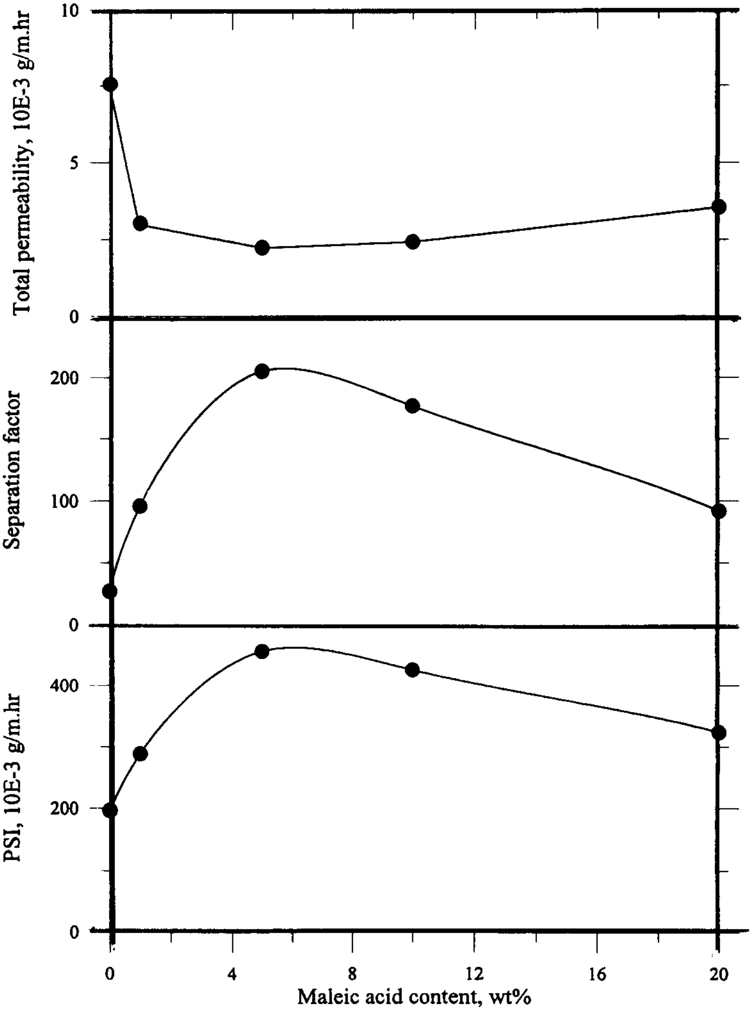

FIG. 6 Effect of maleic acid content on pervaporation performance.

and the membrane exhibits a lower permeability with higher separation factor. The figure shows a parabolic shaped curve and can be explained in terms of the dispersion of excess unreacted crosslinking agent in the membrane with more than 5 wt% maleic acid (22). The reactivity of a functional group on a polymer chain is affected by adjacent neighboring groups. Thus, as reaction proceeds, the accessibility of a crosslinking agent to a functional group on a polymer chain can be restrained even below the stoichiometric quantity of the crosslinking agent. Excess crosslinking agent which does not participate in the reaction becomes dispersed in the membrane, causing an increase in the number of chain end groups in the membrane, which results in an increase in free volume. Therefore, the membranes crosslinked with more than 5 wt% maleic acid show an increase in permeability and a decrease in separation factor with increasing crosslinking agent content. It also shows a maximum PSI value is obtained at 5 wt% maleic acid, suggesting the blend membrane with 5 wt% maleic acid as crosslinking agent gives the best membrane performance. All the blend membranes used for the following discussion are crosslinked with 5 wt% maleic acid.

Figures 7 and 8 give the pervaporation results of a crosslinked (5 wt% maleic acid) blend membrane of PVA/*N*-methylol nylon-6 with different blend ratios. The trend of permeability curves against ethanol content in feed is similar to Figs. 4 and 5. All curves show a maximum value at about 70 wt% ethanol in the feed. They also show that both the permeabilities and plasticizing effect of ethanol–water mixtures on the membrane are reduced with increasing PAA content. This suggests that in the membrane matrix, *N*-methylol nylon-6 is the main component plasticized by ethanol–water mixtures. It is noticeable that the ethanol permeability decreases abruptly with a PVA content of more than 30 wt%, while the water permeability gradually decreases. The separation factor remains mainly unchanged at ethanol contents below 70 wt%, while a sudden increase of separation factor is observed when the ethanol content is higher than 70 wt%. The hydrophilicity of the blend membranes increases with increasing PVA content, therefore the chain mobility in the membrane matrix is more limited at a high ethanol content, leading to a decrease in permeability and an increase in separation factor.

Preferential sorption has been considered to be a prerequisite for preferential permeation (23, 24). According to the solution-diffusion model, both sorption and diffusion aspects should be taken into account. In order to illuminate the relationship between sorption and pervaporation, sorption measurements were conducted at 30°C over the entire concentration range for a chemically crosslinked membrane with 70 wt% PVA content. Figure 9 shows that as the concentration of ethanol in the bulk liquid solution increases, the sorption of total solution in the membrane decreases almost linearly, suggesting the membrane is hydrophilic. On the other hand, the pervaporation curve shows a different trend. The permeability increases to a maximum and then decreases with an increase of ethanol content. This indicates that, in addition to sorption, the diffusion of permeant

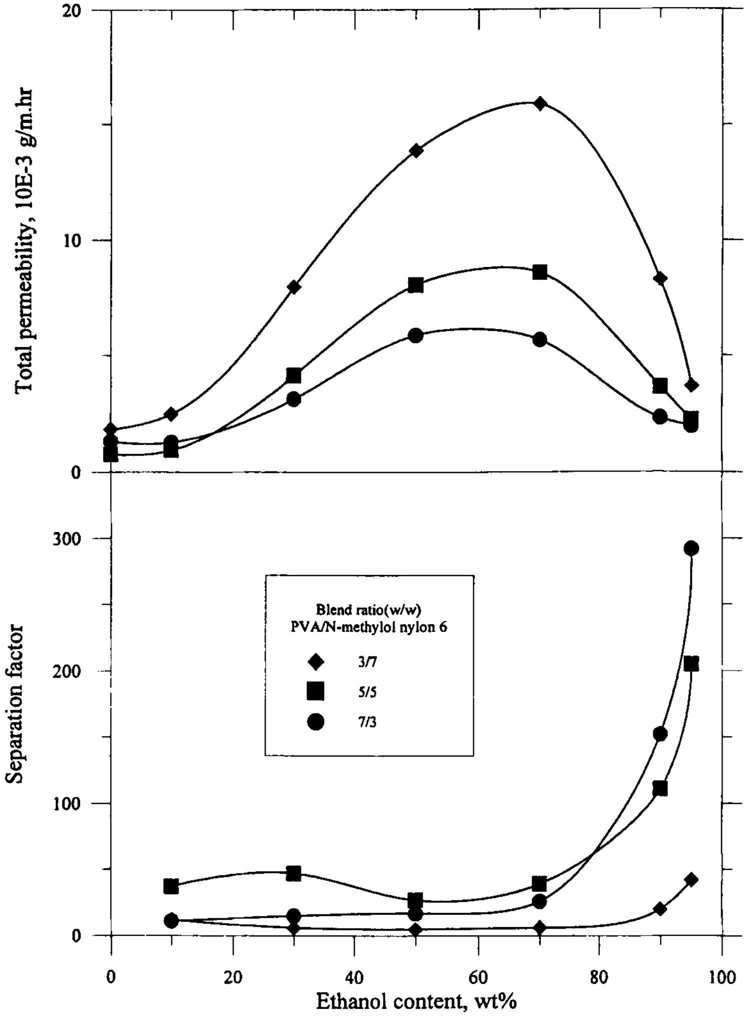

FIG. 7 Overall pervaporation performance versus feed concentration for crosslinked PVA/*N*-methylol nylon-6 blend membranes with different blend ratios. Maleic acid content: 5 wt%.

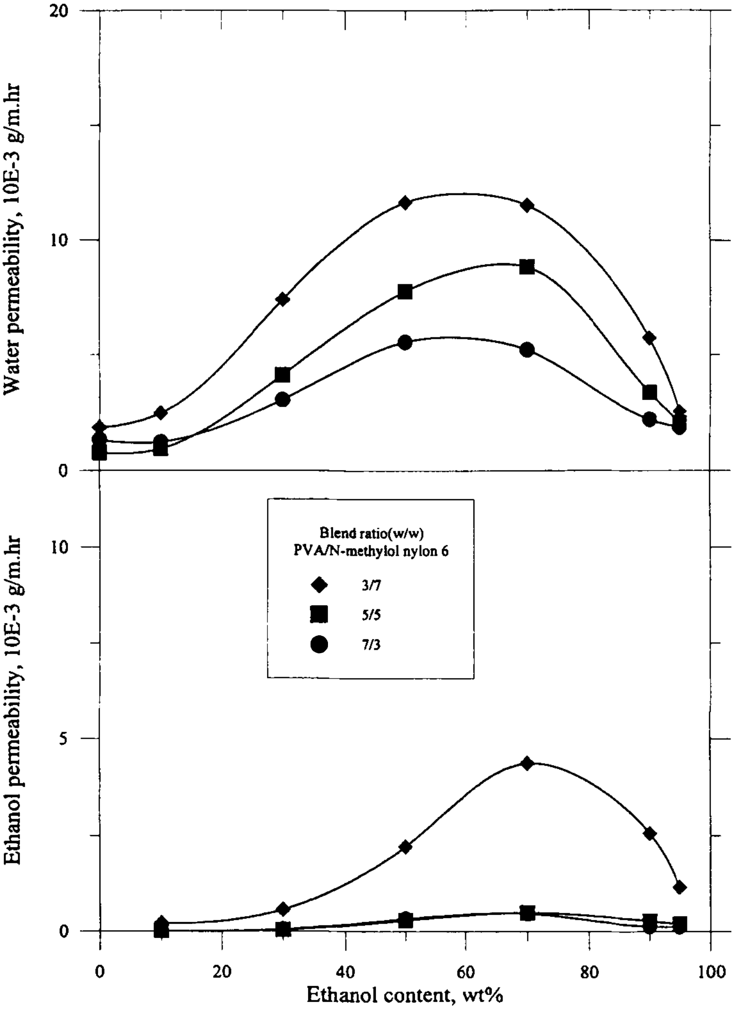

FIG. 8 Individual permeability versus feed concentration for crosslinked PVA/*N*-methylol nylon-6 blend membranes with different blend ratios. Maleic acid content: 5 wt%.

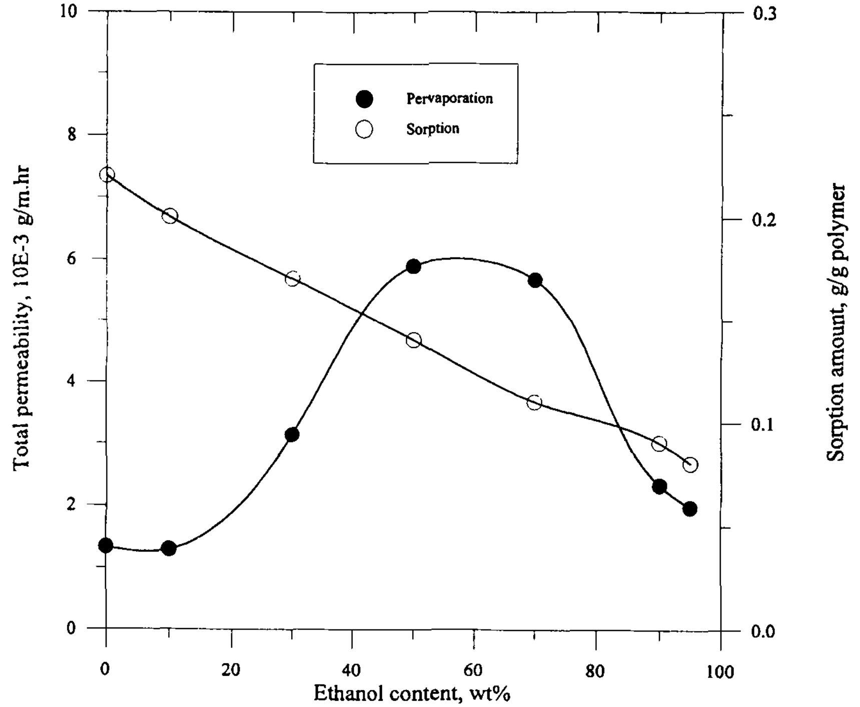

FIG. 9 Pervaporation and sorption data versus feed concentration. Crosslinked PVA/*N*-methylol nylon-6 blend membrane with blend ratio of 70/30 by weight and 5 wt% maleic acid.

through the membrane also plays a very important role in pervaporation due to complicated polymer-permeant and permeant-permeant interactions which cause membrane plasticization. Figure 10 shows the separation characteristics for both pervaporation and sorption. At low organic concentration (<50 wt% ethanol), the two curves are almost identical, while at high organic concentration (>50 wt% ethanol), they deviate from each other. At higher water concentrations, the hydrophilic membrane swells so extensively that selective diffusion does not exist, and the separation mainly depends on sorption properties. At high organic concentration, membrane swelling diminishes so that the major part of the membrane is almost in a dry state and separation now mainly depends on diffusion which leads to better separation performance.

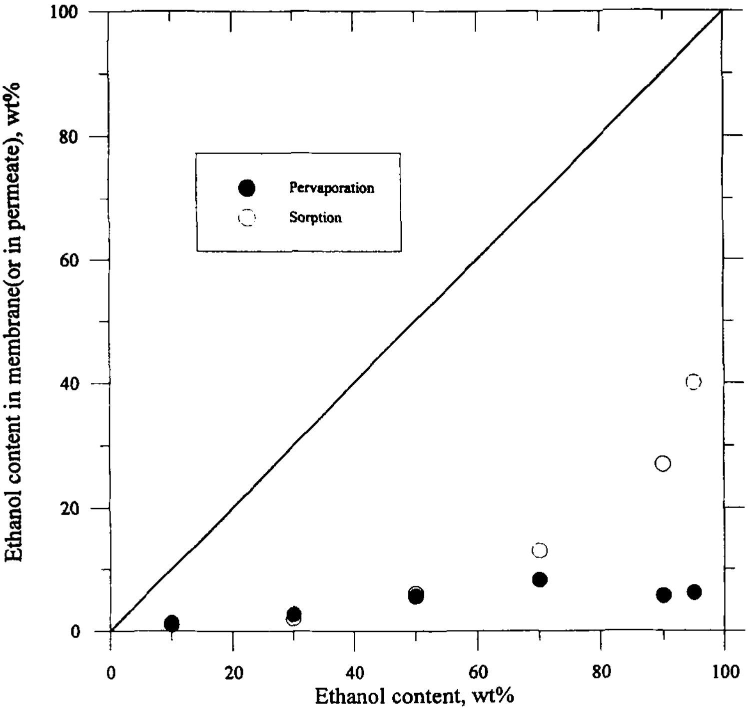

FIG. 10 Separation characteristic of pervaporation and sorption versus feed concentration. Crosslinked PVA/*N*-methylol nylon-6 blend membrane with blend ratio of 70/30 by weight and 5 wt% maleic acid.

CONCLUSIONS

In this study, crosslinked blend membranes of PAA/*N*-methylol nylon-6 and PVA/*N*-methylol nylon-6 were prepared using aluminum nitrate and maleic acid, respectively, as crosslinking agents. The following conclusions can be drawn.

1. All the crosslinked blend membranes are water selective for the separation of ethanol–water mixtures.
2. Both membrane systems are strongly plasticized by ethanol–water mixtures. The plasticizing effect of ethanol mainly acts on the hydrophobic domain, i.e., *N*-methylol nylon-6, while the plasticizing effect of water on the hydrophilic domain, i.e., PAA or PVA, is in the membrane matrix.

3. Enhanced permeation is observed. In some blend systems the water permeability at low water content (5 wt%) is much higher than pure water permeability.
4. For a feed solution of 95 wt% ethanol, the best pervaporation results for both membrane systems are:

   Crosslinked PAA/*N*-methylol nylon-6 blend membrane (blend ratio 70/30 by weight): total permeability = 10 × 10^{-3} g/m·h with a separation factor of 13.

   Crosslinked PVA/*N*-methylol nylon-6 blend membrane (blend ratio 70/30, 5 wt% maleic acid): total permeability = 2 × 10^{-3} g/m·h with a separation of 300.
5. For a hydrophilic membrane, the diffusion is the determining factor of pervaporation performance for the feed solution with a low water content, while the sorption property dominates if the feed solution contains a high water content.

ACKNOWLEDGMENTS

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