

Permselectivities of 2,2'-Dimethyl-4,4'-bis(aminophenoxy)-biphenyl Diphenyl Methane-Based Aromatic Polyamide Membranes for Aqueous Alcohol Mixtures in Pervaporation and Evapomeation

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ABSTRACT: The separation of aqueous alcohol mixtures was carried out by use of a series of novel aromatic polyamide membranes. The aromatic polyamides were prepared by the direct polycondensation of 2,2'-dimethyl-4,4'-bis(aminophenoxy)biphenyl (DBAPB) with various aromatic diacids, such as terephthalic acid (TPAc), 5-*tert*-butylisophthalic acid (TBPAC), and 4,4'-hexafluoroisopropylidenedibenzoic acid (FDAc). The pervaporation and evapomeation performance of these novel aromatic polyamide membranes for dehydrating aqueous alcohol solution were investigated. The solubility of ethanol in the aromatic polyamide membranes is higher than that of water, but the diffusivity of water through the membrane is higher than

that of ethanol. The effect of diffusion selectivity on the membrane separation performances plays an important role in the evapomeation process. Compared with pervaporation, evapomeation effectively increases the permselectivity of water. Moreover, the effect of aromatic diacids on the polymer chain packing density, pervaporation, and evapomeation performance were investigated. It was found that the permeation rate could be increased by introduction of a bulky group into the polymer backbone. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2688–2697, 2003

Key words: pervaporation; evapomeation; polyamide; sorption selectivity; diffusivity selectivity

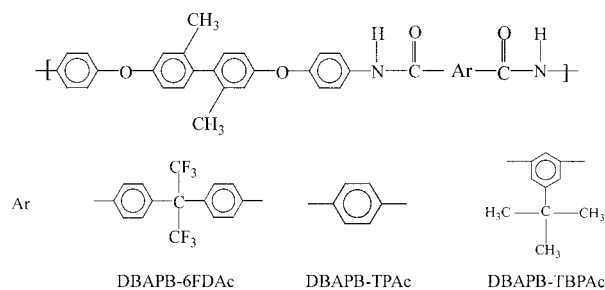
INTRODUCTION

The dehydration of aqueous organic mixtures with azeotrope and/or small differences in boiling point, using conventional separation methods such as azeotropic distillation, solvent extraction, or rectification, are difficult and costly in terms of production of energy and apparatus. Therefore, membrane separation processes offer potentially more economical alternatives for such difficult separation. Pervaporation is one of the membrane separation processes that uses a dense polymeric membrane as a separation barrier between the liquid feed and permeate vapor. Basically, transport in pervaporation takes place in a three-step sequence: (1) sorption into the membrane, (2) diffusion through the membrane, and (3) desorption into the vapor phase.¹ The first two steps are mainly responsible for the permselectivity. Ethanol permselective membranes may be applied to the concentration of dilute aqueous alcohol mixtures. The production cost decreases drastically if the pervaporation

performances are high enough. In addition, with water permselective membrane the pervaporation process has the potential to replace the azeotropic distillation part of the ethanol dehydration system. Thus, to make a pervaporation membrane economically feasible, obtaining a high permeation rate and selectivity is an important factor. However, because organic feed mixtures are directly in contact with polymer membranes in the pervaporation process, the physical and chemical properties of the membranes are often influenced by the feed mixtures by the effects of swelling or shrinking on the membranes.

Evapomeation, a membrane separation technique, was proposed by Uragami et al.^{2,3} to overcome the disadvantages of pervaporation. In this vapor permeation technique, the feed solution is vaporized first and then permeated through the membrane. Thus, the swelling or shrinking of polymer membranes attributed to the feed solutions can be prevented. Many efforts have been made to improve pervaporation and evapomeation performances, for example, polymer grafting, blending, copolymerization, introducing bulky pendant groups into the polymer backbone, and synthesis of new polymers.^{4–8} However, the efficiency of the pervaporation process depends mainly on the

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Scheme 1

intrinsic properties of the polymers used to prepare the membrane. Thus, synthesizing new polymeric materials with good pervaporation performance is exceedingly important. In this work, a series of novel aromatic polyamides based on DBAPB was prepared to investigate the effect of diacid structure on the separation performances. Comparisons of the evaporation and pervaporation performances of the aromatic polyamide membranes for dehydrating aqueous alcohol solution were also investigated. In addition, the effects of feed solution compositions and temperature on the pervaporation and evaporation performance of the prepared membranes were studied.

EXPERIMENTAL

Materials

Polyamides were prepared by the direct polycondensation of DBAPB with various aromatic dicarboxylic acids, such as terephthalic acid (TPAc), 5-*tert*-butylisophthalic acid (TBPAc), and 4,4'-hexafluoroisopropylidenedibenzoic acid (FDAc) in NMP using triphenyl phosphite (TPP) and pyridine as condensing agents.⁹ The polyamide structure is shown in **Scheme 1**. *N,N*-Dimethyl acetamide (DMAc), obtained from Tedia Co., USA, was used without further purification as a solvent. Water was deionized and distilled before use.

Membrane preparation

The polyamide polymer was dissolved in DMAc to form a homogeneous solution of 10 wt % polymer solutions at room temperature. The polymer solution was then cast onto a glass plate to a predetermined thickness using a Gardener knife at room temperature. The cast film was placed in an oven and heated at 80°C for 1 h to evaporate the solvent. The membrane was peeled off from the glass plate and placed in the oven for 24 h to further remove the residue solvent in the membrane. A micrometer was used to measure the average thickness of the polyamide membranes to within $40 \pm 5 \mu\text{m}$.

Pervaporation and evaporation measurement

The pervaporation and evaporation processes were reported in an earlier study.¹⁰ The feed solution was in direct contact with the membrane in the pervaporation apparatus. The effective area was 4.9 cm² and the feed temperature studied was in the range of 25–55°C. The permeation rate was determined by measuring the weight of the permeate. The compositions of the feed solution and the permeate were measured by gas chromatography (GC China Chromatography 8700 T). The separation factor of water/alcohol ($\alpha_{w/a}$) was calculated from

$$\alpha_{w/a} = \frac{Y_w/Y_a}{X_w/X_a}$$

where X_w , X_a , Y_w , and Y_a are the weight fraction of water and alcohol in the feed and permeate, respectively.

The same apparatus was used for evaporation as for pervaporation, except that the feed solution was not in contact with the membrane. The feed solution was vaporized first and then permeated through the membrane. To verify that liquid feed was not in contact with the membrane, we attached a filter paper to the membrane surface facing the feed solution. After the evaporation experiment, we found that the filter paper remained dry, thus confirming that the liquid feed was not in direct contact with the membrane.

Sorption measurement

The polyamide membranes were immersed in several feed mixtures for 24 h at room temperature. They were subsequently blotted between pieces of tissue paper to remove excess solvent and placed in the left tube of a twin setup. The system was evacuated while the left tube was heated with hot water and the right tube was cooled in liquid nitrogen. The composition of the condensed liquid in the right tube was determined by GC.

Degree of swelling

The polyamide membranes were immersed in different feed mixtures for 24 h at different temperatures. The degree of swelling (%) of the membrane was defined by the following equation:

$$\text{Degree of swelling (\%)} = \frac{W_w - W_d}{W_d} \times 100$$

where W_d and W_w denote the weight of dry and swollen membranes, respectively.

TABLE I
Synthesis of Aromatic Polyamides

Polyamide	T_g (°C)	d -spacing (Å)	Solubility in NMP, DMAc, DMSO
DBAPB-TPAc	324	5.29	Good
DBAPB-TBPAC	255	5.30	Good
DBAPB-6FDAc	243	5.87	Good

Characterizations

Wide-angle X-ray diffraction scans were generated by a Philips model PW 1710 diffractometer (Philips, The Netherlands) using Ni-filtered Cu-K α radiation (40 kV, 30 mA). FTIR spectra were recorded on a Jasco FTIR-7000 (Tokyo, Japan). Thermogravimetric data were obtained on a DuPont 2200 apparatus (DuPont, Boston, MA) in flowing nitrogen (60 cm³/min) at a heating rate of 20°C/min. Differential scanning calorimetry analysis was performed on a Perkin-Elmer DSC-7 differential scanning calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT) in flowing nitrogen (60 cm³/min) at a heating rate of 20°C/min. The true density was measured by using a Micromeritics Accucyc 1330 pycnometer (Switzerland), an instrument that measures the volume of the membrane by the nitrogen displacement method. In addition, specific volume is the reciprocal of true density. The bulk density was measured by the method of Archimedes' principle.

$$\rho_{\text{bulk}} = \frac{A}{A - B} \times \rho_w$$

where A is the dry membrane weight in air, B is the membrane weight in water, and ρ_w is the water density.

RESULTS AND DISCUSSION

Effect of diacid structure of the aromatic polyamide on the evapomeation performance

Three types of DBAPB-based aromatic polyamides were prepared by direct polycondensation with aromatic dicarboxylic acids (TPAc, TBPAC, and 6FDAc) using triphenyl phosphite and pyridine as condensa-

tion agents. The results are summarized in Table I. All of the polymers were soluble in polar aprotic solvents such as DMF, NMP, and DMAc. The good solubility is possibly attributable to the introduction of the bulky group into polymer backbone. The glass-transition temperature of these polymers decreases as the molecular volume of dicarboxylic acids increases. These phenomena might result from the fact that the larger pendant group and flexible hexafluoroisopropylidene groups between rigid benzoic rings reduce the polymer packing density and inhibit the mobility of polymer chains. Table II shows the effect of diacid structure on the evapomeation of 90 wt % aqueous ethanol solution through the DBAPB-based aromatic polyamide membranes. Compared with DBAPB-TPAc membrane, the DBAPB-TBPAC and DBAPB-6FDAc membranes with 5-*tert*-butyl pendant group and hexafluoropropane group in polymer backbone, respectively, have a higher permeation rate. These phenomena might result from the fact that the latter aromatic polyamides (DBAPB-TBPAC and DBAPB-6FDAc) have a bulky segment (5-*tert*-butyl pendant group and hexafluoropropane group) in the polymer backbone, which could result in increasing steric hindrance. Thus, the free volumes of the DBAPB-TBPAC and DBAPB-6FDAc membranes are higher than that of the DBAPB-TPAc membrane.

In addition, Table II also shows the effects of diacid structure on the specific volume, swelling degree, and the bulk density of the aromatic polyamides. It can be seen that the specific volume and the swelling degree of the DBAPB-based aromatic polyamide membranes ranked in the following order: DBAPB-6FDAc > DBAPB-TBPAC > DBAPB-TPAc. With respect to molecular structure, the polymer with a larger substituted group is characterized by a higher barrier to the chain rotation than that with a smaller group. The higher barrier to rotation in the polyamide membranes may also inhibit the local segmental motion. Thus, it can be deduced that the polymer packing density is lower when a larger pendant group is introduced into the polymer backbone. The above discussion can explain why the permeation rates of DBAPB-TBPAC and DBAPB-6FDAc membranes are higher than that of the DBAPB-TPAc membrane. These results agree well with the results of the eva-

TABLE II
Effect of Polymer Structure on the Evapomeation Performance, Degree of Swelling, Bulk Density and Specific Volume of the Polyamides^a

Polyamide	Permeation rate (g m ⁻² h)	Separation factor	Degree of swelling (wt %)	Specific volume	Bulk density
DBAPB-TPAc	128	2856	12	0.775	1.29
DBAPB-TBPAC	152	591	13	0.820	1.22
DBAPB-6FDAc	203	292	16	0.847	1.18

^a Feed solution concentration, 90 wt % aqueous ethanol solution; feed solution temperature, 25°C.

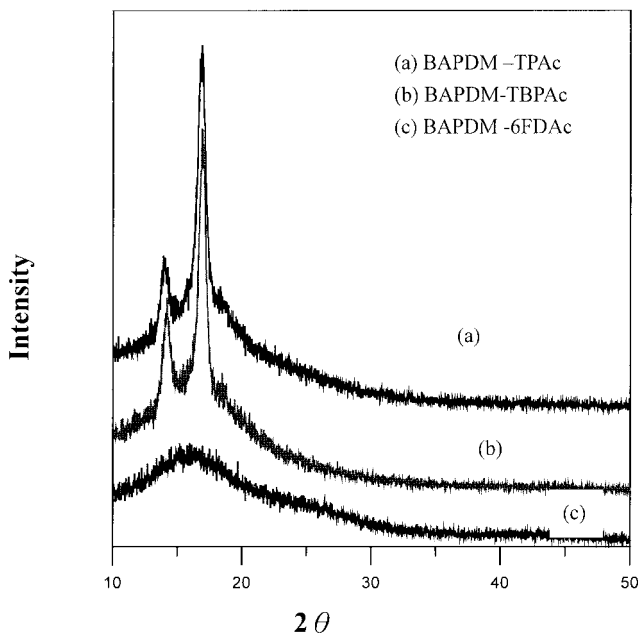


Figure 1 X-ray diffraction measurements of the aromatic polyamides.

pomeation experiment. Furthermore, X-ray diffraction measurements of the polymers indicated that all aromatic polyamides were essentially crystalline except that based on 4,4'-hexafluoroisopropylidenedibenzoic acid (DBAPB-6FDAc). The X-ray diffraction pattern

and *d*-spacing results of the aromatic polyamide are shown in Figure 1 and Table I, respectively. The amorphous structure of aromatic polyamide (DBAPB-6FDAc) could be explained by the fact that the 4,4'-hexafluoroisopropylidenedibenzoic acid has a bulky hexafluoropropane group in the polymer backbone, which could result in increased steric hindrance. Thus, the packing density of polymer chains decreased during the membrane-formation process.

Comparison of the separation performances of the DBAPB-6FDAc membrane between pervaporation and evapomeation

Figure 2 shows the separation performances of the aqueous ethanol solution through the DBAPB-6FDAc membrane by pervaporation and evapomeation. It shows that the water molecules are predominantly permeated through the DBAPB-6FDAc membranes in both methods. It is also shown in Figure 2 that the permeation rate increases with increasing ethanol concentration in the feed solution. These results might be attributable to the plasticizing effect of ethanol. Generally, hydrophobic membranes have a stronger interaction with alcohol than with water. The degree of swelling of the DBAPB-6FDAc membranes also increases with an increase in the ethanol concentration, as shown in Figure 3. When the ethanol concentration in the feed is higher, the amorphous region of the

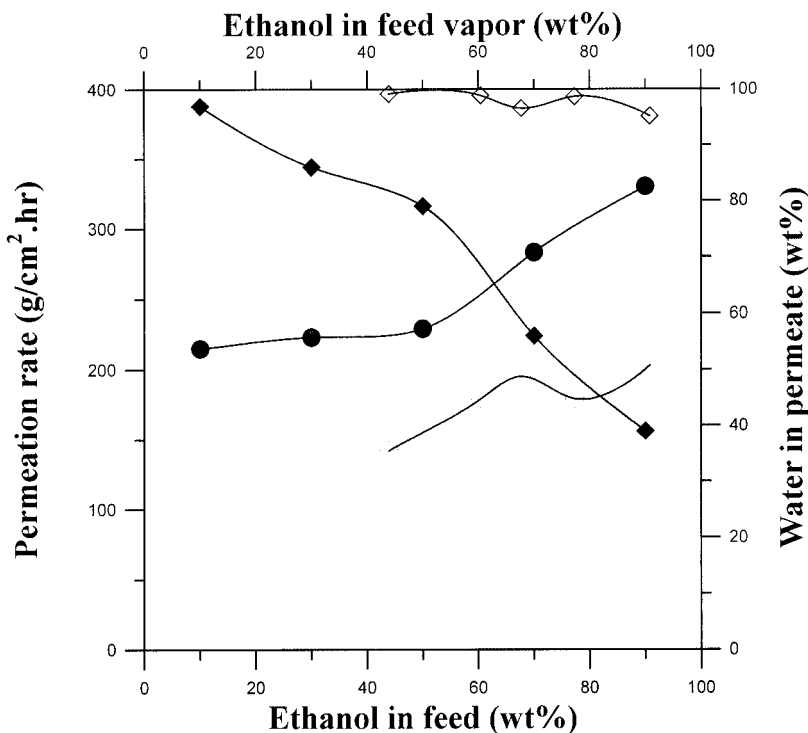


Figure 2 Effect of feed ethanol concentration on the separation performances of DBAPB-6FDAc membrane. Pervaporation: permeation rate (●) and water concentration in permeate (◆). Evapomeation: permeation rate (○) and water concentration in permeate (◇).

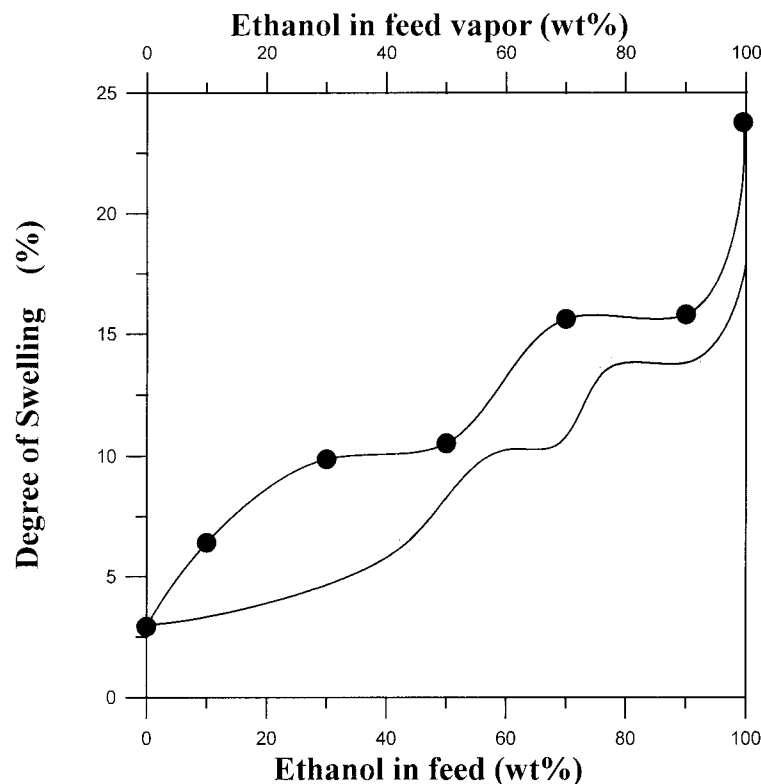


Figure 3 Effect of feed ethanol concentration on the degree of swelling of the DBAPB-6FDAc membrane: pervaporation (●) and evapomeation (○).

membranes is more swollen. Hence, the polymer chains in the swollen region become more flexible and the energy required for diffusive transport also decreases, resulting in an increased permeation rate when the feed ethanol concentration increases. In addition, the permeation rate of evapomeation is lower than that of pervaporation. This phenomenon might result from the fact that the membrane is in direct contact with the feed solution and swollen in the pervaporation process but is not in contact with the liquid feed in the evapomeation process. Thus, the diffusivity of the permeating species in evapomeation is lower than that in pervaporation because the swelling effect caused by the liquid feed is less obvious in evapomeation. The results of swelling degree indicated in Figure 3 are in substantial agreement with the results mentioned above.

Effect of feed ethanol composition on the sorption and diffusion properties of evapomeation through the DBAPB-6FDAc membrane

According to the solution-diffusion model,^{6,11} the permeability (P) of a permeant through a membrane is a product of the solubility (S) and the diffusivity (D). The effects of feed ethanol composition on the sorption and diffusion properties are discussed in this section. As shown in Figure 4, the ethanol concentra-

tion in the membrane is higher than that in the permeate when the vapor ethanol concentration in the feed varies from 40 to 95 wt %. These results can be explained by the strong affinity between ethanol molecules and the aromatic polyamide membrane. In addition, the solubilities of water and ethanol in the DBAPB-6FDAc membrane are 6 and 23 (g/100 g), respectively. It is known that water has low interaction with membranes and consequently low solubility was observed. These results of solubility agree well with the data of permeation mentioned above. Once water molecules are incorporated into the DBAPB-6FDAc membrane, they can easily diffuse through the membrane because the interaction between the water molecule and the membrane is very weak and the molecular size of water is also smaller than that of ethanol. In addition, the sorption experiments were performed to determine the separation factor of solution (α_{solution}) for the DBAPB-6FDAc membranes. For evapomeation, the permeability coefficient represents the product of the solution coefficient and the diffusion coefficient. Thus, the separation factor of evapomeation ($\alpha_{\text{evapomeation}}$) is also expressed as the product of α_{solution} and that of the diffusion $\alpha_{\text{diffusion}}$, as follows:

$$\alpha_{\text{evapomeation}} = \alpha_{\text{solution}} \times \alpha_{\text{diffusion}}$$

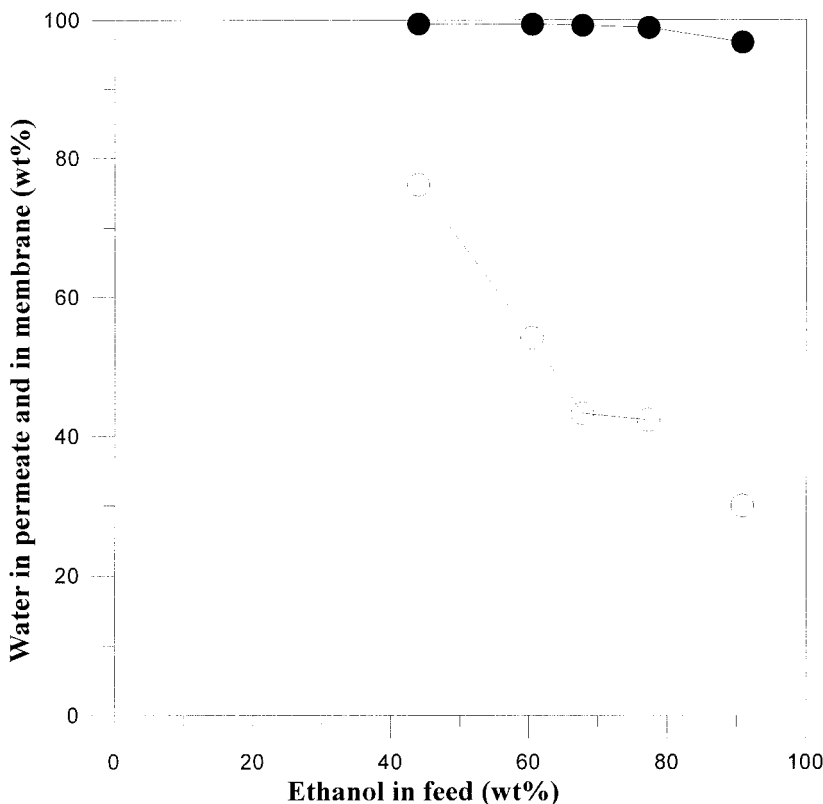


Figure 4 Effect of feed ethanol concentration on evaporation performance: water concentration in the permeate (●); water concentration in the membrane (○).

The results of the separation factor of evaporation, solution, and diffusion are shown in Figure 5. It shows that the separation factor of evaporation and solution increases with increasing the feed ethanol concentration. In general, the separation factor of diffusion was strongly related to the membrane structure: a denser membrane structure results in a higher separation factor of diffusion. Obviously, the diffusion selectivity dominates the behavior of evaporation because the separation factor of evaporation follows the same trend as the diffusion selectivity, but not the trend of the sorption selectivity. These phenomena might be attributable to the fact that the feed solution was vaporized first and then permeated through the membrane. Thus, the swelling of the DBAPB-6FDAc membranes arising from the feed solutions can be prevented.

Temperature effect

Figures 6 and 7 show the effect of feed solution temperature on the permeation rate and separation factor for pervaporation and evaporation of 90 wt % aqueous ethanol solution through the DBAPB-6FDAc membrane, respectively. It shows that the permeation rate (total, water, and ethanol) increases and the separation factor decreases as the feed solution tempera-

ture increases. From these phenomena it may be assumed that the increases of swelling of the membrane matrix at higher temperature results in increased polymer segmental motions. Moreover, according to the free-volume theory, free volume is strongly related to random thermal movement. As temperature increases, the frequency and amplitude of the chain increase accordingly and result in larger free volume, with the activity of permeating molecules increasing at the same time. This facilitates the transport of ethanol molecules along with water molecules, thus reducing the separation factor. Furthermore, compared with the separation factor of pervaporation, it decreases drastically for evaporation of 90 wt % aqueous ethanol solution when the operating temperature is in the range of 15–55°C. These results might be attributed to the increase of partial pressure of ethanol in the vapor phase of the evaporation process with increases in the feed solution temperature, resulting in increases of the liquid zone of the polyamide membrane. Thus, the transport of ethanol molecules along with water molecules results in rapid decreases of the separation factor. However, a strong interaction can be formed at low temperatures and can reduce the plasticizing effect. The data from experiments of swelling also support the above deduction: the degree of swelling of membranes increases with increasing temperature for

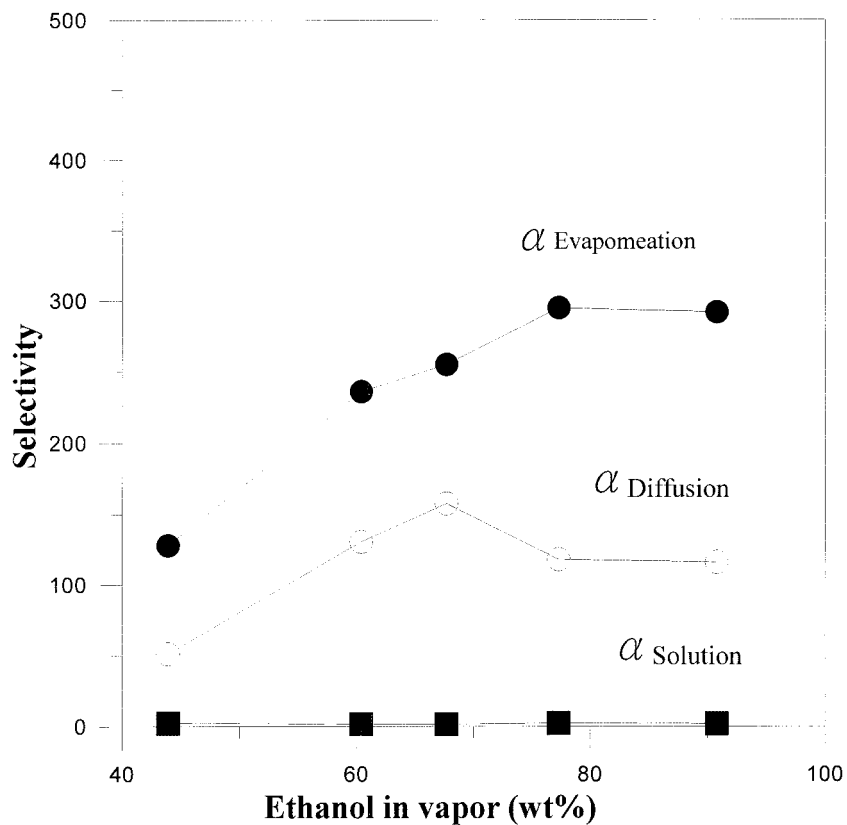


Figure 5 Effect of feed ethanol concentration on separation factor $\alpha_{\text{Evaporation}}$ (●), solution selectivity α_{Solution} (■), and diffusion selectivity $\alpha_{\text{Diffusion}}$ (○) of DBAPB-6FDAc membrane. Operating temperature at 25°C.

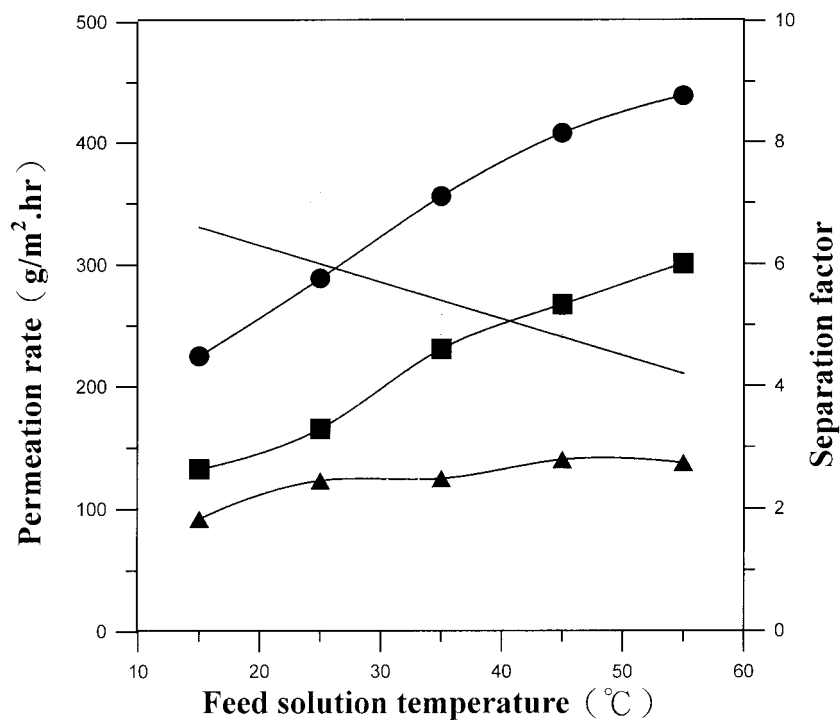


Figure 6 Effect of feed solution temperature on the pervaporation performance of DBAPB-6FDAc membrane: feed solution, 90 wt % aqueous ethanol solution; total permeation rate (●); water permeation rate (▲); ethanol permeation rate (■); separation factor (○).

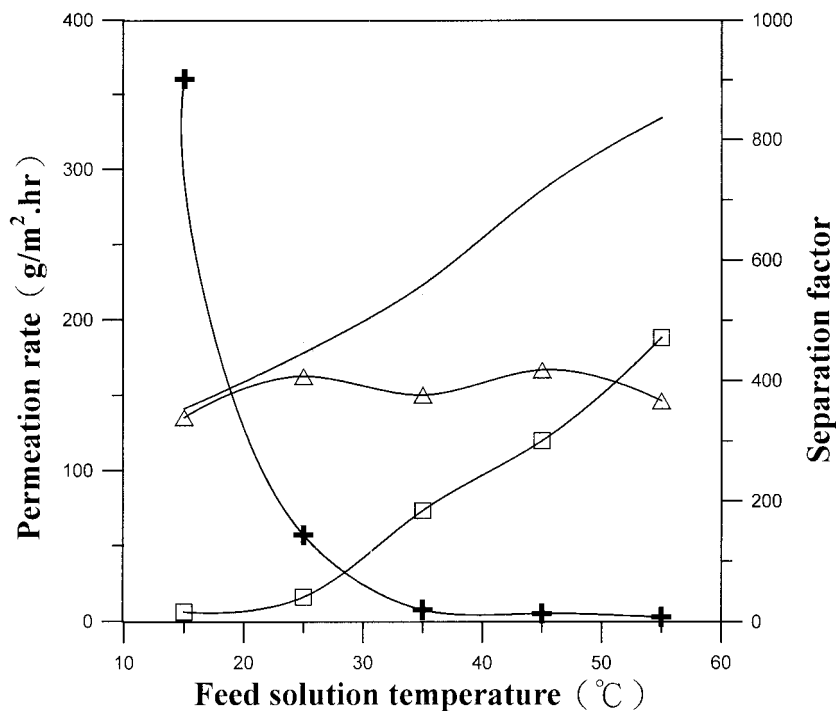


Figure 7 Effect of feed solution temperature on the evaporation performance of DBAPB-6FDAc membrane: feed solution, 90 wt % aqueous ethanol solution; total permeation rate (○); water permeation rate (△); ethanol permeation rate (□); separation factor (+).

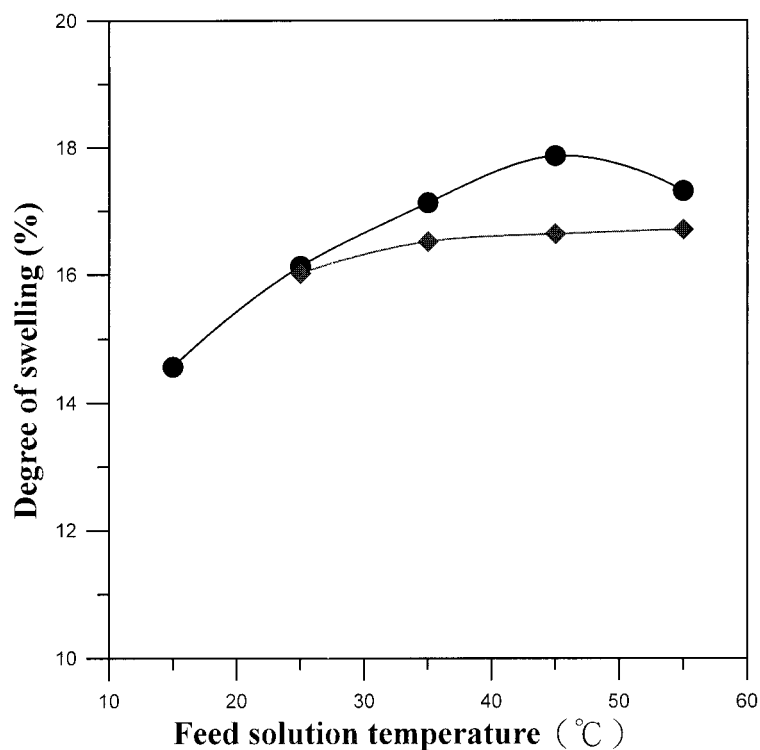


Figure 8 Effect of feed solution temperature on the degree of swelling of the DBAPB-6FDAc membrane: pervaporation (●); evaporation (○).

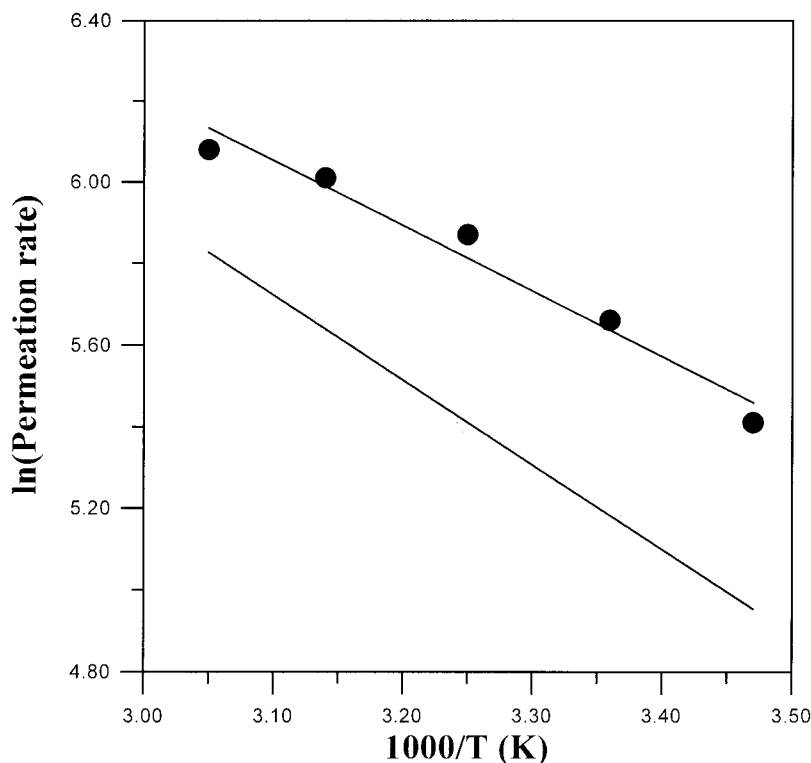


Figure 9 Arrhenius plots of DBAPB-6FDAc membrane evaporation (○) and pervaporation (●); feed ethanol concentration, 90 wt %.

both pervaporation and evaporation separation systems, as shown in Figure 8. In addition, the Arrhenius plot can calculate the activation energy for permeation of a 90 wt % aqueous ethanol solution through DBAPB-6FDAc membrane by pervaporation and evaporation, as shown in Figure 9. The activation energy in pervaporation and evaporation separation processes is 13.3 and 17.3 kcal/mol, respectively. This implies that the evaporation process is more heat sensitive than is the pervaporation process.

Pervaporation and evaporation of alcohol/water mixtures through DBAPB-6FDAc membrane

The pervaporation and evaporation performances of a 90 wt % aqueous alcohol solution through the DBAPB-6FDAc membrane are shown in Table III. An

increase in the separation factor and a decrease in the permeation rate occur as the number of carbon atoms in the alcohol increases. According to the solution/diffusion mechanism, the size of the permeating species is important in both the solution and the diffusion processes. Thus, the molar volumes of the alcohol can explain these phenomena. The molar volumes of methanol, ethanol, *n*-propanol, and *t*-butanol are 40.7, 58.68, 75.14, and 94.88 mL/mol, respectively. The separation factor was found to depend on the molecular length of linear alcohols. Furthermore, the interaction between permeates and polymer membranes can be used to further explain the above phenomena. The degree of swelling of the DBAPB-6FDAc membrane in various alcohol/water mixtures is summarized in Table IV. The degree of swelling follows the order of

TABLE III
Effect of Alcohol/Water Mixtures on the Pervaporation and Evaporation Performance of DBAPB-6FDAc Membrane^a

Mixture	Pervaporation		Evaporation	
	Permeation rate (g m ⁻² h)	α	Permeation rate (g m ⁻² h)	α
MeOH	829.8	1.2	299.7	67.7
EtOH	330	5	199	292
<i>n</i> -PrOH	321	13.5	248	1192
<i>t</i> -BuOH	284	220	218.5	3932

^a Feed alcohol concentration, 90 wt %.

TABLE IV
Swelling Degree of the DBAPB-6FDAc Membrane in Various Alcohol/Water Mixtures

Alcohol/water mixture	Molar volume (mL/mol)	Swelling degree ^a (wt %)
MeOH	40.70	10.56
EtOH	58.68	15.8
<i>n</i> -PrOH	75.14	16.7
<i>t</i> -BuOH	94.88	18.8

^a Feed solution: alcohol/water = 90 wt %.

methanol > ethanol > *n*-propanol > *t*-butanol. That is, the larger-size alcohol has higher affinity for the membrane than does the smaller-size alcohol. Thus, the degree of swelling of the former is higher than that of the latter. Consequently, the solubility of alcohols for the DBAPB-6FDAc membrane is higher than that of water, but the diffusivity of water across the membrane is much higher than that of the alcohols. Uragami et al.¹² also observed these phenomena for various hydrophobic membranes. Therefore, the larger separation factor for the higher alcohols may be explained from the viewpoint of molecular size and the affinity between the DBAPB-6FDAc membrane and the permeating species (alcohols).

CONCLUSIONS

A novel DBAPB-based aromatic polyamide membrane was successfully prepared in this study. The DBAPB-based aromatic polyamide membranes exhibited water selectivity during all process runs. The specific volume of the DBAPB-based aromatic polyamide membranes ranked in the following order:

DBAPB-6FDAc > DBAPB-TBPAc > DBAPB-TPAc. With respect to molecular structure, the polymer with a larger substituted group was characterized by a higher barrier to the chain rotation than was that with a smaller group. Compared with pervaporation, evapomeation effectively increases the permselectivity of water. The activation energy in pervaporation and evapomeation separation processes is 13.3 and 17.3 kcal/mol, respectively. This implies that the evapomeation process is more heat sensitive than is the pervaporation process. In addition, the effects of diffusion selectivity on the membrane separation performances play an important role in the evapomeation process. An increase in the separation factor and a decrease in the permeation rate occur as the number of carbon atoms in the alcohol increases.

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