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Pervaporation of Water/Ethanol Mixture Through Hydrophilically Modified Polyimide Membrane

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Polyimide of pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) was hydrophilically modified by partial replacing of ODA with 3,5-diaminobenzoic acid (DABA) containing a carboxylic group with two amine groups. Pervaporation experiments of water/ethanol mixture were performed and the results demonstrated that both flux and permselectivity increase simultaneously with increasing DABA content in polyimide backbone. From the sorption and temperature-dependent permeation behavior, it could be concluded that the diffusivity of permeant plays a major role in determining the pervaporation performance rather than the solubility.

Keywords: polyimide, diaminobenzoic acid, pervaporation, water/ethanol mixture, hydrophilic modification

INTRODUCTION

In pervaporation process, the flux and permselectivity through polymeric membranes are generally in conflict. In other words, when the flux is high, the permselectivity is low and *vice versa*. Therefore it is important to obtain a material having both high flux and permselectivity simultaneously.

On this aspect, in dehydration of an aqueous ethanol solution, the introduction of hydrophilic group into polymer chain has been frequently attempted since the hydrophilic groups such as -COOH, -OH, and -NHCO- preferentially interact with water.[1] However, the preferential interaction with water normally accompanies swelling of the polymeric membrane material, which results in poor permselectivity. Therefore, the hydrophilic-hydrophobic property of the polymer should be well balanced as a polymeric membrane material for pervaporation of water/ethanol mixture.[1] Practically the hydrophilic-hydrophobic balance has been controlled by blending[2] and crosslinking,[3,4] grafting,[5–9] copolymerization[10–13] and bulk[14] or surface[15,16] modification. Kang et al.[15] introduced the carboxylic acid groups at one

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side of the surfaces of crosslinked poly(vinyl alcohol) membrane. Consequently they found that the surface modification technique was a useful means in obtaining a high performance pervaporation membrane.

In pervaporation of water/ethanol mixture, polyimide exhibited high permselectivity toward water but very low permeability.[17] Thus, in order to increase the permeability while at least maintaining the permselectivity unchanged, polyimide of pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) has been selected as a base membrane material in this work. Subsequently, the polyimide backbone was hydrophilically modified by partial replacing ODA with hydrophilic comonomer 3,5-diaminobenzoic acid (DABA). In this work, the bulk of the membrane was hydrophilically modified instead of one side of the surfaces as was in Reference 15. Pervaporation behavior of water/ethanol mixture was investigated through the membranes containing varying amount of DABA in the polyimide.

EXPERIMENTAL

Materials

PMDA (from Aldrich, U.S.A.) and ODA (from TCI, Japan) were sublimed twice to be purified, and DABA (from Aldrich, U.S.A.) was purified by recrystallization in water followed by sublimation. The other chemicals were used without further purification.

Preparation of Poly(amic Acid)

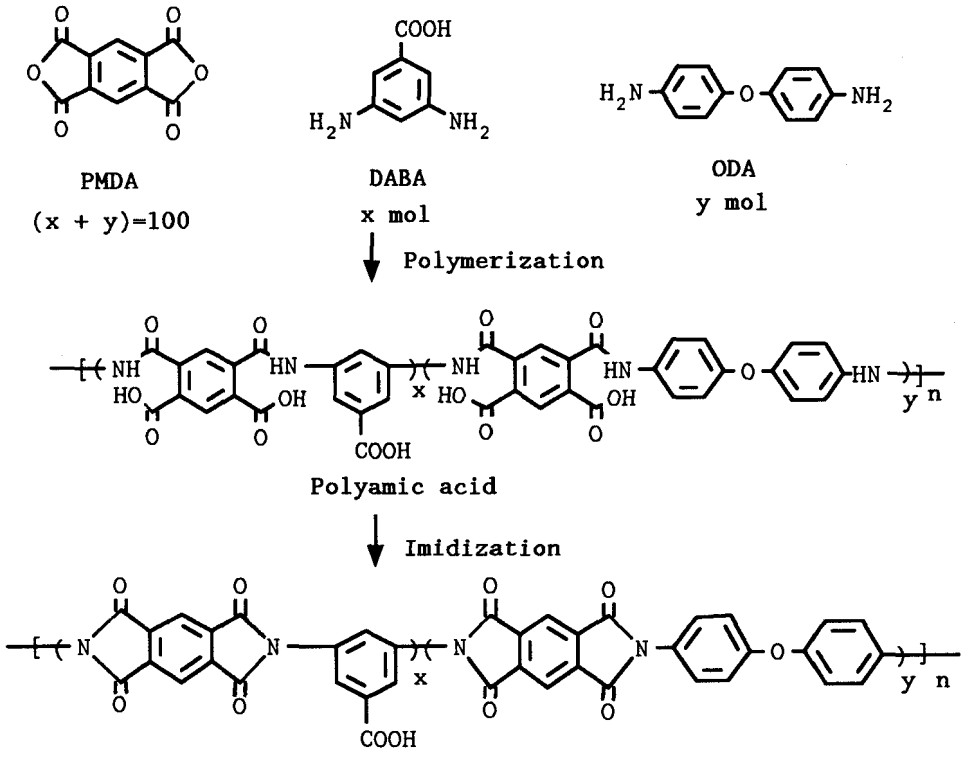
The measured amount of DABA and its two equivalence of PMDA with N-methyl pyrrolidinone (NMP) were mixed into a reaction flask equipped with a mechanical stirrer and allowed to react at room temperature for one hour. ODA and the remainder of PMDA were added into the reaction flask and again allowed to react at room temperature for 10 hours. The inherent viscosities of 0-, 10-, 20-, 30- and 40-mole % DABA poly(amic acid) solution in NMP (0.5 g/100 ml) were 1.44, 1.09, 0.85, 0.38 and 0.20, respectively. The viscous poly(amic acid) solution obtained was stored in a dark and cool place (< 5°C).

Solution Casting and Thermal Imidization of Poly(amic Acid)

The poly(amic acid) solution was cast on a glass plate, followed by placing it into an oven preset at 80°C for 30 minutes. Subsequently, the oven temperature was raised to 200°C with increasing rate of 4°C/min and maintained for 3 hours. Finally the sample was heat-treated at 300°C for 30 minutes. The thickness of film was controlled by a doctor's knife. A reaction scheme and structure of the modified polyimide was presented in Scheme I.

Pervaporation Experiments

Pervaporation experiment was carried out at 40°C by an ordinary manner. The effective membrane area was 19.6 cm^2. The downstream side pressure was main-



SCHEME I

tained between 1–2 torr during the experimental period. Pervaporation performance was characterized in terms of the flux and the permselectivity at a steady state. The steady state flux, J, was obtained by:

$$J = Q/At \tag{1}$$

where Q is the total amount of permeate during the time interval t with an effective membrane area A. The permselectivity, α, is defined as a usual manner by:

$$\alpha = \frac{(x_w^p/x_e^p)}{(x_w^f/x_e^f)} \tag{2}$$

where x is the weight fraction, the superscripts p and f stand for permeate and feed, the subscripts w and e for water and ethanol, respectively. The permeation composition was analyzed with a gas chromatograph (Varian VISTA 6000, stainless steel Porapak Q column with thermal conductivity detector).

Sorption Experiments

A piece of dry, pre-weighed membrane was immersed into a given water/ethanol solution at 30°C. After reaching equilibrium, the membrane was taken out, blotted

between filter papers and then weighed immediately. The sorption results give rise to the solubility, defined as mg of dissolved permeant in membrane per 100 mg of dry membrane.

RESULTS AND DISCUSSION

Pervaporation

Specific physico-chemical interactions, for instance the hydrogen bonding interaction between a membrane and one of the permeants, enhance the preferential sorption giving rise to higher permselectivity.[6,12] The carboxylic acid group as a hydrogen bonding site with water, in this work, was incorporated into the polyimide backbone. DABA was selected as a comonomer for carboxylic acid source because it contains a carboxylic acid group in addition to two amine groups. Thus, by partial replacing ODA with DABA, the amount of carboxylic acid of the resulting modified polyimide membrane was readily controlled. Therefore, the introduction of DABA into the polyimide results in the membrane more hydrophilic and water to be preferentially sorbed.

Figures 1–4 depict the pervaporation performance with varying amount of DABA. All the membranes containing 10-, 20-, 30- and 40-mole % DABA demonstrate the typical pervaporation behavior. That is, the flux increases and the permselectivity decreases with the water concentration in the feed.

In order to investigate the effect of the carboxylic acid concentration in the modified polyimide, the flux and permselectivity were plotted against the DABA content in Fig. 5. The flux and permselectivity increase simultaneously with increasing DABA content and reach maxima at around 30-mole % of DABA. This result is very surprising because, as described previously, a trade-off normally exists

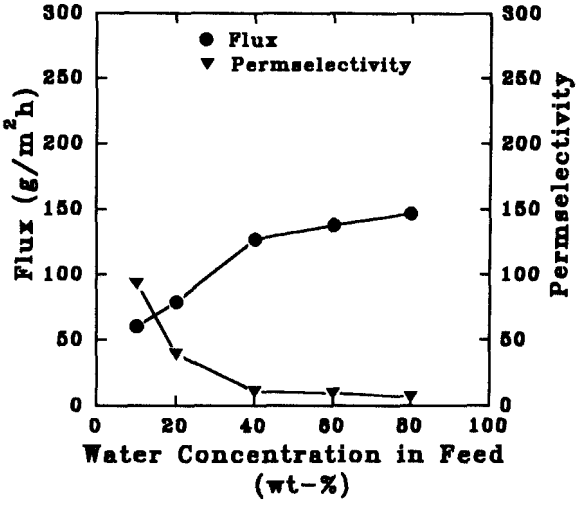


FIGURE 1 The effect of feed composition on the flux and permselectivity throgh 10-mole % DABA polyimide membrane at 40°C.

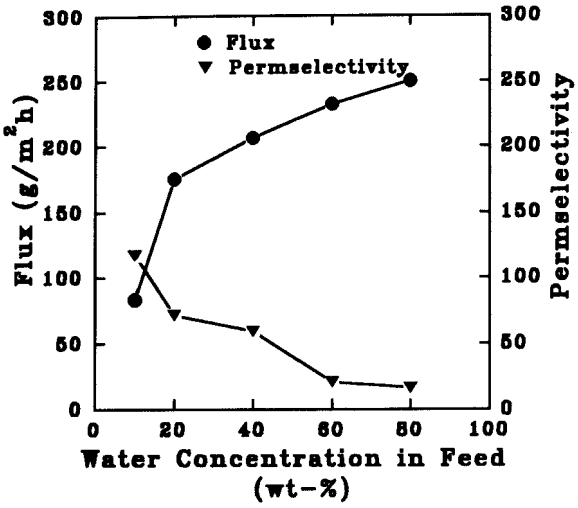


FIGURE 2 The effect of feed composition on the flux and permselectivity through 20-mole % DABA polyimide membrane at 40°C.

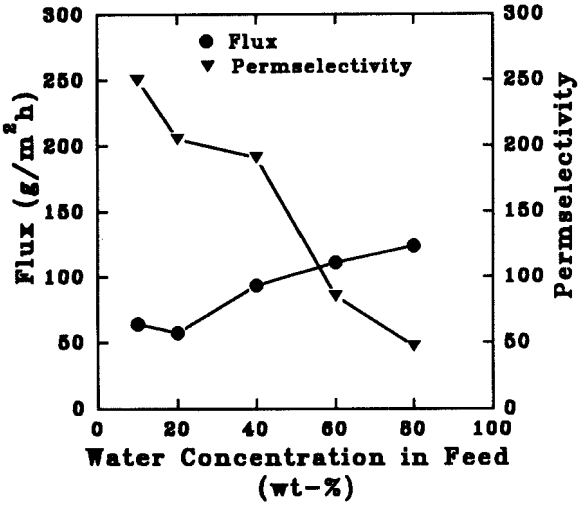


FIGURE 3 The effect of feed composition on the flux and permselectivity through 30-mole % DABA polyimide membrane at 40°C.

between the flux and permselectivity among polymeric membranes. The increase in both the flux and permselectivity mainly stems from the increased water flux while depressing the ethanol flux as shown in Fig. 6. The increased water flux is presumably associated with the hydrogen bonding ability of water toward the hydrophilic carboxylic acid in the membrane. This is because the hydrogen bond strength of the carboxylic acid toward water has been known to be greater than ethanol.[12] The enhanced pervaporation behavior through the modified polyimide membrane is in accordance with the previous work on pervaporation through

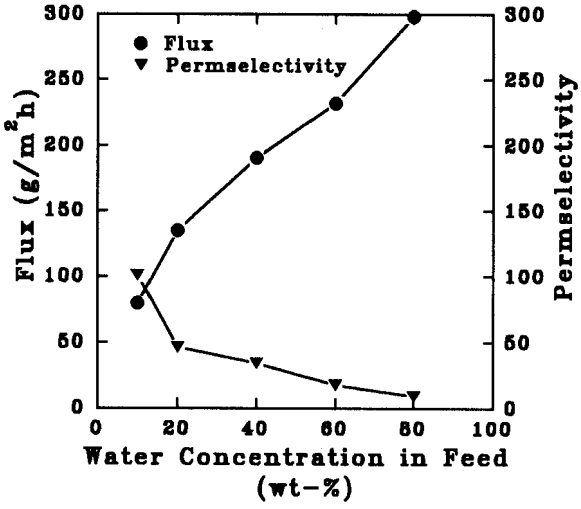


FIGURE 4 The effect of feed composition on the flux and permselectivity through 40-mole % DABA polyimide membrane at 40°C.

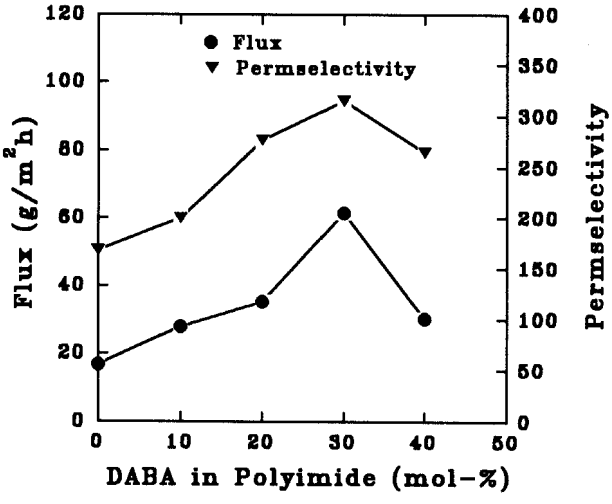


FIGURE 5 The effect of DABA content in the modified polyimide membrane on the flux and permselectivity at a fixed feed composition of 10 wt % water.

hydrophilically surface-modified poly(vinyl alcohol) membrane as shown in Fig. 7 by Kang et al.[15] They introduced carboxylic acid groups at the one side of the surfaces of the crosslinked poly(vinyl alcohol) membrane by reacting with monochloroacetic acid. The reaction time with monochloroacetic acid was used as a measure of the carboxylic acid content in Fig. 7 because the carboxylic acid concentration could not be easily measured, and also because the carboxylic acid concentration was found to increase qualitatively with the reaction time.

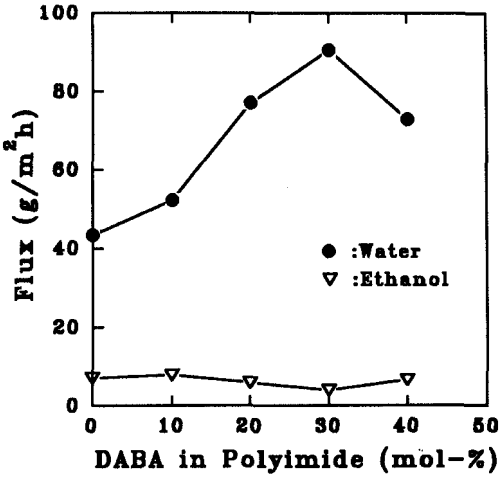


FIGURE 6 Water and ethanol flux through the modified polyimide membrane with varying content of DABA at a fixed feed composition of 10 wt % water.

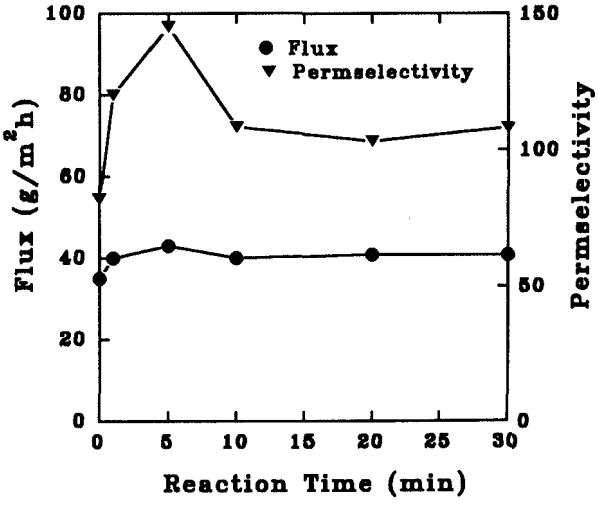


FIGURE 7 The effect of reaction time t with monochloroacetic acid on the flux and permselectivity through the surface-modified poly(vinyl alcohol) membrane.[15]

Sorption Behavior

According to the solution-diffusion mechanism, the permselectivity is contributed from both diffusivity selectivity, α_d, and solubility selectivity, α_s, as described by Koros et al.[18]

$$\alpha = \alpha_d \alpha_s \tag{3}$$

Upon incorporating the carboxylic acid into the polyimide backbone, the solubility selectivity was expected to increase owing to the possible hydrogen bonds between the carboxylic acid and water. However, the solubility selectivity was not evaluated here because of the difficulty in measuring the water concentration in the membrane species. Nonetheless, the overall sorption experiments were carried out to measure the swelling extent at 40°C and the results are summarized in Table I. The solubility of ethanol is generally higher than that of water in most membranes. Unexpectedly, the solubility varies insignificantly (only few percent) with the DABA content, whereas both the flux and permselectivity increase markedly (Fig. 5). It seems that although the carboxylic acid groups are incorporated into the membrane material, the swelling would be depressed due to the intrinsic chain rigidity of the polyimide and the solubility difference, thus, becomes insignificant. Therefore it could be concluded that the solubility selectivity may not play an important role in determining the pervaporation performance, i.e., the effect of the diffusivity selectivity might be dominant. However, we do not have direct evidence because of the difficulty in measuring diffusivity in a pervaporation membrane.

Temperature-Dependent Permeation

Pervaporation experiments were carried out at different temperatures. The results were depicted as an Arrhenius plot in Fig. 8. The apparent activation energies (E_a) for water permeation were calculated from the slope of Fig. 8 and summarized in Table II. The E_a value decreases with DABA content. This implies that the water permeation mechanism could be different. In the previous section, it is claimed that the diffusivity selectivity could be an important factor in determining pervaporation performance. Therefore it might be plausible the E_a decrease would be primarily associated with the decrease in diffusion activation energy. In the case of 0-mole % DABA, a permeant, for instance water, should open the rigid polyimide chain to diffuse through and thus E_a is high. However, when the carboxylic acid group is present, there will be a specific interaction with water. That is to say, the carboxylic acid group would specifically bind with water and free it in the direction of the downstream side, which is conceptually analogous to the facilitated transport in solid membrane. Therefore, the apparent overall activation energy for water permeation decreases with the DABA content.

TABLE I

Solubility of water/ethanol mixture in modified polyimide membrane at 30°C[a]

DABA Content (mole %) / Sorbant	0	10	20	30
Water	1.4	1.0	3.6	1.5
20 % Water	5.6	3.0	6.0	3.4
Ethanol	7.1	8.3	7.7	6.7

[a] Solubility unit (mg sorbant per 100 mg of dry polymer).

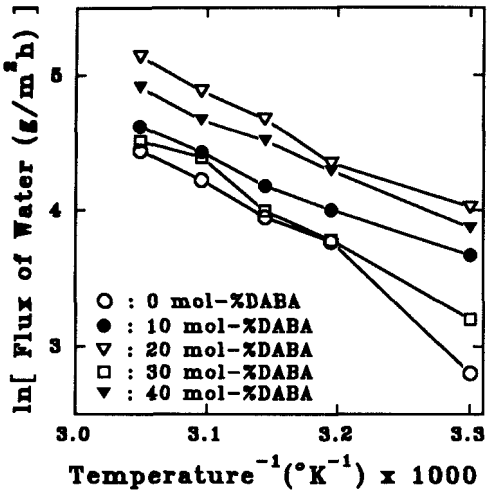


FIGURE 8 The effect of temperature on water flux through the modified polyimide membrane with varying content of DABA.

TABLE II

The apparent activation energy (E_a) for water permeation through modified polyimide membrane

DABA Content (mole %)	0	10	20	30	40
E_a (J/mole)	57.0	43.9	31.8	33.0	25.4

CONCLUSION

Introducing hydrophilic carboxylic acid group into the polyimide of PMDA and ODA results in the simultaneous increase in both the flux and permselectivity. Therefore, it is confirmed that the hydrophilic modification method could be a useful means in developing a good membrane material for pervaporation of water/ethanol mixture. In addition, it may be concluded that the diffusivity selectivity would be a main factor in controlling the pervaporation performance rather than the solubility in this particular system.

Acknowledgment

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