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Pervaporation of Water/Ethanol Mixtures by an Aromatic Polyetherimide Membrane

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Abstract

The pervaporation of water/ethanol mixtures through an aromatic polyetherimide membrane was attempted. The membrane was laboratory prepared using the solution casting technique. The sorption characteristics in relation to pervaporation were also studied. It was found that the preferential sorption was altered when the liquid composition was changed, whereas the water component permeated through the membrane preferentially over the whole range of feed mixture compositions. The experimental results were analyzed in terms of sorption ratio and permeation ratio to characterize nonideality of sorption and pervaporation. The effects of some operating parameters, including temperature, feed concentration, and permeate pressure, on the pervaporation performance were also investigated.

Key Words: Aromatic polyetherimide; Pervaporation; Separation of water/ethanol; Permeation ratio; Sorption ratio

INTRODUCTION

Pervaporation is a membrane separation process currently being studied by both industry and academia with increased attention as one of the versatile separation techniques in chemical and associated industries. Unlike evaporation and distillation, pervaporation is a rate-governed separation process based on the difference in permeation rates of permeating components through a membrane. It also differs from other membrane processes such as reverse osmosis, ultrafiltration, and membrane gas separation in that pervaporation involves a phase change of permeant from liquid to vapor phase. Many membranes made from different polymers using different preparation techniques have been tested for pervaporation separation of organic–aqueous and organic–organic solutions (*1*). In particular, the separation of ethanol–water mixtures has become the classic example for membrane pervaporation due to the attractiveness of alcohol fuels production by fermentation.

Mass transfer through a pervaporation membrane has been investigated intensively. However, the transport mechanism is not yet well elucidated. The solution-diffusion model is generally accepted for describing mass transfer in the pervaporation process, though alternative approaches have been presented (*2–4*). According to the solution-diffusion model (*5*), pervaporation consists of three consecutive steps: 1) sorption of components from the liquid phase at the membrane surface, 2) diffusion of the sorbed component through the membrane, and 3) desorption from the opposite side of the membrane into the vapor phase, the driving force being the chemical potential gradient across the membrane. It is generally considered that desorption is a fast, nonselective step, and sorption and diffusion govern the permeability and selectivity. The applicability of the solution-diffusion model has been reported by many investigators, assuming an ideal sorption and a concentration-dependent diffusion. However, the assumption of ideal sorption has been experimentally proven to not be the case normally, i.e., the concentration of a component in the membrane is not proportional to its concentration in the bulk solution (*6–11*). This means that one of the components is preferentially sorbed by the membrane. From a thermodynamic point of view, hydrophilic membranes tend to sorb the hydrophilic component. It is surprising to note that in some hydrophobic polymers, pure water is hardly sorbed, whereas in the presence of ethanol, water is sorbed preferentially (*6*). Based on studies of sorption and pervaporation of water/ethanol mixtures in cellulose acetate, polysulfone, and several ion-exchange membranes, it was claimed that the component which is sorbed preferentially will also permeate through the membrane preferentially, and the preferential sorption contributes to a large extent to the selective permeation (*6*, *8*). On the other hand, there are some reports in which a reverse situation was observed for other permeant/polymer systems (*9*, *12*, *13*). Therefore, more study is needed to gain insight into sorption characteristics in relation to pervaporation.

The objective of this work was to investigate the preferential sorption of two competing components in the liquid phase in connection with pervaporation. The system water/ethanol/aromatic polyetherimide was chosen for this purpose. Although aromatic polyetherimide has been tested in screening membrane materials for pervaporation (*14*, *15*), no attempt has so far been made to test the effects of operating variables on the pervaporation performance. Hence, our next objective was concerned with the study of the effects of such operating parameters as temperature, feed concentration, and permeate pressure on the permeation flux and separation factor.

THEORETICAL

The performance of a pervaporation membrane can be characterized in terms of permeation flux and separation factor. For the pervaporation of a binary liquid mixture, there is usually no linear relationship between the permeation flux and its concentration in the feed mixture due to complex interactions between the membrane material and the permeating components. Defining an ideal permeation as that permeation in which the permeation flux of a component is proportional to its feed concentration, Huang and Lin (*16*) introduced the permeation ratio in order to measure the deviation of the real permeation flux from the ideal one:

$$\Theta_i = J_i/X_iJ_i^o \tag{1}$$

where Θ is the permeation ratio; J and J^o are the real and the ideal permeation fluxes, respectively; X is the mole fraction in the feed; and subscript i represents Component i. When $\Theta_i > 1$, the permeation of Component i is enhanced by the presence of the other component; when $\Theta_i < 1$, the permeation of Component i is retarded by the other component. The permeation ratio can be used to explain how the interactions between membrane and permeating components influence the permeation.

The separation factor for the pervaporation of a binary mixture is conventionally defined as

$$\alpha = \frac{(X_p/X_f)}{(1 - X_p)/(1 - X_f)} \tag{2}$$

where X_p and X_f are the mole fractions of Component i in the permeate and the feed, respectively. Usually the preferentially permeating component is denoted as Component i, so that the separation factor is greater than unity.

According to the solution-diffusion model, if the pressure on the downstream side is very small, then

$$\alpha \propto \alpha_S\alpha_D \tag{3}$$

where α_D is called the diffusion selectivity, which is determined by the difference in the molecular sizes of permeating components; α_S is called the sorption selectivity, and as a first approximation it may be defined by Eq. (4) in analogy to Eq. (2):

$$\alpha_S = \frac{(X_s/X_f)}{(1 - X_s)/(1 - X_f)} \tag{4}$$

where X_s represents the mole fraction of Component i in the polymer sorbed phase. It is obvious that if Component i is preferentially sorbed, then $\alpha_S > 1$.

Similar to the permeation ratio as defined by Eq. (1), we introduce a sorption ratio in this study to characterize the sorption behavior of a binary liquid mixture.

$$\Phi_i = Q_i/X_iQ_i^o \tag{5}$$

where Φ_i is the sorption ratio of Component i, and Q_i^o and Q_i are the amount of Component i sorbed from the pure and mixed solutions, respectively, per unit weight of polymer membrane. When $\Phi_i < 1$, the sorption of Component i is reduced due to the presence of the other component; when $\Phi_i > 1$, the sorption of Component i is increased by the presence of the other component. Especially when $\Phi_i = 1$, the two components sorb onto the polymer membrane independently, i.e., ideal sorption occurs. Thus the deviation of Φ_i from unity is a measure of the nonideality of sorption.

EXPERIMENTAL

Membrane Preparation

Aromatic polyetherimide (Ultem 1000, supplied by General Electric Co.) was dried at 150°C for 8 h in an oven with forced air circulation, as suggested by the supplier. The dried polymer was then dissolved in *N*,*N*-dimethyl acetamide (reagent grade, supplied by BDH Chemicals) to form a homogeneous solution of 20.6 wt%. The membrane was prepared by casting the polymer solution on a glass plate to a nominal thickness of 300 μm. The casting atmosphere was ambient (23°C, relative humidity 50%). The cast film was then air dried at room temperature in a dust-free, environmentally controlled chamber (supplied by D.F.S. Inc., France). The thickness of the dry membrane was ~160 μm.

Pervaporation Experiment

The flow diagram of the pervaporation apparatus used in the present study is shown schematically in Fig. 1. The permeation cell, whose design is very similar to that reported previously (*17*), consisted of two detachable stainless steel parts which were provided with inlet/outlet openings for the flow of feed solution and an outlet opening for the withdrawal of permeated product. A porous stainless steel plate was embedded in one part of the cell to support the membrane. The two parts of the cell were clamped and

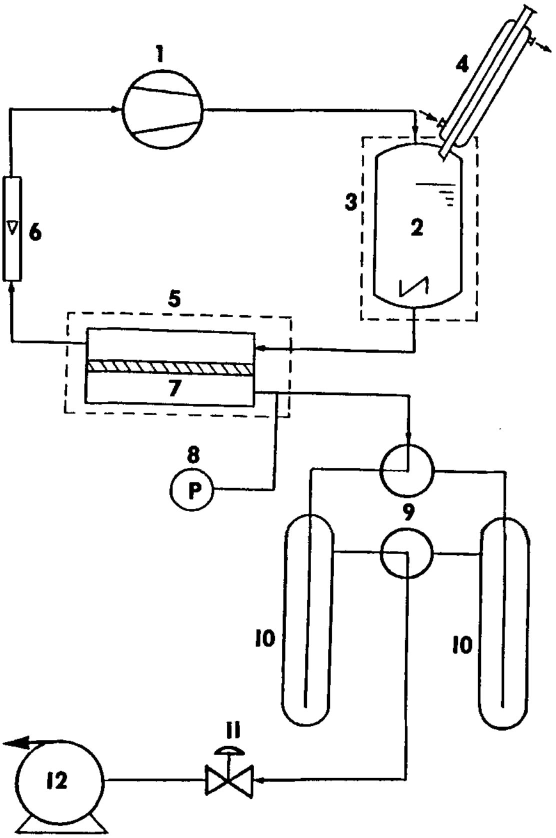

FIG. 1. The flow diagram of experimental pervaporation setup. (1) Circulation pump; (2) feed tank; (3) heating bath; (4) overhead condenser; (5) isothermal chamber; (6) flowmeter; (7) membrane unit; (8) vacuum gauge; (9) switch valve; (10) cold trap; (11) vacuum regulator; (12) vacuum pump.

sealed tightly using two rubber O-rings. The effective area of the membrane in the pervaporation cell was 21.22 cm^2.

The feed solution was circulated from a feed tank, which was equipped with an overhead condenser to prevent any loss of feed due to evaporation, to the feed side of the permeation cell using a Masterflex peristaltic pump. The feed circulation rate was sufficiently high so that the concentration variation from the inlet to the outlet of the feed chamber was negligible. This means that the membrane unit was a differential pervaporator and that the primary experimental data were local properties of the membrane.

The permeate side of the membrane was connected to two cold traps immersed in liquid nitrogen, followed by a two-stage Edwards vacuum pump to supply the necessary driving force for pervaporation. The permeate product was initially condensed and collected in one of the cold traps, and then the cold trap was switched to the other after steady state was reached. The permeation rate was determined gravimetrically by weighing the permeate sample collected for a predetermined period of time. The composition of the sample was determined by using a Waters Associates differential refractormeter (model R401).

For each experimental run, the amount of permeate product removed by membrane pervaporation was kept below 0.5% of the initial feed load. The downstream pressure was controlled by a vacuum regulation valve.

Liquid Sorption Experiment

The preweighed dry membrane was immersed in a liquid sorbate of known composition to equilibrate at constant temperature for 36 h. Then the membrane was blotted, weighed, and quickly placed in a dry container. The container was connected to a vacuum pump leading to a collection trap cooled by liquid nitrogen. The liquid sorbed by the membrane was thus desorbed and collected in the trap, and then weighed and analyzed for composition. The total amount of liquid sorbed by the membrane was determined from the sorption uptake, and the sorption data so obtained was ensured by weighing the liquid collected in the trap during desorption.

RESULTS AND DISCUSSION

Liquid Sorption Experiment

Figure 2 shows the results of the liquid sorption experiment. As the concentration of ethanol in the bulk liquid solution increases, the sorption of ethanol in the membrane increases monotonically but not linearly, while water sorption increases to a maximum and then decreases. Accordingly, sorption of the water/ethanol mixture passes through a maximum at an ethanol mole fraction of about 0.43. The sorption ratio is shown in Fig. 3. Regardless of the liquid composition, a sorption ratio greater than unity is observed for both components in the binary mixture, indicating positive deviation from ideal sorption. The sorption of one component increases with the addition of the other component; the two components enhance each other with respect to their sorption due to polymer–permeant and permeant–permeant interactions.

The mole fraction of ethanol in the membrane sorbed phase versus the mole fraction of ethanol in the bulk solution is plotted in Fig. 4. It is

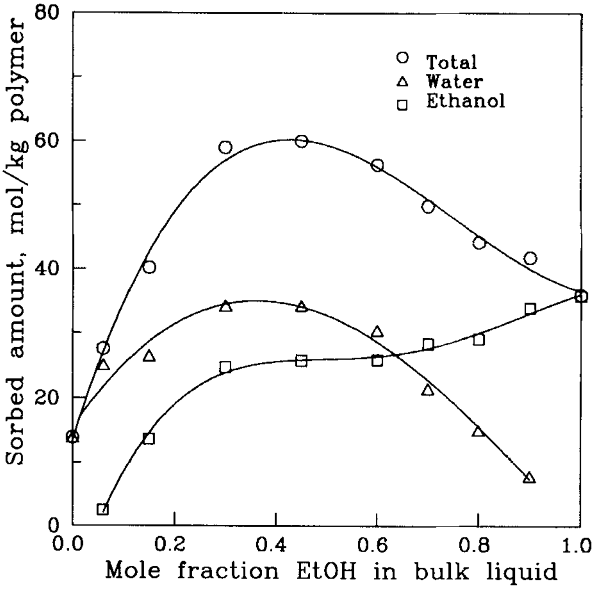

FIG. 2. The sorption data for binary liquid mixtures of water/ethanol in aromatic polyetherimide membrane. Temperature, 37°C.

interesting to note that ethanol is sorbed preferentially at feed ethanol mole fractions below 0.43, and water is sorbed preferentially at higher feed ethanol concentrations. In these two different sorption regions, the selective sorption will oppositely influence the selective permeation of water, which is the preferentially permeating component, as will be discussed later.

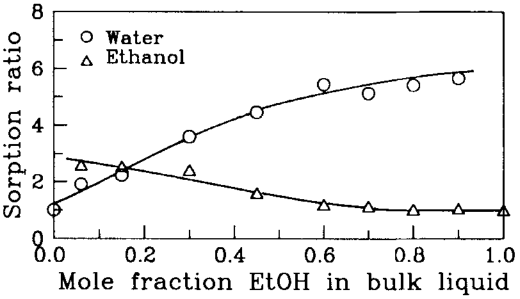

FIG. 3. The sorption ratio versus liquid composition. Temperature, 37°C.

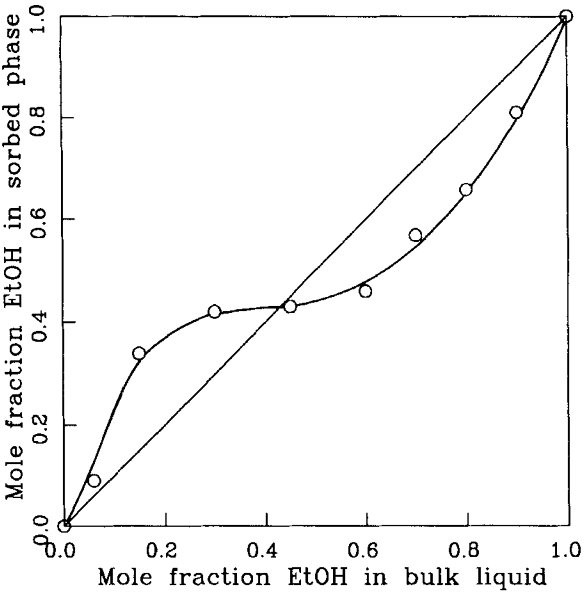

FIG. 4. The mole fraction of ethanol in membrane sorbed phase versus the mole fraction of ethanol in bulk liquid phase. Temperature, 37°C.

Pervaporation Experiment

The total and the partial permeation fluxes for water/ethanol mixtures at 37°C and at a permeate pressure of 133 Pa (1 mmHg) are shown in Fig. 5. As the concentration of ethanol in the feed increases, ethanol flux increases, and water flux decreases more significantly, resulting in a decrease in the total flux of the water/ethanol mixture. It should be noted that the total flux changes slowly in the feed concentration range corresponding to the maximum sorption.

The permeation ratio as a function of feed ethanol concentration is shown in Fig. 6. There exists a wide range of feed compositions in which ethanol permeation deviates from ideal behavior positively, and the reverse situation is observed for water permeation. By comparing Figs. 6 and 3, it can be seen that for a given feed concentration the permeation ratio of ethanol differs from its sorption ratio slightly, but the difference between permeation ratio and sorption ratio for the water component is relatively dramatic. These results are attributed to the fact that the feed concentration affects the mobilities of different permeating components to a different degree, as is generally observed (*18*, *19*).

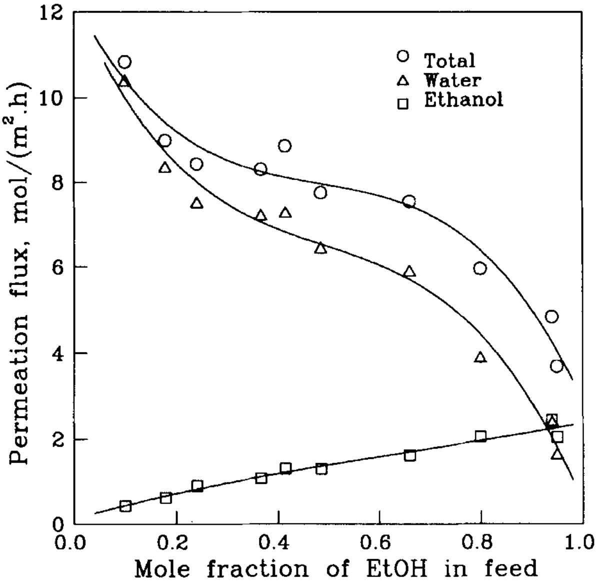

FIG. 5. The total and the partial permeation fluxes versus feed concentration. Temperature, 37°C. Permeate pressure, 133 Pa.

The corresponding data for the mole fraction of ethanol in the permeate versus the mole fraction of ethanol in the feed solution are presented in Fig. 7. Despite the existence of preferential sorption of ethanol at feed ethanol mole fractions below 0.43, the water component is enriched in the membrane permeated product over the whole range of compositions of ethanol/water feed mixtures. This means that preferential sorption does

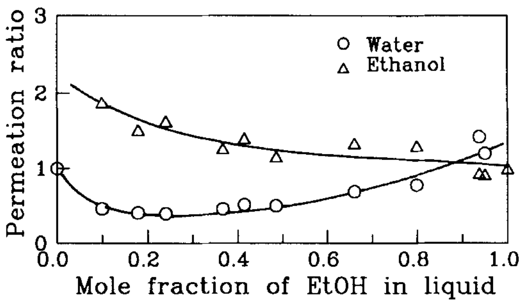

FIG. 6. Permeation ratio as a function of feed concentration.

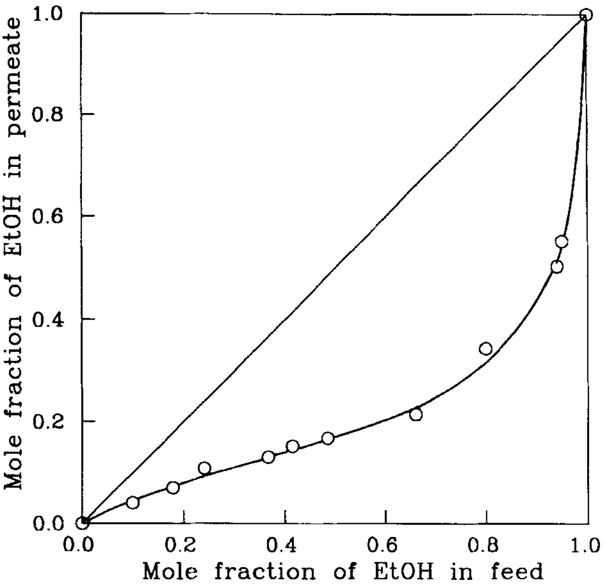

FIG. 7. The mole fraction of ethanol in permeate versus the mole fraction of ethanol in feed.

not necessarily give rise to preferential permeation. This result confirms that pervaporation separations are governed not only by the sorption factor but also by the relative mobility of the permeating components through the membrane. Figure 8 shows the separation factor as a function of feed ethanol concentration. For comparison, the sorption selectivity is also presented in Fig. 8. As can be seen, both separation factor and sorption selectivity increase with an increase in the concentration of ethanol in the feed. It has to be noted that the sorption selectivity passes through a value of unity. Therefore, the selective sorption of water/ethanol mixtures in the membrane contributes to preferential permeation of the water component positively in the range of high ethanol concentrations and negatively in the range of low ethanol concentrations. For a given feed concentration, the separation factor of pervaporation is higher than sorption selectivity, suggesting that water molecules are more mobile in the membrane than are ethanol molecules. This is obvious because the water molecule is smaller than the ethanol molecule.

Figure 9 shows the permeation data for pure water, pure ethanol, and a water/ethanol mixture with an ethanol mole fraction of 0.415 as a function of permeate pressure; the temperature was 37°C in all these experiments. Regardless of feed composition, the permeation flux decreases naturally

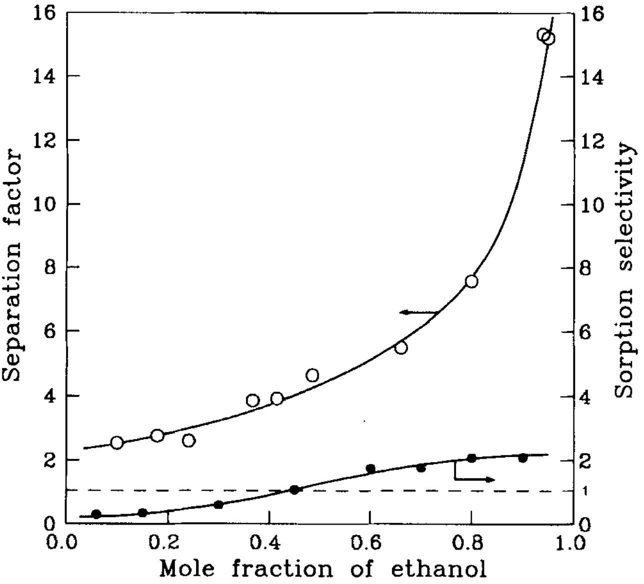

FIG. 8. The separation factor of pervaporation and the sorption selectivity versus the mole fraction of ethanol in feed.

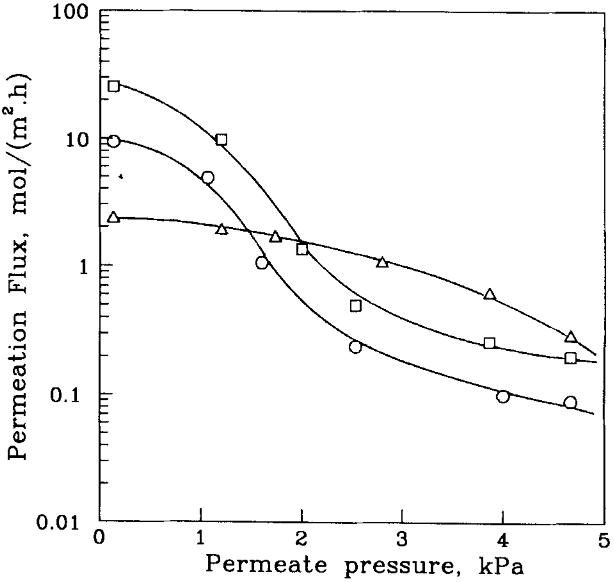

FIG. 9. The effect of permeate pressure on the permeation fluxes of pure water (□), pure ethanol (△), and a water/ethanol mixture of ethanol mole fraction 0.415 (○). *Temperature*, 37°C.

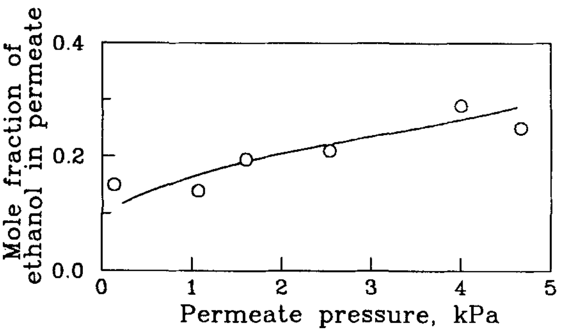

FIG. 10. The effect of permeate pressure on permeate concentration. Temperature, 37°C. Feed ethanol concentration, 0.415.

with an increase in the permeate pressure due to a decrease in the transmembrane driving force. However, water permeation is affected by permeate pressure more significantly in comparison with ethanol permeation because of the difference in their volatilities. Thus it is expected that for the binary mixture permeation, the ethanol concentration in the permeate increases with an increase in permeate pressure. This is indeed the case, as shown in Fig. 10.

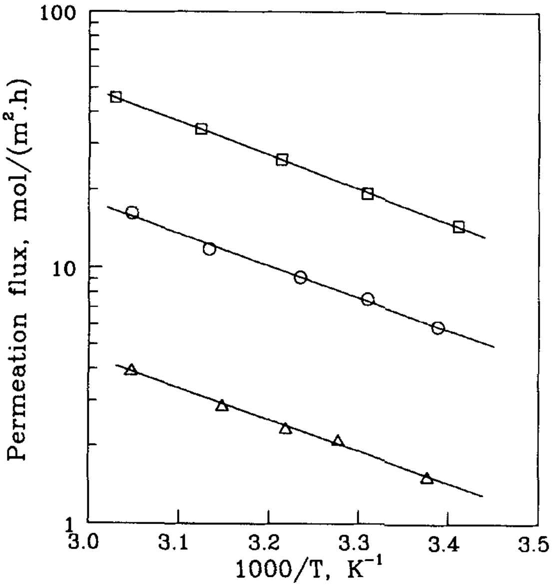

FIG. 11. The effect of temperature on the permeation fluxes of pure water (□), pure ethanol (△), and a binary mixture (ethanol mole fraction 0.415) (○). Permeate pressure, 133 Pa.

TABLE 1
Activation Energy of Pervaporation

Feed ethanol mole fraction	Activation energy (kJ/mol)
0.0	24.86
0.415	23.78
1.0	23.47

The permeation data of pure water, pure ethanol, and the water/ethanol mixture are plotted against the reciprocal of the operating temperature in degrees Kelvin in Fig. 11. An Arrhenius type of relationship seems to be appropriate to describe the temperature effect on permeation flux in the temperature range of interest. The apparent activation energy for permeation is slightly concentration dependent, as presented in Table 1. The temperature dependence of the separation factor is determined by the relative value of the activation energy of the permeating components. Consequently, the separation factor for the pervaporation of the water/ethanol mixture, shown in Fig. 12, is nearly constant over the temperature range studied.

CONCLUSIONS

Liquid-phase sorption with reference to pervaporation for the system water/ethanol/aromatic polyetherimide was investigated, and the effects of some operating conditions on the pervaporation performance were tested. The following conclusions can be drawn from this study.

(1) The preferential sorption characteristics for water/ethanol mixtures in an aromatic polyetherimide membrane can be altered when the concentration of the liquid mixture is changed.

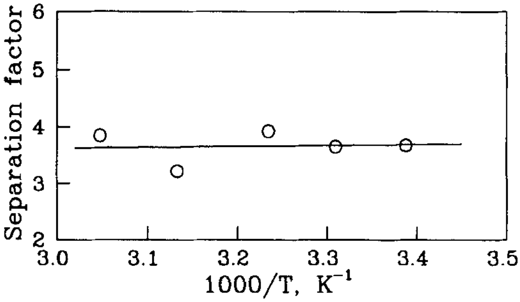

FIG. 12. Separation factor versus reciprocal of absolute temperature. Feed ethanol mole fraction, 0.415. Permeate pressure, 133 Pa.

(2) The aromatic polyetherimide membrane exhibits preferential permeation to the water component over the whole range of feed compositions.
(3) The preferential permeation is affected, but is not determined, by preferential sorption from the liquid phase.
(4) A new empirical term, the sorption ratio, was introduced as a measure of the nonideality of sorption.
(5) The pervaporation performance of the membrane is affected by such operating parameters as temperature, feed concentration, and permeate pressure.

Acknowledgments

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