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Dehydration of Isopropanol by Pervaporation Using Aromatic Polyetherimide Membranes

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ABSTRACT

Aromatic polyetherimide membranes were prepared by the phase inversion method and tested for the pervaporation separation of water from isopropanol with emphasis on the breaking of azeotropic composition and the dehydration of high concentrations of isopropanol. It was found that the membrane selectivity was enhanced by partial evaporation of the solvent in the cast polymer films prior to the gelation step during membrane formation. The membrane performance was shown to be dependent on the feed concentration and the operating temperature. At a feed temperature of 25°C and a permeate pressure of 133 Pa, separation factors of 173 and 384 were achieved for the dehydration of isopropanol solutions at 0.68 (azeotropic composition) and 0.96 mole fractions isopropanol, respectively, with reasonably high permeation rates. The utility of the membranes for the proposed separation was demonstrated; however, these membranes were not prepared under optimized conditions and thus a continuous study is required to rationalize the effects of membrane preparation parameters on membrane performance.

Key Words. Pervaporation; Dehydration of isopropanol; Asymmetric membrane; Aromatic polyetherimide

INTRODUCTION

Pervaporation is a membrane process for the separation of liquid mixtures. In this process the feed liquid is introduced to one side of a membrane and the permeate is removed in the vapor state from the other side. The mass transport through the membrane can be induced by applying vacuum on the permeate side. The separation is governed by the chemical nature of the permeating species and the membrane material, the morphology of the membrane, and the process operation conditions. A comprehensive treatment of theory and practice of pervaporation processes can be found in a book edited by Huang (1). One of the promising industrial applications is the dehydration of alcohols, in particular ethanol and isopropanol. In Japan at Ohgaki, there is a plant designed and built by Mitsui Zosen of Tokyo to dehydrate isopropanol from 87 to 99.7 wt% with a capacity of 500 kg/h using the GFT polyvinyl alcohol composite membrane.

Since the separation is based on the relative permeation rates of different components, pervaporation is effective for the separation of azeotropic and close-boiling mixtures, which is difficult by thermodynamics-governed processes such as distillation. Pervaporation involves a phase change of a fraction of feed liquid to the vapor phase, and therefore, from the energy consumption point of view, pervaporation is especially promising when the component to be removed from a mixture is at low concentrations.

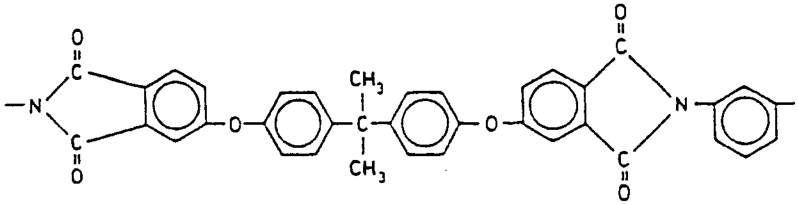
The separation potential of pervaporation has been recognized since the late 1950s (2). However, the permeation fluxes of the early membranes were too low to allow for practical use. Although many efforts have since been made toward the development of membrane materials in an attempt to improve their intrinsic permeation properties, the separation potential of a membrane material will be fully utilized only when the effective thickness of the membrane is minimized. One approach of increasing permeation flux is the use of asymmetric membranes in which a thin skin layer is supported on a microporous substructure and thus the mass transport resistance of the membrane is decreased substantially. Integrally skinned asymmetric membranes were first developed by Loeb and Sourirajan (3) for reverse osmosis separations using the phase inversion technique, which is nowadays the most common method for the preparation of asymmetric membranes for various applications. Unfortunately, most asymmetric reverse osmosis membranes are not very selective for pervaporation separation because the skin layers of the membranes prepared by a traditional phase inversion process are likely to be defective. It is thus often believed that this type of membrane is unsuitable for pervaporation separations (4, 5). Nevertheless, it is encouraging that several integrally skinned asymmetric membranes have been developed for gas–gas and organic vapor–gas separations from polymers including poly(ether sulfone), polyimide, and polyetherimide (6–9). In all cases the membranes were formed via a phase inversion process in which either a solvent evaporation step or a dual bath gelation step was introduced. Using the same principle, it is expected that membranes with structures suitable for pervaporation could be produced by proper control of the parameters involved in the procedure for membrane preparation. This consideration is supported by the fact that the commercial asymmetric cellulose acetate (CA) membrane originally developed for gas separations exhibited impressive pervaporation performance (10) although some laboratory-prepared CA membranes were not highly selective (11–13). Recently, Maeda et al. (14) reported an asymmetric poly(parabanic acid) membrane that showed fairly good selectivity for the pervaporation of acetic acid–water mixtures.

The objective of this work is to demonstrate that asymmetric aromatic polyetherimide membranes are applicable to the dehydration of isopropanol by pervaporation. Aromatic polyetherimide was chosen since it is known that asymmetric gas separation membranes can be produced from this polymer and also that this polymer has excellent thermal stability, mechanical strength, and chemical resistance (15). Although dense polyetherimide films have been tested for pervaporation (14, 16), the permeation flux is very low and no attempt has so far been made to introduce asymmetricity to the membrane structure in order to increase the permeation rate. In this study the membranes were prepared by the phase inversion method and tested for the pervaporation of water–isopropanol mixtures with emphasis on the breaking of its azeotropic composition as well as the dehydration of isopropanol at relatively high concentrations.

EXPERIMENTAL

Materials

Aromatic polyetherimide (Ultem 1000), constituting the repeat unit shown, was kindly supplied by GE Plastics Canada. This polymer was dried at 150°C for 8 hours in an oven with forced air circulation. *N,N*-Dimethyl acetamide was used as solvent for the preparation of the membrane casting solution. Isopropanol was obtained from J. T. Baker Chemical Co. Both chemicals were reagent grade and used without further purification. Water was deionized and distilled before use.



Membrane Preparation

The polyetherimide material was dissolved in *N*,*N*-dimethyl acetamide to form a homogeneous solution of 25 wt%. The polymer solution was cast on Pyrex glass plates to a nominal thickness of 275 μm. The casting atmosphere was ambient (temperature, 23°C; relative humidity, <60%). The cast films were then immersed into a gelation medium (ice-cold water, 3°C) immediately or allowed to rest for a predetermined period of evaporation of solvent in the polymer films before being gelled. Finally, the membranes were air-dried.

Pervaporation

The pervaporation equipment and the experimental procedure are described in detail elsewhere (17). The permeation cell consisted of two detachable stainless steel parts. The upper part was a cylindrical chamber which served as a feed reservoir. The membrane was mounted in the lower part of the cell, and the effective area for permeation was 8.55 cm^2. Vacuum was applied to the downstream side of the membrane. The permeate vapor was initially condensed and collected in one of two cold traps, and then the cold trap was switched to the other after a permeation steady-state was reached. The permeation rate was determined gravimetrically by weighing the permeate sample collected for a predetermined period of time, and the permeate composition was determined by refractometric measurement.

In all the experiments, about 220 mL feed liquid was charged to the permeation cell, and the feed solution was well stirred by using a magnetic stirrer. The amount of permeate removed by membrane was kept below 0.5% of the initial feed load so that the concentration variation of feed solution was negligible. The operation temperature was controlled by running thermostatted water through a jacket that covered the permeation unit. The downstream pressure was maintained below 133 Pa (1 mmHg) with a two-stage Edwards vacuum pump.

Membrane Performance Characterization

The pervaporation performance of a membrane is characterized in terms of permeation flux, J in mol/($m^2 \cdot h$), and separation factor, α, which is expressed as

$$\alpha = [Y/(1 - Y)]/[X/(1 - X)]$$

where X and Y are the concentrations of the feed and permeate, respectively, in mole fractions of the preferentially permeable component (in this case, water). Since there is usually a trade-off between membrane permeability and selectivity, Huang and Yeom (18, 19) introduced a composite parameter, namely the pervaporation separation index (PSI), which is expressed as the product of J and α. When $\alpha = 1$, no separation occurs, but the corresponding pervaporation separation index may still be very high, depending on the flux, as in the case of a highly porous membrane. Therefore, in this study the pervaporation separation index is now defined as the product of J and $(\alpha - 1)$; thus, a pervaporation separation index of zero means either zero separation or zero flux.

RESULTS AND DISCUSSION

Table 1 lists the three membranes used in the study. The difference in the thickness of these membranes indicates, to some extent, their different structures. The preparation conditions of the membranes were the same except for the solvent evaporation step. Note that in the solvent evaporation step, the initially clear nascent films became turbid because of the phase separation in the surface region, which was induced by the solvent loss from the film surface. This step is considered critical for the preparation of defect-free asymmetric membranes (20). It needs to be mentioned that when the evaporation time is sufficiently long, a completely dry membrane results, and that the membrane structure may be asymmetric or symmetric, depending on the specific operation conditions. This is the case for the PEI-D membrane. Unlike the other two membranes, a very dense structure was observed in the cross-section of the PEI-D membrane under a scanning electron microscope. This membrane was eliminated from further pervaporation test due to its very low permeation rate.

Figure 1 shows the experimental data for the mole fraction of isopropanol in the permeate versus the mole fraction of isopropanol in the feed

TABLE 1

Specifications of the Polyetherimide Membranes[a]

Membrane identification	Dry membrane thickness (μm)	Physical appearance
PEI-D[b]	36	Transparent
PEI-DW[c]	141	Opaque
PEI-W[d]	129	Opaque

[a] The membrane preparation conditions were the same except for the solvent evaporation step.

[b] Evaporation step: 80°C, 10 minutes.

[c] Evaporation step: 80°C, 2 minutes.

[d] No solvent evaporation.

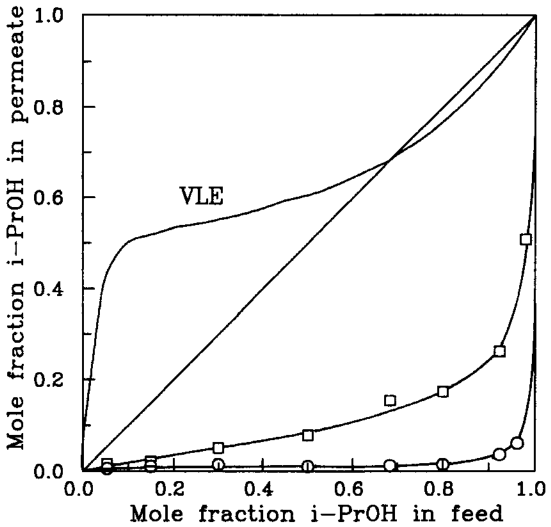


FIG. 1 The mole fraction of isopropanol in the permeate versus the mole fraction of isopropanol in the feed for the PEI-DW membrane (○) and the PEI-W membrane (□) at 25°C.

for the other two membranes, PEI-W and PEI-DW. It also shows the vapor–liquid equilibrium (VLE) data for the isopropanol–water solutions at a pressure of 101.3 kPa. It is shown that the permeate composition is far richer in water than the saturated vapor in the entire range of feed compositions. Obviously, these membranes can be used to dehydrate aqueous isopropanol solutions, and the isopropanol–water azeotropic composition can be shifted by using membrane pervaporation. Of the two membranes tested, PEI-DW exhibited higher permeation selectivity. This observation shows that membrane selectivity was enhanced by including partial solvent evaporation to give "dry" phase inversion prior to gelation for the "wet" phase inversion during the course of membrane formation.

The permeation flux data of the PEI-DW membrane at 25°C are shown in Fig. 2. The total permeation flux decreased with an increase in the feed isopropanol concentration. At the azeotropic composition (0.68 mole fraction isopropanol), the permeation flux was 2.5 mol/m^2·h, and the permeation flux decreased to 0.8 mol/m^2·h at a feed isopropanol mole fraction of 0.96. The partial flux of isopropanol increased over a small range of feed concentration and then decreased to a minimum at a concentration close to the azeotropic composition; higher feed isopropanol concentrations led to an increase of isopropanol flux. However, the change in the

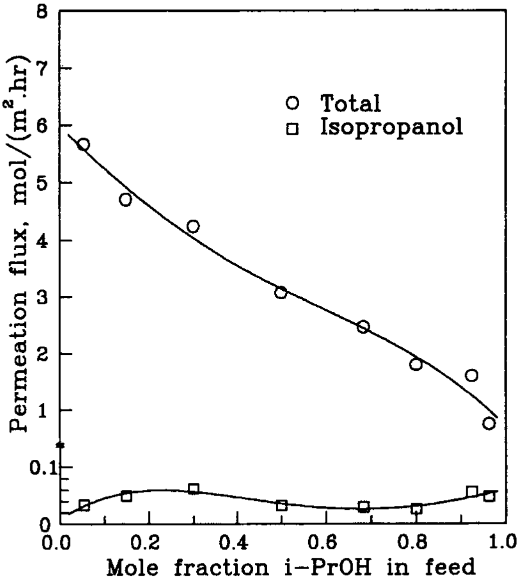


FIG. 2 The permeation flux as a function of feed concentration for the PEI-DW membrane. Temperature: 25°C.

isopropanol flux is not significant as compared to the total permeation flux. Figure 3 shows the permeation flux data for the PEI-W membrane. It can be seen that the total flux slightly increased when the feed isopropanol mole fraction was increased up to ~0.4, above which the total flux decreased significantly, whereas the partial flux of isopropanol increased continuously. The total permeation rate for the PEI-W membrane is several times higher than for the PEI-DW membrane. The difference in the pattern of permeation fluxes for the two membranes under study is presumably caused by the difference in the membrane structures.

The data for separation factor as a function of feed concentration are plotted in Fig. 4. Interestingly, high separation factors for water removal are observed at high feed isopropanol concentrations. Hence, the membranes are effective for the dehydration of high concentrations of isopropanol. This is what we desired for the proposed separation. Separation factors of 173 and 384 were achieved for the dehydration of isopropanol solutions at 0.68 (azeotropic composition) and 0.96 mole fractions isopropanol, respectively, with the PEI-DW membrane. Comparing the two curves in Fig. 4 shows that the concentration dependence of the separation factor for the PEI-DW membrane is much more significant than for the

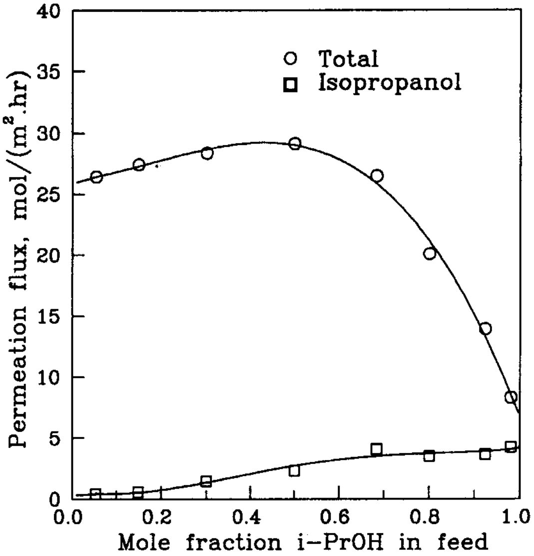


FIG. 3 The permeation flux as a function of feed concentration for the PEI-W membrane. Temperature: 25°C.

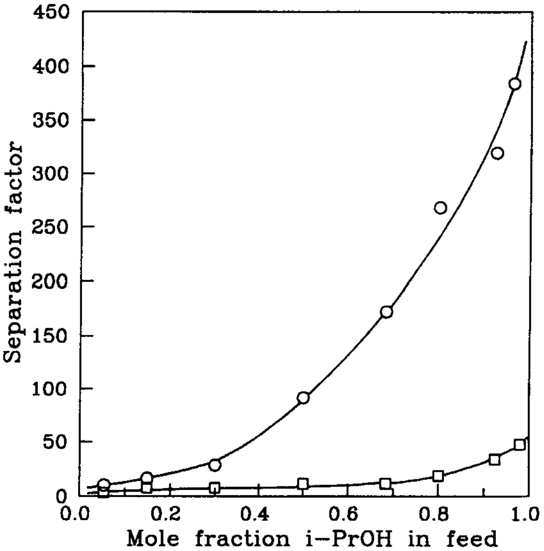


FIG. 4 The effect of feed isopropanol concentration on the separation factor. Membranes: PEI-DW (○) and PEI-W (□). Temperature: 25°C.

PEI-W membrane. This also suggests that the membrane selectivity depends on the membrane structure.

By looking at the above pervaporation experimental data, it is clear that there is a trade-off between the permeation flux and the separation factor for the two membranes. This can be explained qualitatively. Due to the solvent evaporation step prior to gelation in the membrane preparation procedure, the membrane skin layer becomes thicker and the possibility of the existence of big pores on the membrane surface becomes smaller, resulting in higher selectivity and lower permeability. This consideration agrees with the results of Feng et al. (6) who tested the effects of the solvent evaporation period on the membrane performance for the separation of organic vapors from gas streams. It should be pointed out that it is possible to obtain a membrane with both higher permeability and higher selectivity than another membrane by proper control of membrane preparation conditions, which was not attempted here, as observed in previous work (6). In an ideal asymmetric membrane, the skin layer should be defect-free and extremely thin, and the substructure should be highly porous but strong enough to provide sufficient mechanical support to the skin layer.

In light of the permeability–selectivity trade-off, the pervaporation separation index may be used as a composite parameter to evaluate the pervaporation performance. Figure 5 is a plot of the pervaporation separation index versus the feed concentration. It is shown that the pervaporation separation index tends to increase with increasing feed isopropanol concentration and then decreases when the mole fraction of isopropanol is above 0.92. The change in the pervaporation separation index is not uniform for the two membranes. Depending on the feed concentration, the pervaporation separation index for one membrane may be higher than for the other. However, though the permeation flux and separation factor for the two membranes are quite different, the corresponding pervaporation separation index values do not differ significantly since a low permeability is compensated for by a high selectivity, or vice versa.

The membranes were further tested for the dehydration of the isopropanol–water azeotrope as well as high concentrations of isopropanol at elevated temperatures. The experimental results are illustrated in Figs. 6–9 where the pervaporation data are plotted against the reciprocal of the operating temperature. In general, increasing temperature leads to a higher permeation flux and a lower separation factor. The temperature dependence of permeation flux seems to follow an Arrhenius type of relation in the temperature range of interest, whereas the temperature effect on separation is less significant. This observation is particularly evident for the PEI-W membrane, as shown in Figs. 8 and 9, since the permeating

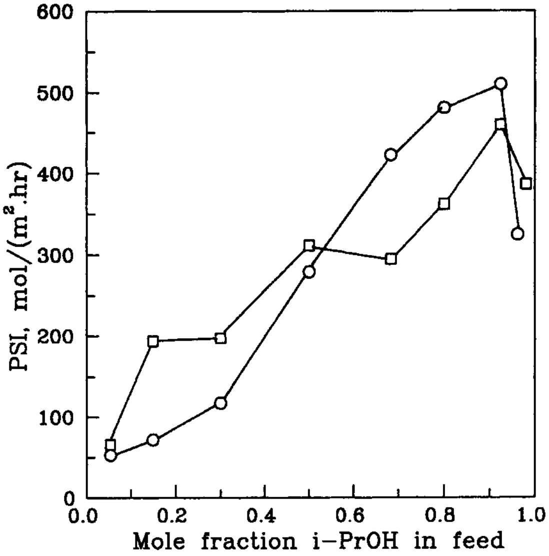


FIG. 5 The pervaporation separation index (PSI) versus feed concentration. Membranes: PEI-DW (○) and PEI-W (□). Temperature: 25°C.

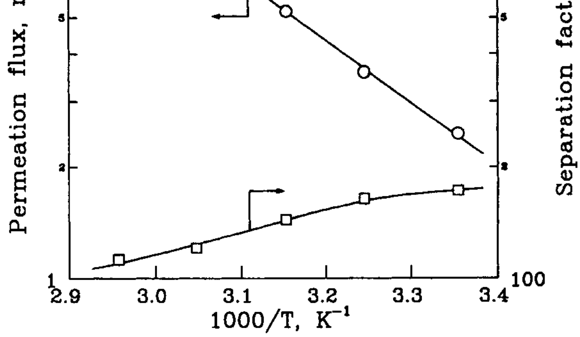


FIG. 6 The effect of temperature on the permeation flux and the separation factor. Membrane: PEI-DW. Feed concentration: 0.68 mole fraction isopropanol (azeotropic composition).

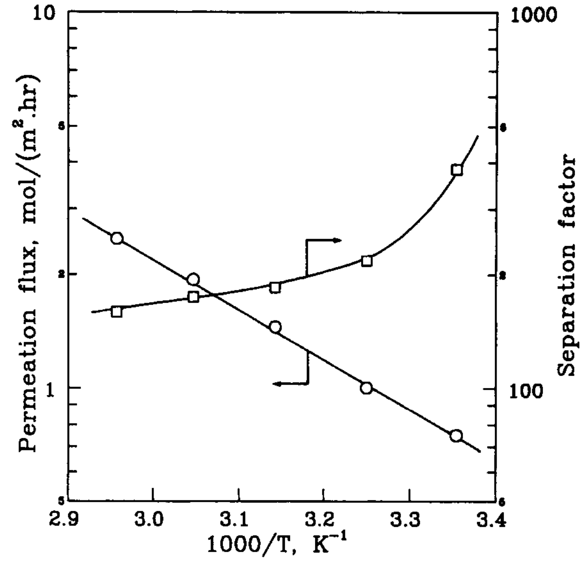


FIG. 7 The effect of temperature on the permeation flux and the separation factor. Membrane: PEI-DW. Feed concentration: 0.96 mole fraction isopropanol.

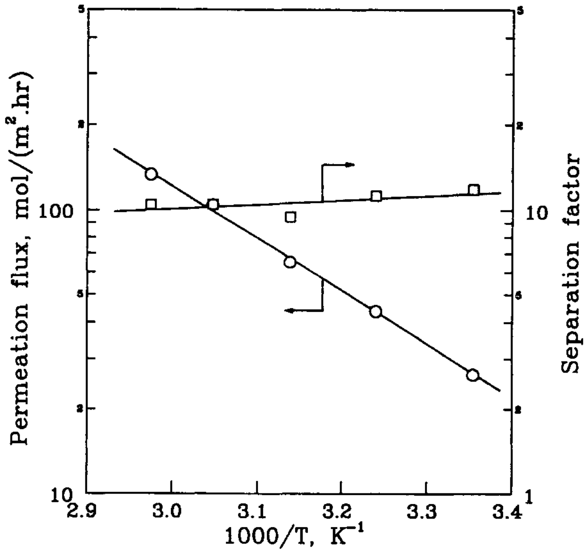


FIG. 8 The effect of temperature on the permeation flux and the separation factor. Membrane: PEI-W. Feed concentration: 0.68 mole fraction isopropanol (azeotropic composition).

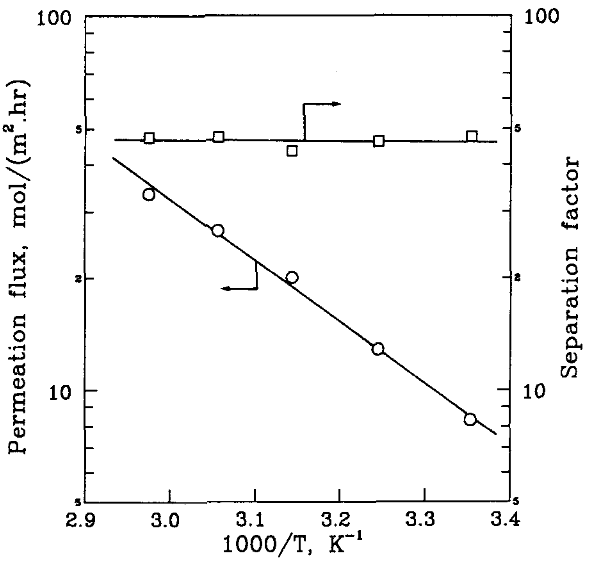


FIG. 9 The effect of temperature on the permeation flux and the separation factor. Membrane: PEI-W. Feed concentration: 0.98 mole fraction isopropanol.

components cannot be effectively differentiated by a low selective membrane. Note that for both membranes the activation energy for the permeation of the isopropanol–water azeotrope is larger than for the permeation of high concentrations of isopropanol, as reflected by the slopes of the flux vs temperature plots. Presumably, this is due to the tendency of isopropanol to associate with water at the azeotrope composition. All the above observations further indicate that pervaporation separation depends on both the membrane structure and the interactions between permeating components.

CONCLUSIONS

Laboratory prepared asymmetric polyetherimide membranes were studied for the separation of isopropanol–water mixtures, and the following conclusions can be drawn from the observations made in the study.

1. Asymmetric aromatic polyetherimide membranes prepared by phase inversion method are applicable for the dehydration of aqueous isopropanol solutions.

2. Membrane selectivity can be enhanced by partial evaporation of the solvent in the cast polymer film before the gelation step in the membrane preparation.
3. At 25°C, a permeation flux of 2.5 mol/($m^2 \cdot h$) and a separation factor of 173 were achieved for the breaking of the isopropanol–water azeotrope by using the asymmetric membrane. A higher separation (α = 384) with a lower flux [0.8 mol/($m^2 \cdot h$)] was observed for the dehydration of isopropanol at 0.96 mole fraction.
4. The separation factor, in general, decreases with an increase in temperature, whereas the corresponding permeation flux increases more significantly.

This study demonstrates the applicability of asymmetric polyetherimide membranes for pervaporation, but the membranes used here were not prepared under optimized conditions. A continuous effort to investigate the effects of various membrane preparation parameters on membrane performance is needed.

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