SEPARATIONS

Pervaporation of Alcohols and Methyl tert-Butyl Ether through a Dense Poly(2,6-dimethyl-1,4-phenylene oxide) Membrane

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Pervaporation separation and swelling experiments of methanol/methyl tert-butyl ether mixtures were performed by using a flat-sheet, dense poly(2,6-dimethyl-1,4-phenylene oxide) membrane prepared from a chloroform casting solvent. The effect of the feed composition on the membrane performance was described by the permeability of the components, the separation factor, and the sorption selectivity. The effect of the feed temperature on the separation was also studied, and the Arrhenius activation energy for permeability was determined over the whole range of feed composition. Pervaporation operations offered a maximum methanol selectivity of 5.4 and an overall normalized flux of 110 kg m⁻² h⁻¹. Pervaporation and sorption experiments were also conducted using ethanol, propanol, butanol, and octanol to study the effect of the size of the alcohol molecule on the transport across the membrane.

1. Introduction

In pervaporation processes, a liquid mixture is in contact with one side of a dense membrane, and the permeate is removed as a vapor from the opposite side of the membrane. The mass transport through the membrane, which is generally described by the solution/diffusion model, involves three steps: sorption, diffusion, and desorption. Additional resistances due to concentration polarization in the feed side and due to the mass transfer toward the vacuum trap in the permeate side should be considered. Thus, permselective properties of the membrane can be explained in terms of differences in the relative solubility and diffusivity in the membrane of the liquid mixture components.

Applications of pervaporation can be included in three general categories: dehydration of organics, removal of organic pollutants from dilute aqueous solutions, and separation of organic/organic mixtures. Methanol/methyl tert-butyl ether (MTBE) is one example of an organic/organic mixture that can be separated, and there are numerous papers dealing with this possibility. MTBE is an octane enhancer used as a replacement for toxic lead and lead compounds in car fuel. The production process of MTBE includes a simple and economical alternative to the present separation process. The present study tries to investigate the performance of a poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) membrane in a pervaporation process for the separation of methanol/MTBE mixtures. PPO is a glassy polymer at room temperature, having high permeability to gases because of the absence of polar groups in the polymer backbone. The high free volume and the ease of the rotational motion of the phenyl rings contribute to the high gas diffusivity exhibited by dense PPO films. In addition, PPO possesses excellent mechanical and thermal properties and is resistant to several chemicals.

Table 1. Results of Studies on the Separation of Methanol/MTBE Mixtures by Pervaporation

<table>
<thead>
<tr>
<th>polymer</th>
<th>methanol in the feed (wt %)</th>
<th>temp (°C)</th>
<th>normalized flux (kg m⁻² h⁻¹)</th>
<th>selectivity ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA</td>
<td>20</td>
<td>30</td>
<td>4.2</td>
<td>22</td>
</tr>
<tr>
<td>PAA/PVA</td>
<td>20</td>
<td>30</td>
<td>2.5</td>
<td>23</td>
</tr>
<tr>
<td>PAA/SSA</td>
<td>20</td>
<td>30</td>
<td>1.6</td>
<td>24</td>
</tr>
<tr>
<td>CTA</td>
<td>20</td>
<td>30</td>
<td>0.5</td>
<td>25</td>
</tr>
<tr>
<td>CA</td>
<td>20</td>
<td>22</td>
<td>0.15</td>
<td>21</td>
</tr>
<tr>
<td>HEC/agarose</td>
<td>30</td>
<td>30</td>
<td>0.47</td>
<td>22</td>
</tr>
<tr>
<td>PVA/alumina</td>
<td>30</td>
<td>20</td>
<td>0.5</td>
<td>23</td>
</tr>
<tr>
<td>PVP/alumina</td>
<td>30</td>
<td>20</td>
<td>0.5</td>
<td>24</td>
</tr>
<tr>
<td>SEC/pDMAAC</td>
<td>12.3</td>
<td>20</td>
<td>10.4</td>
<td>25</td>
</tr>
<tr>
<td>CS</td>
<td>20</td>
<td>30</td>
<td>3.4</td>
<td>26</td>
</tr>
</tbody>
</table>

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The experiments were carried out in the pervaporation apparatus described elsewhere. The effective membrane surface area was 28 cm². The feed was circulated over the membrane sample through meander-type channels. The feed pressure was kept at 1.0 bar. The permeate stream was evacuated by means of a vacuum pump, and the permeate was collected alternatively in two traps cooled by liquid nitrogen. The downstream pressure was monitored by a pressure transducer and was maintained below 0.1 Torr. The fluxes were determined by weighing the sample collected within a predetermined time interval. In the case of methanol/MTBE mixtures, the feed and permeate compositions were determined by measuring their refractive index with an Abbé-type refractometer model 60/ED. The pervaporation selectivity of the membrane was studied in terms of the separation factor, $\alpha$, which is defined as

$$\alpha = \frac{(w_1/w_2)_{\text{permeate}}}{(w_1/w_2)_{\text{feed}}}$$

where $w$ are the weight fractions of the relevant component in the feed and permeate, respectively. Indexes 1 and 2 refer to methanol and MTBE, respectively.

Sample history and relaxation phenomena are very important in membrane processes where glassy polymers, such as PPO, are used. In the present work, thermal and chemical preconditioning of the PPO membrane prior to the pervaporation experiments were conducted by methanol permeation experiments at 50 °C. In each operation run, several samples were collected to determine the total flux as well as the composition of the permeate. The alternative use of two cold traps allowed the permeate to be continuously sampled without interrupting the experiment. It was observed that the membrane exhibited initially high fluxes, which then gradually moved to a steady-state value. The data given in this paper correspond to the final steady-state values.

### 2. Experimental Section

#### 2.1. Materials

PPO powder of an intrinsic viscosity of 1.57 dL/g in chloroform at 25 °C and a density of 1.04 g/cm³ was supplied by General Electric. Analytical-grade chloroform, purchased from Aldrich Chemicals, was used as the solvent in the preparation of the PPO membrane. Methanol, ethanol, 2-propanol, 1-butanol, and 1-octanol were supplied from Merck. MTBE was purchased from Fluka. Physicochemical properties of solvents are given in Table 2. All of the chemicals were of analytical purity grade with concentrations of 97–99%. No further purification was carried out for the solvents used in the pervaporation and sorption experiments.

#### 2.2. Membrane Preparation

In this study, the concentration of the PPO casting solution was 4 wt% in chloroform. A total of 4 mL of the solution of PPO was spread smoothly over a leveled glass plate inside an O ring of about 10 cm inner diameter made of stainless steel. The casting ring was then covered with a filter paper to keep out dust. After 24 h at a temperature of 25 °C, the membrane was removed very cautiously from the glass plate by immersing the whole plate in a water bath. After drying at 25 °C for 24 h in a fume hood, the membrane was further dried for 72 h in a vacuum to remove the last traces of solvent. The average thickness of the obtained film was 37.7 μm.

#### 2.3. Sorption Experiments

The swelling properties of the membrane in the liquids were measured gravimetrically. Preweighed dry PPO membranes were immersed for 48 h in a closed bottle containing either methanol, ethanol, 2-propanol, 1-butanol, 1-octanol, MTBE, or a mixture of methanol and MTBE. The bottle was placed in a thermostated bath at 30 °C. Then, the swollen membrane was taken out of the liquid, wiped out with tissue paper, and weighed again. The increment in weight is equal to the weight of the liquid sorbed by the membrane. Each swelling experiment was carried out at least two times.

## Table 2. Chemical Formula, Molecular Weight, Molar Volume at 20 °C, Diffusional Cross Section, Boiling Point, and Density for the Liquids Used in This Work

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Chemical Formula</th>
<th>Molecular Weight</th>
<th>Molar Volume at 20 °C</th>
<th>$\sigma$ (Å²)</th>
<th>$T_b$ (°C)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>C2H5OH</td>
<td>46.07</td>
<td>0.7893</td>
<td>1177</td>
<td>78.2</td>
<td>0.7809</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C2H5OH</td>
<td>46.07</td>
<td>0.7893</td>
<td>1177</td>
<td>78.2</td>
<td>0.7809</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>C4H9OH</td>
<td>74.12</td>
<td>0.8093</td>
<td>1177</td>
<td>78.2</td>
<td>0.7809</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>C4H9OH</td>
<td>74.12</td>
<td>0.8093</td>
<td>1177</td>
<td>78.2</td>
<td>0.7809</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>C8H17OH</td>
<td>130.23</td>
<td>0.8193</td>
<td>1177</td>
<td>78.2</td>
<td>0.7809</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>(CH3)3COCH3</td>
<td>88.15</td>
<td>0.7809</td>
<td>1177</td>
<td>78.2</td>
<td>0.7809</td>
</tr>
</tbody>
</table>

$\sigma$ is the hard-sphere diameter.
as the liquid molar volume shows that, in the case of alcohols, their solubility in the PPO membrane decreases with increasing size of the molecule. In fact, a regression analysis indicates that the mean correlation coefficient between the solubility and molar volume is 0.93. This behavior suggests that the sorption of alcohol in the membrane depends not only on the affinity between the penetrant and polymer but also on the molecular volume of the penetrant. Burshe et al.45 observed a similar behavior when testing poly(vinyl acetate) (PVA) membranes using water/alcohol mixtures. They found that, in the case of alcohols, the polarity decreases with an increase in the carbon number and, therefore, the extent of sorption also decreases. From Table 3, it is seen that the solubility of MTBE is smaller than those of alcohols. In particular, if the solubility of MTBE is compared with those of butanol and octanol, because the MTBE molar volume is between the values of butanol and octanol, its solubility is lower than those of both because of lower polarity.

Table 3 also shows that the permeation rate across the membrane with alcohol is molecular size. It must be mentioned that methanol and ethanol fluxes are significantly higher than the fluxes of the other alcohols. On the contrary, MTBE flux is smaller than those of the alcohols, with the exception of octanol. The examination of pervaporation and sorption data suggests that the solubility of the compounds in the PPO membrane is not the only characteristic responsible for the observed different permeation rates. An estimation of the diffusivity of the permeants in the membrane was made by assuming the validity of Fick’s law in our system. The classic Fick’s law can be expressed as follows:

\[
J_i = -D_i \frac{dC_i}{dx} \quad (2)
\]

where \(D_i\) is the Fickian diffusion coefficient of component \(i\) and \(C_i\) is the penetrant concentration in the membrane. The diffusion coefficient depends usually on the penetrant concentration in the membrane, and it also changes across the membrane as a function of the distance.46 Because the latter information could not be obtained with accuracy in our system, we expressed Fick’s law as follows:

\[
J_i = \frac{D_{i,f}C_{i,f} - C_{i,p}}{l} \quad (3)
\]

where \(D_{i,f}\) is a mean diffusion coefficient of component \(i\), \(l\) is the membrane thickness, and \(C_{i,f}\) and \(C_{i,p}\) are the concentrations of component \(i\) at the membrane feed and permeate sides, respectively. In the present study, the permeate side was kept at sufficiently reduced pressure (less than 0.1 Torr) and \(C_{i,p}\) was assumed to be zero.

Although the film thickness changes in the pervaporation experiments, it was assumed that the thickness of the PPO membrane is the value of the dry sample. Consequently, an apparent diffusion coefficient in PPO was calculated by using the following equation:

\[
D_i = \frac{J_i}{C_{i,f}} \quad (4)
\]

The obtained apparent diffusion coefficients are given in Table 3. It should be pointed out that, although the apparent diffusion coefficient is not the true diffusion coefficient, it is presented to compare the diffusivities of the different compounds. As far as the alcohols are concerned, there is a noticeable difference in their diffusivities in the membrane; i.e., the diffusion coefficient of methanol is 1 order of magnitude higher than that of octanol. In addition, the values of \(D_i\) of methanol and ethanol are significantly higher than those of the other alcohols. This fact suggests that the diffusivity is important for permeation rates. On the other hand, it is known that the alcohol molecules are polar, with the ability to form hydrogen bonds through their hydroxyl groups. This implies the capability of the formation of alcohol clusters in the PPO membrane. For example, Nguyen et al.47 observed the formation of alcohol clusters in a poly(dimethylsiloxane) membrane, and they concluded that clustering increased the solubility in the membrane, although the diffusivity was decreased. The clustering probably occurs more with the smaller alcohols, so if alcohol clustering occurs in the PPO membrane, a lower diffusivity for alcohols with lower molecular size would be expected. However, diffusivities of methanol and ethanol in the PPO membrane are larger than those of higher alcohols. On the other hand, an analysis of the effect of shape and size of the penetrate molecule on the diffusivity can also be made in terms of a diffusional cross section of the penetrants, \(a_i\), given in Table 2. A regression analysis shows that there was not a linear correlation between \(D_i\) and \(a_i\), but there is a noticeable reduction in the diffusivity in the PPO membrane for molecules with a diffusional cross section larger than approximately 22–25 Å². In fact, diffusivity in the membrane is dependent on both the size of the penetrant and the polymer structure. PPO is a semicrystalline polymer. The presence of crystalline entities in the PPO membrane, which can be regarded as impermeable to the solvent transport, reduces the configurational mobility of the nearby chains and increases the path length of diffusion via tortuosity. The results obtained suggest that the restriction to the diffusion produced by the microstructure is more important for alcohols with a molecular size larger than some critical value.

Table 3. Normalized Pervaporation Flux, Solubility, and Concentration-Averaged Diffusion Coefficient of Pure Compounds

<table>
<thead>
<tr>
<th>Component</th>
<th>Flux (J) (kg mol m⁻² h⁻¹)</th>
<th>Solubility (S) (g/g)</th>
<th>(D_i) (10⁻¹¹ m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH</td>
<td>35.3</td>
<td>0.173</td>
<td>5.4</td>
</tr>
<tr>
<td>C₂H₅OH</td>
<td>31.2</td>
<td>0.161</td>
<td>4.8</td>
</tr>
<tr>
<td>C₃H₇OH</td>
<td>8.28</td>
<td>0.122</td>
<td>1.7</td>
</tr>
<tr>
<td>C₄H₉OH</td>
<td>3.39</td>
<td>0.101</td>
<td>0.9</td>
</tr>
<tr>
<td>C₅H₁₁OH</td>
<td>1.34</td>
<td>0.071</td>
<td>0.5</td>
</tr>
<tr>
<td>C₆H₁₃OH</td>
<td>2.04</td>
<td>0.057</td>
<td>0.64</td>
</tr>
<tr>
<td>CH₃OC(CH₃)₂CH₃</td>
<td>2.04</td>
<td>0.057</td>
<td>0.64</td>
</tr>
</tbody>
</table>

The effect of the feed composition on the flux and selectivity was investigated over the whole mixture concentration range for methanol/MTBE mixtures at 30 °C. Figure 1 shows the total flux and methanol selectivity as a function of the feed mixture composition. It can be seen that the flux increases with the methanol content in the feed. For example, the flux goes from 7.3 to 18.4 kg mol m⁻² h⁻¹ when the methanol weight fraction is increased from 0.14 to 0.69. The PPO membrane is selective toward methanol, with a selectivity factor ranging between 2.6 and 5.4. The variation of the
selectivity upon feed composition follows a complicated pattern, and the typical "tradeoff" between flux and selectivity is not observed in this case, because for methanol-rich mixtures, both flux and selectivity increase with the methanol content. It should be pointed out that the minimum in selectivity is due to a maximum in the MTBE flux, as will be discussed later. On the other hand, a comparison between the pervaporation performance of PPO and the values reported for other membrane materials indicates that the fluxes can be considered satisfactory, but the selectivity is rather low.

The partial fluxes of methanol and MTBE, which were calculated by using both the total flux and permeate composition data, are plotted in Figure 2 as a function of the methanol content in the feed. The methanol flux increases with its content in the feed, whereas the MTBE flux initially keeps nearly constant and finally decreases. This behavior can be explained as follows: methanol molecules occupy most of the dissolution sites available in the polymer matrix, so the MTBE solution is severely restricted, and thus MTBE permeates slower, which results in an increase of the methanol selectivity of the PPO membrane, as observed in Figure 1. However, Wijmans\textsuperscript{48} has shown that the analysis of the membrane performance in terms of its flux is not recommended because this quantity includes not only the membrane properties but also the effect of the operating conditions in the pervaporation process. A better understanding of the process is achieved if the permeabilities of the permeants are considered instead of their permeation rates. The permeability of the membrane toward the components, which is an intrinsic membrane transport property, is characterized by the permeability coefficient. Such a coefficient can be determined if the flux of component \( i \) through the membrane is expressed as follows:\textsuperscript{48}

\[
J_i = P_i \frac{f_{i,f} - f_{i,p}}{l} \tag{5}
\]

where \( P_i \) is the apparent permeability coefficient and \( f_{i,f} \) and \( f_{i,p} \) are the fugacities of component \( i \) in the feed and permeate sides, respectively. The fugacities can be expressed as follows:

\[
f_{i,f} = \gamma_i X p_i^o \tag{6}
\]

\[
f_{i,p} = Y_i p_p \tag{7}
\]

where \( \gamma_i \) is the activity coefficient, \( p_i^o \) is the saturation vapor pressure of component \( i \) at temperature \( T \) of the feed, and \( p_p \) is the total pressure in the permeate. Values of \( P_i \) for each component were calculated using the following expression:

\[
P_i = \frac{J_i}{\gamma_i X p_i^o - Y_i p_p} \approx \frac{J_i}{\gamma_i X p_i^o} \tag{8}
\]

An important parameter needed to calculate the permeability coefficient is the activity coefficient. In the present work, values of \( \gamma_i \) for methanol and MTBE at 30 °C were taken from Coto et al.\textsuperscript{49} as a function of the methanol mole fraction in their mixture, and \( p_i^o \) were calculated with the extended Antoine equation. The apparent permeability coefficients of methanol and MTBE, which are shown in Figure 3 as a function of the variation of the methanol content in the feed, exhibit a very nonideal behavior. As can be seen, the permeability of methanol increases steadily as the methanol content in the feed increases. In contrast, the permeability of MTBE shows a nonmonotonic behavior, with a maximum at about 50/50 wt % feed composition. According to the solution/diffusion model, the permeability of a dense PPO membrane is determined by the solubility and diffusivity of the permeants. Because both
sorption and diffusion are dependent on the liquid composition in the membrane, also the permeability characteristics of the membrane are influenced by the composition.

The analysis of the sorption properties of the membrane toward methanol/MTBE mixtures can shed light on the behavior observed for the permeability. The sorption of a binary liquid mixture in a polymer can be characterized by the overall sorption, which represents the total amount of liquid inside the membrane. The results of the swelling measurements with mixtures of methanol and MTBE in PPO are presented in Figure 4 as a function of the methanol content in the mixtures. It can be observed that the higher the methanol content in the feed, the more the membrane is swollen. As an example, the degree of swelling goes from 0.06 for pure MTBE to 0.207 for pure methanol. The composition of the liquid sorbed in the PPO membrane was estimated by a model derived from the Flory–Huggins theory, which makes a statistical calculation of the different configurations of a polymer/solvent system upon some assumptions on molecular shapes and interactions. The theory enables sorption modeling using a single parameter, which is a reflection of the polymer/solvent affinity. The lower the value of this parameter, the higher the sorption and thus the higher the affinity. Furthermore, the model was extended by Mulder to describe the sorption of binary liquid mixtures. According to this model, at a given volume fraction of liquid i in the feed, $v_i$, the volume fraction in the membrane, $\phi_i$, can be calculated by the following equations:

$$\ln\left(\frac{\phi_i}{\phi_2}\right) - \ln\left(\frac{v_i}{v_2}\right) = (r - 1) \ln\left(\frac{\phi_2}{v_2}\right) - g_{12}(\phi_1, v_1, v_2, \phi_2) - \phi_1 - \phi_3(x_{13} - r_x) + u_1\phi_2\frac{\partial g_{12}}{\partial \phi_1} - v_1\phi_2\frac{\partial g_{12}}{\partial v_1}$$

$$\phi_1 + \phi_2 + \phi_3 = 1$$

where $g_{12}$ is the liquid/liquid interaction parameter, $x_{13}$ is the polymer/liquid parameter, indexes 1 and 2 refer to the methanol and MTBE, respectively, index 3 refers to the PPO polymer, and $u_i$ is the relative volume fraction of component i in the sorbed liquid:

$$u_i = \frac{\phi_i}{1 - \phi_3}$$

Values of the weight fraction of polymer were obtained from the swelling experiments by using mixtures of methanol and MTBE at different concentrations. The volume fraction of polymer was easily calculated from its weight fraction data by assuming that there is no change of volume upon mixing and the penetrant in the ternary mixture has the same density as that in the liquid binary mixture. The interaction parameter between the liquids and polymer, which were assumed to be concentration-independent, were calculated from swelling experiments by using either pure methanol or pure MTBE. On the other hand, the liquid/polymer interaction parameter, $x_{13}$, can be expressed as follows:

$$x_{13} = -\frac{\ln(1 - \phi_3) + \phi_3}{\phi_3}$$

The value of $x_{13}$ for methanol (1.6) is smaller than that of MTBE (2.5), indicating that the methanol is more soluble than MTBE in the PPO membrane, as was mentioned in section 2.1. The binary liquid interaction parameter was calculated using the following expression:

$$g_{12} = \frac{1}{x_1v_2} \left( x_1 \ln \frac{x_1}{v_1} + x_2 \ln \frac{x_2}{v_2} + \frac{\Delta G^E}{RT} \right)$$

where $x_i$ is the molar fraction of component i, $\Delta G^E$ is the excess free energy of mixing, and $R$ is the gas constant. For methanol/MTBE mixtures, values of $\Delta G^E$ as a function of the mixture composition at 30 °C were taken from Coto et al. Thus, the dependence of $g_{12}$ on $v_i$ was expressed by a fourth-order polynomial relationship:

$$g_{12} = 2.532v_1^4 - 6.356v_1^3 + 6.222v_1^2 - 3.406v_1 + 1.715$$

Values of absolute, $\phi_i$, and relative, $u_i$, volume fractions of methanol and MTBE in the PPO membrane were calculated from eqs 9–11 and are given in Figures 4 and 5. It is clearly shown that methanol is preferen-
coefficient but also in the driving force. In the present study, activation energy values were obtained from Arrhenius-type plots of the flux. The correlation coefficients obtained, which lie in the range 0.90–0.99. As can be seen, the activation energy of pervaporation process can be calculated from Arrhenius plots of the permeability coefficient of each component. Thus, the activation energy for permeation is regarded as a combination of the activation energy of diffusion and the enthalpy of sorption of the permeants in the membrane.

The data presented in Figure 6 were used to determine the apparent permeability coefficient by using eq. 8. The saturation vapor pressures at different temperatures were calculated by means of the extended Antoine equation. Values for the activity coefficient of methanol/MTBE mixtures at different temperatures were found in the literature or estimated following Wilson and NRTL methods.

### Table 4. Activation Energy (kJ/mol) for the Permeability Coefficient of Methanol and MTBE in Mixtures with Different Methanol Volume Fractions

<table>
<thead>
<tr>
<th>(v_1)</th>
<th>1.0</th>
<th>0.9</th>
<th>0.7</th>
<th>0.5</th>
<th>0.3</th>
<th>0.15</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_p)(methanol)</td>
<td>32.6</td>
<td>20.9</td>
<td>15.8</td>
<td>6.9</td>
<td>31.7</td>
<td>21.5</td>
<td></td>
</tr>
<tr>
<td>(E_p)(MTBE)</td>
<td>86.2</td>
<td>55.2</td>
<td>38.8</td>
<td>61.1</td>
<td>64.5</td>
<td>71.3</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6. Normalized flux for methanol/MTBE mixtures vs feed temperature with different methanol volume fractions: 1 (●), 0.9 (■), 0.7 (▲), 0.5 (△), 0.3 (*)\(,\) 0.15 (●), 0 (+).
increasing the feed temperature, as can be observed in Figure 7; i.e., the partial fluxes of MTBE were more affected by the temperature than those of methanol. With regard to the effect of the feed composition on the activation energy, it is observed that, for MTBE-rich mixtures, the activation energy of methanol and MTBE decreases with the methanol content in the feed mixture, whereas, for methanol-rich mixtures, the increase in the methanol concentration gives rise to an increase in the activation energies of both components. Temperature variation may affect the polymer relaxation associated with the membrane swelling/plasticization and the interaction between methanol, MTBE, and the PPO polymer, and it may also cause the fusion of the less perfect crystalites in the polymer matrix. Because of the fact that the effect of these phenomena on the solution and diffusion of methanol/MTBE mixtures may be very complex, at the moment we have no plausible explanation for the variation of the activation energy with composition. According to some authors, it can be speculated that the increase in swelling of the PPO membrane at increasing methanol content results in a lowering of the energetic barrier for diffusion owing to the possible plasticization by the methanol.

4. Conclusions

The pervaporation separation for the mixture of methanol and MTBE by using a PPO membrane was investigated. The membrane preferentially permeated methanol over the whole range of composition. The permeability coefficient of methanol increases with the methanol content in the feed. This may be attributed to the membrane swelling, if not plasticization, caused by methanol. The permeability of MTBE showed a nonmonotonic behavior with the feed composition.

The total amount of liquid sorbed in the PPO membrane increases with the concentration of methanol. This fact indicates that methanol has a higher solubility in PPO than MTBE. The Flory—Huggins model predicts that the membrane has preferential sorption toward methanol over the whole range of feed composition. Both sorption and diffusion processes account for the permselective properties of the membrane.

The temperature dependence of the overall flux followed an Arrhenius relationship over the concentration range of 0–100% methanol. The activation energies for the permeation of methanol and MTBE were 32.6 and 71.3 kJ/mol, respectively.

Pervaporation and sorption measurements by using five different alcohols showed that the permeation rate, solubility, and diffusivity increased with the compound molecular size. It can be inferred that pervaporation of pure compounds is governed by both sorption and diffusion processes in the PPO membrane.

Acknowledgment

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