Coupled Diffusion of Water and Ethanol in a Polyimide Membrane

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In this work, the sorption and steady state permeation of water-ethanol mixture in an aromatic polyimide membrane was investigated with the objective of revealing the coupling effects of water and ethanol in their course of diffusion. The solubility of the water-ethanol mixture in the membrane was determined by means of swelling-distillation techniques. The sorption behavior was interpreted in terms of the thermodynamic equilibrium equations. The Maxwell-Stefan mass transfer model was employed as a framework for modeling diffusion. Model equations derived therefrom enable us to calculate coupled fluxes of water and ethanol from the experimental data. The coupling effects in the diffusion of water and ethanol were revealed by comparing the calculated coupled flux with non-coupling flux, which was calculated by integration of the Fickian first law using independent diffusion coefficients. Furthermore, the implication of the sole adjustable parameter included in the derived model equations was discussed.

INTRODUCTION

Separation of liquid mixtures by means of permeable polymer membranes is a subject of great interest from a technological point of view. Diffusion of the penetrants in the membranes from glassy polymers plays an important role in membrane performance. For polar liquid components, the diffusion behavior is generally complex. The complexity may arise from strong interaction between the penetrants, interaction of the penetrants with different segments of the membrane polymer, and consecutive plasticization effects of the penetrants on the polymer. In this case, coupled diffusion generally occurs, which implies that that diffusivity of one penetrant is influenced by the presence and movement of the other penetrants (1). Recently, Uchytil et al. (2) have evidenced coupled transport of acetic acid and water in polyvinyl alcohol membranes by using a differential permeation method to measurements of fluxes.

Most of the models for interpreting coupled diffusion in polymer membranes are based on the free volume and dual mobility concepts. The coupling effects in the pervaporation process, which is usually described by the solution-diffusion mechanism (3), can be exacted from experimental data by model fitting (4, 5). A pioneering work by Brun et al. (6) proposes the so-called "exponential six-coefficients model," which has four concentration-coefficients. However, the coefficients have not been given a strict physical interpretation, and have to be acquired by fitting of equations with several adjustable parameters. This work is an attempt to elucidate the coupling effects in diffusion of penetrants from binary mixtures, in terms of the Maxwell-Stefan mass transfer model. It is known that the Maxwell-Stefan model was originally established, starting from the concept of irreversible thermodynamics,
for a description of steady state diffusion in gaseous mixtures (7). In the case where diffusion of small molecules against a background of polymer membrane is involved, this model can still be useful if the membrane polymer as "the third component" remains at rest and no swelling of the membrane is observed when diffusion occurs. During steady state diffusion of liquid mixtures across polymer membranes, the membranes would also remain in the state of swelling equilibrium; we therefore use the Maxwell-Stefan model as a framework for modeling this diffusion process. Recently, several generalized expressions of the Maxwell-Stefan model have been used for liquid diffusion (8). Starting from a generalized expression of the Maxwell-Stefan model, we obtain in this work useful model equations containing one adjustable parameter. This parameter has the meaning of the coupling effect in the diffusion of the binary mixture, and can be derived by model calculations.

The membrane-liquid mixtures chosen in this study comprise water, ethanol and polyimide membrane. The solubility of a water-ethanol mixture in a polyimide membrane, which is essential for calculations of component fluxes, is presented in the first part of this paper. Further discussion, which is based on the Flory-Huggins thermodynamic theory (9), is on the deviation of their solubility behaviors from the ideal sorption assumption. In the second part, the diffusion behaviors of the liquid mixture are investigated, with the aim of extracting the coupled effects in diffusion of water and ethanol from experimental data.

Model for Interpreting Coupled Diffusion in Polymer Membranes Based on Maxwell-Stefan Theory

The Maxwell-Stefan equation gives an equal relationship of driving force with diffusion resistance for steady-state diffusions (10). Equation 1 is a generalized expression of the Maxwell-Stefan equation (11), which is suitable for the occasions where mass transport in polymeric matrices is involved:

$$\frac{d\mu_i}{dx} = RT \sum_{j=1}^{n} \phi_j (v_j - v_i) \frac{D_{ji}}{D_{ij}}$$

(1)

where $-d\mu_i$ is chemical potential variation of component $i$ in the direction of diffusion. $RT\phi_j (v_j - v_i) dx/D_{ij}$ is partial resistance exerted by component $j$ on component $i$ ($j \neq i$). $v_j$ is absolute velocity of component $j$. $D_{ji}$ is mutual diffusion coefficient of component $j$ and $i$. $\phi_i$ is volume fraction of component $i$ at a diffusion distance $x$.

We apply the Maxwell-Stefan equation to steady state diffusion in a polyimide membrane basing on following assumptions: (I) during steady state diffusion, the membrane remains at swelling equilibrium state; (II) the swelling degree of the membrane is low enough; in addition, the polymer will be in the glassy state under experimental temperature conditions so that convective flow in the membrane is negligible, and (III) the diffusion is only in the $x$-direction. In addition, Eq 1 has included only one modification compared to the original expression of the Maxwell-Stefan equation: molar fraction of components, $X_j$, present in the original expression is replaced by $\phi_j$; the physical argument is that when a polymer membrane is involved, $\phi_j$ rather than $X$ is a realistic measure of the probability that the frictional effect of component $j$ contributes to the total frictional force exerted on component $i$ (11). Rearranging Eq 1 gives

$$\frac{d\ln \phi_i}{dx} = \sum_{j=1}^{n} \phi_j (v_j - v_i) \frac{D_{ij}}{D_{ji}}$$

(2)

with

$$D_{ij} = D_{ji} \frac{d \ln \alpha_i}{d \ln \alpha_j}$$

(3)

where $\alpha_i$ is the activity of component $i$. In the case of diffusion of a single component in a polymer membrane, Fick's first law in the form as Eq 4 can be easily derived from Eq 2 if using the polymer as a focused frame ($v_m = 0$, Hittorf frame of reference). The index $m$ refers to polymer membrane.

$$J_i = -D_{ij} \frac{d\mu_i}{dx}$$

(4)

with

$$D_{ij} = \frac{D_{im}}{1 - \phi_i}$$

(5)

$J_i$ is the molar flux of component $i$. $D_{ij}$ is the diffusion coefficient in the polymer matrix in the Hittorf frame of reference. The relationship of Hittorf's 's diffusion coefficient with Fick's diffusion coefficient is the same as what Eq 5 expresses (12); $D_{ij}$ in Eq 2 must therefore be the diffusion coefficient in Fick's frame of reference.

In the case of diffusion of a binary mixture in a polymer membrane, the following equations can be derived from Eq 2 if the Hittorf frame of reference is also used:

$$\frac{d\phi_1}{dx} = \frac{\phi_1 j_2}{D_{21}} - \frac{\phi_2 j_1}{D_{12}} - \frac{(1 - \phi_1 - \phi_2) j_1}{D_{im}}$$

(6)

$$\frac{d\phi_2}{dx} = \frac{\phi_2 j_1}{D_{12}} - \frac{\phi_1 j_2}{D_{21}} - \frac{(1 - \phi_1 - \phi_2) j_2}{D_{im}}$$

(7)

where $j_1$ and $j_2$ are coupled fluxes in volume of component 1 and 2, respectively. The cross-term $D_{ij}$ is understood as mutual diffusion coefficient of component $i$ and component in $j$ Fick's frame of reference, and we therefore assume this term to be symmetric, i.e. $D_{ij} = D_{ji}$. Analysis of Eq 5 in terms of the Flory-Huggins thermodynamic theory (13) reveals that $D_{12}$ is strongly linked to the interaction of the two components between themselves and with the polymer, as well as the concentrations of all the components present in the system. Hence, it is reasonable to argue that $D_{12}$ has included the factors that can bring about the coupled diffusion.
In order to derive the coupled fluxes from the Maxwell-Stefan equation, a numerical integration is required. In the literature pertaining to the Maxwell-Stefan equation, there are several approximate approaches reported to solve this equation or its derivatives. Stewart et al. (14) simplified the integration by replacing component concentrations, which are variables in the equation, with averaged concentrations. Another typical approximation converted the Maxwell-Stefan equation from the differential form into a difference form, and applied a Stewart-like approximation (15) and obtain the model equations as Eq 8 and 9. Particulars of this approach are described in Appendix 1.

\[
\left[ \frac{j_1}{D_{1m}} + \frac{j_2}{D_{2m}} \right] x = \ln \frac{1 - (\Phi_1 + \Phi_2)}{1 - (\Phi_1^0 + \Phi_2^0)} \tag{8}
\]

\[
\frac{j_1 + j_2}{D_{12}} x = \ln \left\{ \frac{j_1 + j_2}{j_2} Q \frac{\Phi_2 - \Phi_1}{j_1} + 1 - Q \right\} \tag{9}
\]

where \( \Phi_i \) is volume fraction of component \( i \) at diffusing distance \( x \), \( \Phi_i^0 \) is volume fraction at the interface of the polymer membrane where \( x = 0 \). The model equations show the concentration profiles of the penetrants across the membrane under steady state conditions. Knowledge of the diffusion profiles is important for understanding the nature of mass transport in polymer membranes and may help in designing appropriate polymer membranes for separation processes. Equations 8–9 clearly show that for steady state diffusion, the overall concentration of the binary mixture, \( \Phi_1 + \Phi_2 \), decreases in an exponential manner with diffusing distance. The concentration profile of each component is also an exponential function of \( x \) and depends on the value for \( D_{12} \). Mulder et al. (16) obtained steady concentration profiles of a binary mixture in a cellulose acetate membrane by means of the film-stack technique. It appears that the model equations developed here can give an appropriate description to the nonlinear profiles measured by the authors.

A combination of Eq 8 and Eq 9 enables coupled fluxes to be calculated by a Gilliland-like iterative method, if the boundary conditions of the membrane, \( \Phi_1^0 \) and \( \Phi_2^0 \), and all the equation coefficients are known. In brief, \( j_1 \) is estimated in a first attempt and \( j_2 \) is computed by solving Eq 8 at the estimated \( j_1 \). This iterative process is continued until a set of fluxes can fulfill the two equations within an admitted error range. However, \( D_{12} \) in general cannot be predicted theoretically. \( D_{12} \) is here taken as an adjustable model parameter to be determined. Once the boundary conditions and the water volume fraction in the permeate, \( \psi_1 \), which is connected with the volume fluxes through a relationship

\[
\psi_1 = \frac{j_1}{j_1 + j_2} = 1 - \frac{j_2}{j_1 + j_2} \tag{11}
\]

are given, \( D_{12} \) and the coupled fluxes can be simultaneously derived using Eqs 8 and 9. Pervaporation of the water/ethanol mixture in a polyimide membrane will be tested over entire composition range of the mixture and the permeate composition \( \psi_1 \) will be measured.

The diffusion coefficient of a liquid penetrant in polymer membranes usually is concentration dependent; it should be a function of diffusing distance. However, the concentration dependence in general cannot be predicted theoretically. In this work, the diffusion coefficients, \( D_{1m} \) and \( D_{2m} \) in Eqs 8 and 9 are replaced by Crank’s mean diffusion coefficients (17), which can be calculated using Fick’s first law and knowledge of flux values for pure components.

**EXPERIMENTAL**

Preparation of the polyimide membrane was reported in our previous paper (18). The \( T_g \) of this polymer was measured at 196°C using a Netzsch-Geratebau DSC-200. Solubility of water-ethanol mixture in polyimide membrane is determined in the swelling-distillation experiment, which has been adopted by other investigators (19). The overall sorption of the mixture is measured by weighting the swollen film at swelling equilibrium. The liquid absorbed by the membrane is removed by a vacuum pump and condensed in a tube cooled by liquid nitrogen. A gas chromatograph, equipped with a thermal conductivity detector, is employed to determine the composition of the collected liquid. The solubility of each component, \( \psi_1^0 \) or \( \psi_2^0 \), is subsequently calculated. The accuracy of the solubility data is estimated to be within about ±5%, which is calculated from the spread of values obtained for different runs with the liquid mixture of the same composition.

The pervaporation apparatus used in this work and the experimental procedures have been described elsewhere (20). In brief, the liquid mixture contacts with one side of the polymer membrane while permeate on the other side of the membrane is removed into a vapor phase by means of vacuum desorption. Pressure at the permeate side is maintained around 0.1 mmHg. The permeate mixtures are continuously collected in a trap cooled by liquid nitrogen and then weighted. Composition analysis of the permeate is performed on the gas chromatograph.

For steady state pervaporation, it is in general assumed that solution equilibrium establishes at the
membrane/liquid interface. Thus, $\phi_i^0$ in Eq 8 and 9 is taken to equal to the measured solubility, $\phi_i^{sol}$, at $x = \delta$ where $\delta$, membrane thickness, is taken as small, i.e., $\phi_i^0 \sim 0$, because the pressure on the permeate side of the membrane is kept very low in our experiments.

**RESULTS AND DISCUSSION**

**Solubility of Water-Ethanol Mixture in Polyimide Membrane**

Figures 1 and 2 show the solubility of the water-ethanol mixture in the polyimide membrane. It is apparent from the data in the Figures that over the entire composition range of the mixture, the solubility of the mixture is considerably low, and the solubility by weight, $w_i^{sol}$, of each component is consistently less than 0.1. It is generally assumed that under low solubility conditions, the solution behavior in polymer membranes follows Henry's law, i.e., the solubility of a solvent is proportional to its molar fraction in the liquid outside the membrane. However, this ideal hypothesis fails to describe the solution behaviors of the mixture studied here, since the sorption curve of ethanol is markedly nonlinear as observed in Fig. 1. Values indicated by the dotted curve in Fig. 1 were calculated using Eq 12 (22): 

$$w_i^{sol} = \phi_i \gamma_i X_i$$

where $\gamma_i$ is the activity coefficient in the water-ethanol liquid mixture, and has the meaning of a correction factor to Henry's law. $\gamma_i$ values are calculated using widely accepted Wilson activity equations (Appendix 2) (23, 24), in which two adjustable parameters are given in Table 1. The calculated solubility for ethanol is found to be higher than the corresponding experimental value. It is apparent that Eq 12, although it has taken into account the thermodynamic reality of the water-ethanol binary mixture, is still inadequate to describe the sorption behavior of the water-ethanol mixture in the polyimide membrane. This sorption behavior appears to be associated with the thermodynamic properties of the polyimide-water-ethanol ternary mixture.

Starting from classical Flory-Huggins thermodynamic theory, Krigbaum et al. (25) have derived an equation to calculate sorption composition (Appendix 2). This equation makes it clear that the sorption composition, $\mu_1$, is related to a parameter $x_{13} - b_{23}$, where $x_{13}$ and $x_{23}$ are, respectively, the interaction parameter of the polymer with component 1 and component 2 in the ternary system. We prove that the $\mu_1$ value for the water-ethanol mixture is, as expected, sensitive to the difference $x_{13} - b_{23}$. At $(x_{13} - b_{23}) = 0.75$; a good mutual agreement between the experimental and calculated $\mu_1$ can be achieved, as shown in Fig. 2.

![Fig. 1. Solubility of ethanol $w_i^{sol}$ in polyimide membrane vs molar fraction of ethanol $X_i$ in the mixture at 20°C. □: experimental values; ---: values calculated in terms of Eq 12.](image)

![Fig. 2. Volume fraction of water in the permeate $u_i$ and in the sorption $u_i$ at 20°C. ○: experimental values of $u_i$; □: measured values of $u_i$; ······: calculated $u_i$ at $x_{13} - b_{23} = 0.75$; ······: calculated $u_i$ at $x_{13} - b_{23} = 1.10$.](image)

<table>
<thead>
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<th>Table 1. Specific Parameters for Water, Ethanol and Polyimide Membrane.</th>
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<td><strong>Sorption coefficient</strong>:</td>
</tr>
<tr>
<td>$\varphi_1$ (water) = $9.7 \times 10^{-2}$, $\varphi_2$ (ethanol) = $9.3 \times 10^{-2}$</td>
</tr>
<tr>
<td><strong>Wilson activity equations</strong>:</td>
</tr>
<tr>
<td>$\Lambda_{12} = 0.94$, $\Lambda_{21} = 0.15$</td>
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<tr>
<td><strong>Membrane density</strong>:</td>
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<td><strong>Membrane thickness</strong>:</td>
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<td><strong>Interaction parameters</strong>:</td>
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<td><strong>Pure component fluxes</strong> ($10^{-3}$ kg · m$^{-2}$ h$^{-1}$):</td>
</tr>
<tr>
<td>62.3 for water, 4.9 for ethanol</td>
</tr>
<tr>
<td><strong>Diffusion coefficients</strong>:</td>
</tr>
<tr>
<td>$D_{1,m} = 25.5 \times 10^{-13}$ m$^{2}$ · s$^{-1}$, $D_{2,m} = 2.1 \times 10^{-12}$ m$^{2}$ · s$^{-1}$</td>
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* $e_1$ are determined by fitting pure water solubility or pure ethanol solubility into Eq 12.

* The two parameters are calculated from vapor-liquid equilibrium data in the literature (22, 23).
Table 1 gives interaction parameters of a polyimide membrane with pure water ($\chi_{13}^0$) and pure ethanol ($\chi_{23}^0$). They are estimated using the following relationship (26):

$$\ln \phi_i^r + (1 - \phi_i^r) + \chi_{ij}^0 (1 - \phi_i^r)^2 = 0$$  \hspace{1cm} (13)

where $\phi_i^r$ is the volume fraction of pure component $i$ in the polymer. If $\chi_{13}$ is calculated at $\chi_{23}^0 - \chi_{13}^0 = 1.10$, the calculated values are, however, lower than the experimental values over the entire composition range. It is apparent that the nature of the interaction in the binary system of polymer/pure solvent is different from that in the ternary system. This phenomenon may arise from preferential solvation effects, which would bring about the two solvents acting with different segments of the polymer. From the Flory-Huggins thermodynamic theory (27), it follows that the distinction in the interaction parameters, i.e., $\chi_{13}^0 - \chi_{23}^0 = 0.75$ against $\chi_{23}^0 = 1.10$, is interpretable if concentration dependence is introduced into the interaction parameters, $\chi_{13}$ and $\chi_{23}$.

**Coupling Effect Between Water and Ethanol Diffusion in Polyimide Membrane**

In this part, we first investigate non-coupling diffusion for purposes of comparison. If the diffusion of water and ethanol is independent from each other, the corresponding non-coupling permeation fluxes can be calculated using Eq 14, which is derived by integration of Fick’s first law (28):

$$j_i = \frac{V_i \cdot m_i}{M_i \cdot \delta_j} \cdot \frac{\partial}{\partial \delta_j} \left( u_i^0 - u_i^\delta \right)$$  \hspace{1cm} (14)

where $M_i$ is molar weight of component $i$, $u_i^0$ and $u_i^\delta$ is, respectively, weight fraction of this component at membrane/liquid interface and the permeate side of the membrane. $D_{im}$ values listed in Table 1 were obtained by calculation of this equation using values for $j_i$ and $u_i^\delta$ of pure components given in Table 1. The mean diffusion coefficient of water is considerably higher than that of ethanol; this is qualitatively consistent with the respective molar volumes of the two components ($18.0 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ for water and $58.4 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ for ethanol); the larger the penetrant, the lower its mobility in the membrane. The broken curves in Figs. 3-4 are indicative of the non-coupling fluxes obtained by calculation of Eq 14 using solubility values of the water-ethanol mixture. It is observed that over the entire composition range of the mixture, water non-coupling fluxes are consistently higher than that of ethanol. At a low concentration of ethanol in the mixture, the ethanol non-coupling flux is very small.

Permeate compositions, $\psi_1$, measured in pervaporation tests are shown in Fig. 2. From the values for $\psi_1$ together with the values for $\Phi_i^\psi$, coupled permeation fluxes are derived using an iteration method. The iterative procedures are as follows: substitution of Eqs 8 and 10 into Eq 9 gives an equation containing two unknown parameters, $D_{12}^F$ and $j_1$. Furthermore, $D_{12}^F$ is estimated in a first attempt, and a set of fluxes are then obtained using this equation and Eq 9. This iteration is repeated until a set of fluxes precisely match Eq 11. The calculated coupled fluxes are indicated by the solid curves in Figs. 3-4. Error bars on the curves indicate accuracy for the predicted fluxes, which originates from the experimental error limits of the swelling measurements. Following from the accuracy of ±5% estimated for the solubility data, an accuracy of

![Fig. 3. Water fluxes in polyimide membrane at 20°C. O: experimental values; =...= calculated values for non-coupling diffusion, ---: calculated values for coupled diffusion.](image)

![Fig. 4. Ethanol fluxes in polyimide membrane at 20°C. △: experimental values; ---: calculated values for non-coupling diffusion, ---: calculated values for coupled diffusion.](image)
±10% is estimated for the coupled fluxes and also the non-coupling fluxes. It is observed in Figs. 3-4 that for ethanol, the coupled flux is larger than the non-coupled flux, but for water, the coupled flux is lower than the non-coupled flux. It therefore is clear that the mobility of water in the polyimide membrane is reduced by frictional interaction with ethanol, and the mobility of ethanol is enhanced by the faster-moving water. Moreover, the agreement between the calculated coupled fluxes and measured fluxes is very good for both water and ethanol except at a very low water concentration (weight fraction <10%). We consider that the deviation observed is induced by the concentration dependence of the diffusion coefficients.

Figure 5 shows the calculated $D'_{12}$ plotted against water concentration in the mixture. It is apparent that $D'_{12}$ is concentration dependent. $D'_{12}$ values over the entire composition range of the mixture lie in the range $D'_{2m}$ to $D'_{1m}$. As mentioned earlier, $D'_{12}$ is considered the mutual diffusion coefficient of water and ethanol, i.e., an effective diffusion coefficient of water-ethanol mixture. Thus, $D'_{2m} < D'_{12} < D'_{1m}$ may indicate that the coupling effects make the diffusivity of the binary mixture higher than that of ethanol and lower than that of water. Furthermore, the result that $D'_{12}$ is close to $D'_{1m}$ at a high concentration of water may indicate that the coupling effects make the binary mixture exhibit a diffusion behavior similar to that of water in this case. This deduction is supported by the experimental results shown in Figs. 3-4: at a water concentration larger than 80%, water flux approaches the non-coupling value, and ethanol flux is considerable higher than its non-coupling flux, which is almost zero. It is observed also in Figs. 3-4 that water shows much lower fluxes than the non-coupling fluxes, and ethanol fluxes appear very close to its

non-coupling fluxes at a water concentration lower than 15% where $D'_{12}$ is very close to $D'_{2m}$. This indicates that the coupling effects make the binary mixture exhibit a similar diffusion behavior to ethanol in such a case. It therefore is concluded that $D'_{12}$ implies the mutual diffusion coefficient of water and ethanol, and stands for the coupling effects in the diffusion of water and ethanol.

**CONCLUSIONS**

Starting from the Maxwell-Stefan equation, we have obtained useful model equations whereby the coupling effects in the diffusion of binary mixture can be extracted from experimental data by model fitting. Our results have shown that the mutual friction between water and ethanol promotes the moving of ethanol and slows down the moving of water. The model parameter $D'_{12}$ implies the mutual diffusion coefficient of water and ethanol, and can stand for the coupling effects in the diffusion of the two components. One of the advantages of the model equations developed may be that only one coupling parameter need be determined. In the literature, the coupled fluxes were also predicted, but by numerical integration of modified Fick’s first law containing several concentration-dependent diffusion coefficients. However, such integration was associated with an empirical simplification of the equations accomplished by removing some fitting parameters. Although this study chooses a water-ethanol binary mixture as a model system, the results reported here may help in modeling diffusion for other complex systems.

**APPENDIX 1: SOLUTION FOR THE MAXWELL-STEFAN EQUATIONS**

The following definitions have been used to derive Eq 6, 7 from Eq 2:

\[ J_i = c_i v_i \]  
\[ j_i = J_i v_i \]  
\[ \phi_i = c_i v_i \]

where $J_i$ is molar flux, $c_i$ is mole concentration, $j_i$ is volume flux, $V_i$ is partial molar volume. According to Laplacian transformation principles, image functions of $d\phi_i/dx$, $\phi_i$, and a constant are given by as:

\[ \frac{d\phi_i}{dx} = -\phi_i^0 + p\phi_i \]  
\[ \phi_i^* = \phi_i \]  
\[ 1^* = \frac{1}{p} \]

where $p$ is Laplacian operator and $\phi_i^0$ is a boundary condition at $x = 0$. Laplacian transformation of Eq A4 and A5 leads to
- $\phi_1^0 + p\phi_1 = \\
\frac{j_1}{D_{1m}} \phi_1 - \frac{j_2}{D_{2m}} \phi_2 - \frac{j_1}{D_{1m}} \frac{1}{p} + \frac{j_1}{D_{1m}} \phi_1 + \frac{j_1}{D_{1m}} \phi_2 \tag{A7}
- $\phi_2^0 + p\phi_2 = \\
\frac{j_1}{D_{12}} \phi_2 - \frac{j_2}{D_{22}} \phi_1 - \frac{j_2}{D_{2m}} \frac{1}{p} + \frac{j_2}{D_{2m}} \phi_1 + \frac{j_2}{D_{2m}} \phi_2 \tag{A8}
A7 + A8 gives

$$\bar{y} = \frac{y^0}{p - \lambda} + \left(\frac{1}{p} - \frac{1}{p - \lambda}\right) \tag{A9}$$

with

$$y = \phi_1 + \phi_2, \tag{A10}$$
$$\lambda = \frac{j_1}{D_{1m}} + \frac{j_2}{D_{2m}} \tag{A11}$$
Inverse Laplacian transformation of Eq A9 using Eqs A4, A5 and A12 gives Eq A13.

$$\frac{1}{p - \lambda} = e^\lambda \tag{A12}$$

$$\left(\frac{j_1}{D_{1m}} + \frac{j_2}{D_{2m}}\right) x = \ln \left[\frac{1 - \phi_1 - \phi_2}{1 - \phi_1^0 - \phi_2^0}\right] \tag{A13}$$

However, Eq A13 is inadequate to determine the volume fraction of each penetrant $\phi_1$ and $\phi_2$. Furthermore, $A7 \times \frac{j_1 + j_2}{j_2} \times \phi_1 - A8 \times \frac{j_1 + j_2}{j_1}$ gives the following expression:

$$\left[\frac{j_1 + j_2}{j_1} \phi_1^0 - \frac{j_1 + j_2}{j_2} \phi_2^0\right] - \left[\frac{j_1 + j_2}{j_2} \phi_2 - \frac{j_1 + j_2}{j_1} \phi_1\right]
= (1 - \phi_1) \frac{j_1 + j_2}{D_{12}} \frac{1}{p} \tag{A14}$$
with

$$\phi_1 = \frac{1}{D_{12} - \frac{1}{D_{1m}}} \tag{A15}$$

through dividing each side of Eq A14 by $\lambda$ we have Eq A16. Inverse Laplacian transformation of Eq A16 leads to Eq 9.

$$\left[\frac{j_1 + j_2}{j_1} \phi_1^0 - \frac{j_1 + j_2}{j_2} \phi_2^0\right] \frac{1}{p - \lambda} + \\
\left[\frac{j_1 + j_2}{j_2} \phi_2 - \frac{j_1 + j_2}{j_1} \phi_1\right] = -(1 - \phi_1) \left[\frac{1}{p} - \frac{1}{p - \lambda}\right] \tag{A16}$$

with

$$\lambda = \left[\frac{p - \frac{j_1 + j_2}{D_{12}}}{\frac{1}{D_{12}} - \frac{1}{D_{1m}}} \right] \tag{A17}$$

### APPENDIX 2: CALCULATION OF THE SORPTION OF THE BINARY MIXTURE

#### Activities

The calculation of the activity coefficients is based on the Wilson equation:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + \\
\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_{12}} \tag{A18}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) - \\
\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_{12}} \tag{A19}$$

#### Sorption Compositions

The sorption compositions $u_i$ are calculated according to the following expression:

$$\ln \frac{\phi_1}{\phi_2} = \ln \frac{v_1}{v_2} + \ln \frac{\phi_2}{\phi_1} - \chi_{12} (\phi_2 - \phi_1) - \\
\chi_{12} (v_1 - v_2) - \phi_3 (x_{13} - x_{23}) \tag{A20}$$

$$\phi_1 = (1 - \phi_3) u_1 \tag{A21}$$
$$\phi_2 = (1 - \phi_3) x_1 \tag{A22}$$
$$l = V_1 / V_2 \tag{A23}$$

where $v_1$ and $v_2$, respectively, refer to water and ethanol volume fraction in the feed. $x_{12}$ of water with ethanol is calculated according to a fourth grade polynomial relation taken from the literature (13).

### LIST OF SYMBOLS

- $a_i$: thermodynamic activity of component $i$
- $c_i$: molar concentration (mol · L$^{-1}$)
- $D_{12}$: interaction parameter in generalized Maxwell-Stefan equation (m$^2$ · s$^{-1}$)
- $D_{1m}$ ($D_{2m}$) diffusion coefficient of water (ethanol) in polymer membrane (m$^2$ · s$^{-1}$)
- $J_i$: volume flux of component $i$ (m · h$^{-1}$)
- $J_i^t$: molar flux of component $i$ (mol · hm$^{-1}$ · m$^2$)
- $l$: ratio in molar volume of water to ethanol
- $M_i$: molar weight of component $i$ (g · mol$^{-1}$)
- $n$: number of components
- $p$: Laplacian operator
- $\nu_i$: mean velocity of molecule $i$ (m · s$^{-1}$)
- $V_i$: partial molar volume of component $i$ (m$^3$ · mol$^{-1}$)
- $\omega_{1}^e$: equilibrium solubility (weight fraction) of component $i$ in polymer membrane
- $\omega_i$: weight fraction of component $i$ in polymer membrane
- $x$: axis coordinate perpendicular to film surface
Coupled Diffusion of Water and Ethanol in a Polyimide Membrane

\[ X_i \] \quad \text{molar fraction of component } i \\
\phi_i^{eq} \quad \text{equilibrium solubility (volume fraction) of component } i \text{ in polymer film} \\
\phi_i \quad \text{volume fraction of component } i \text{ in polymer film} \\
\phi_i^0 \quad \text{volume fraction of component } i \text{ in the polymer film at feed side} (x = 0) \\
\phi_i^p \quad \text{volume fraction of component } i \text{ at permeate side} (x = \delta) \\
\phi_i^s \quad \text{solubility (volume fraction) of pure component } i \\
\psi_i \quad \text{volume fraction of water in permeate} \\
\gamma_i \quad \text{activity coefficient of component } i \\
\mu_i \quad \text{chemical potential of component } i \\
(\text{J} \cdot \text{mol}^{-1}) \\
\chi_{ij} \quad \text{interaction parameter of component } i \text{ with } j \\
\rho_m \quad \text{density of the swollen membrane} \quad (\text{kg} \cdot \text{m}^{-3})

Indices

1. water \\
2. ethanol \\
3. polymer \\
m. membrane

REFERENCES