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Highlighting Thermodynamic Coupling Effects in Alcohol/Water Pervaporation across Polymeric Membranes

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Supporting Information

ABSTRACT: The pervaporation of binary alcohol/water mixtures across polymeric membranes is modeled by combining the Maxwell–Stefan (M-S) diffusion formulation with the Flory–Huggins (F-H) description of sorption equilibrium. The combined M-S/F-H model shows that the flux of each penetrant species is coupled to the driving force of its partner penetrant. Two types of coupling contributions can be distinguished: (i) coupling arising out of thermodynamic non-idealities in the polymer matrix and (ii) thermodynamic coupling. The focus of this article is on the contribution of thermodynamic coupling, which is quantified by the set of coefficients $\Gamma_{ij} = \sum_{m} a_{m} \ln a_{m}$, where $a_{m}$ the activity of species $i$, is dependent on the volume fraction $\phi_{m}$ of both penetrants in the polymeric membrane. Detailed analyses of published experimental data for pervaporation of ethanol/water feed mixtures of varying compositions in both hydrophobic (poly(dimethylsiloxane)) and hydrophilic (cellulose acetate, polyimide, and polyvinyl alcohol/polyacrylonitrile composite) membranes show that in all cases, the cross-coefficients $\Gamma_{ij}$ ($i \neq j$) are negative and may attain large magnitudes in relation to the diagonal elements $\Gamma_{ii}$. The net result is that the permeation fluxes of each penetrant are suppressed by its partner, resulting in mutual slowing down of permeation fluxes. If thermodynamic coupling effects are ignored, significantly higher fluxes are anticipated than those that are experimentally observed.

INTRODUCTION

Separations of alcohol/water mixtures by pervaporation across polymeric membranes are of industrial interest because of the high separation selectivities that are achievable.1–9 Alcohol-selective separations are achievable with hydrophobic membranes such as poly(dimethylsiloxane) (PDMS).3–5,10 With hydrophilic membranes (e.g., cellulose acetate (CA), polyimide, and poly(vinyl alcohol)/polyacrylonitrile (PVA/PAN) composites), the separations are selective to water.5,11–13 Water-selective separations are also achieved by exploiting size exclusion in hydrophobic perfluorinated polymer membranes.14,15 For process development and design purposes, robust and accurate models are necessary for calculation of the permeation fluxes. Chemical potential gradients, $d\mu/dx$, are the fundamentally correct driving forces for transport of penetrants across polymeric membranes.6,16–18 The chemical potentials of the penetrants in the polymer matrix are most conveniently described by the Flory–Huggins (F-H) model that relates the component activities $a_{i}$ to the volume fractions, $\phi_{i}$.8,19–21 For ternary mixtures of two penetrants (1, 2), and the polymer matrix ($m$), there are three interaction parameters in the F-H description of phase equilibrium: $\chi_{12}$, $\chi_{1m}$, and $\chi_{2m}$. The F-H model for the component activities of the penetrants is written as follows:

$$\ln a_{i} = \ln(\phi_{i}) + (1 - \phi_{i}) - \phi_{i} \frac{\chi_{1i}}{V_{1}} - \phi_{i} \frac{\chi_{2i}}{V_{2}} + \left(\chi_{1m} \phi_{1} + \chi_{2m} \phi_{2}\right)$$

$$+ \frac{\chi_{12}}{V_{1}V_{2}} \phi_{1} \phi_{2} \phi_{m} \frac{\partial a_{m}}{\partial a_{1}} - \frac{\chi_{12}}{V_{1}V_{2}} \phi_{1} \phi_{2} \phi_{m} \frac{\partial a_{m}}{\partial a_{2}}$$

$$\ln a_{1} = \ln(\phi_{1}) + (1 - \phi_{1}) - \phi_{1} \frac{\chi_{11}}{V_{1}} - \phi_{1} \frac{\chi_{12}}{V_{1}V_{2}} + \left(\chi_{1m} \phi_{1} + \chi_{2m} \phi_{2}\right)$$

$$+ \frac{\chi_{12}}{V_{1}V_{2}} \phi_{1} \phi_{2} \phi_{m} \frac{\partial a_{m}}{\partial a_{1}} - \frac{\chi_{12}}{V_{1}V_{2}} \phi_{1} \phi_{2} \phi_{m} \frac{\partial a_{m}}{\partial a_{2}}$$

In eq 1, $V_{i}$ are the partial molar volumes, and we define

$$u_{2} = \frac{\phi_{2}}{\phi_{1} + \phi_{2}}; \ u_{1} = 1 - u_{2} = \frac{\phi_{1}}{\phi_{1} + \phi_{2}}; \ \phi_{m}$$

$$= 1 - (\phi_{1} + \phi_{2})$$

In the Maxwell–Stefan (M-S) diffusion formulation, which is firmly rooted in the theory of irreversible thermodynamics,
the volumetric permeation fluxes, \( N_i^V \), expressed in \( \text{m}^3 \text{ m}^{-2} \text{ s}^{-1} \), are related to the chemical potential gradients as \(^{16-18} \):

\[
- \frac{\phi_i}{RT} \frac{d\mu_i}{dz} = \frac{(\phi_i N_i^V - \phi_j N_j^V)}{D_{12}^V} + \frac{\phi_j N_j^V}{D_{1m}^V}
\]

\[
- \frac{\phi_j}{RT} \frac{d\mu_j}{dz} = \frac{(\phi_j N_j^V - \phi_i N_i^V)}{D_{21}^V} + \frac{\phi_i N_i^V}{D_{2m}^V}
\]

(2)

Detailed derivations of eq 2 are provided in the Supporting Information. Essentially, in the M-S model, the chemical potential driving force acting on a penetrant species (left member) is balanced by (i) friction with partner penetrant (first right member = \( 1 \rightarrow 2 \) friction) and (ii) friction between the penetrant and the polymer matrix (second right member).\(^ {18} \) The molar flux of component \( i \), expressed in \( \text{mol m}^{-2} \text{ s}^{-1} \), is \( N_i^{\text{molar}} = \phi_i N_i^V \). The mass flux of component \( i \), expressed as \( \text{kg m}^{-2} \text{ s}^{-1} \), is \( N_i^{\text{mass}} = \rho_i N_i^{\text{molar}} \), where \( \rho_i \) is the liquid-phase mass density of the pure component \( i \), with molar mass \( M_i \).

The M-S diffusivities for penetrant–membrane interactions, \( D_{jm}^V \), are often strongly influenced by the volume fractions of penetrants due to swelling\(^ {1,3,6,16} \):

\[
D_{1m}^V = D_{1m}^V(0) \exp(\epsilon_{11} \phi_1 + \epsilon_{12} \phi_2);
D_{2m}^V = D_{2m}^V(0) \exp(\epsilon_{21} \phi_1 + \epsilon_{22} \phi_2)
\]

(3)

In eq 3, \( \epsilon_{ii} \), \( \epsilon_{ij} \) are termed plasticization coefficients. More detailed discussions on the interpretation of the magnitude, and signs, of \( \epsilon \) are available in the literature.\(^ {2,3,22,23} \)

The M-S diffusivities \( D_{12}^V \) and \( D_{21}^V = D_{21}^V(0) \) quantify the extent to which the mobilities of the penetrants are correlated to each other; correlation effects have the effect of slowing down the transport of the more mobile partners due to correlation motions with tardier partners in the polymer matrix.\(^ {17,18} \)

Let us define a \( 2 \times 2 \) dimensional matrix \([\Lambda]\) whose elements are given by

\[
\begin{bmatrix}
\Lambda_{11} & \Lambda_{12} \\
\Lambda_{21} & \Lambda_{22}
\end{bmatrix} = \begin{bmatrix}
D_{1m}^V \phi_m + \phi_j D_{1m}^V & D_{1m}^V \phi_j D_{2m}^V \\
D_{2m}^V \phi_i D_{1m}^V & D_{2m}^V \phi_m + \phi_i D_{2m}^V
\end{bmatrix}
\]

(4)

The ratios \( \frac{D_{ij}^V}{D_{12}^V} \) and \( \frac{D_{ij}^V}{D_{21}^V} \) quantify the degrees of correlations; only one of these is independent because \( \frac{D_{ij}^V}{D_{12}^V} = \frac{D_{ii}^V}{D_{12}^V} \frac{\pi_{ii} \rho_i}{\pi_{12} \rho_2} \). We may estimate \( D_{12}^V \) using the Vignes interpolation formula\(^ {24} \) for diffusion in binary liquid mixtures, adapted as follows\(^ {17} \):

\[
(D_{12}^V / V_2) = \left( D_{1m}^V / V_2 \right) \phi_i / (\phi_i + \phi_j) \left( D_{2m}^V / V_1 \right) \phi_j / (\phi_i + \phi_j)
\]

(5)

with the limiting scenarios

\[
\phi_2 \to 0, \; D_{12}^V = D_{1m}^V; \quad \phi_1 \to 0, \; D_{21}^V = D_{2m}^V
\]

(6)

Alternatively, the degree of correlations \( \frac{D_{ij}^V}{D_{12}^V} \) may be fitted to match experimental data on mixture permeation.\(^ {18} \)

In the limiting scenario in which correlation effects are considered to be of negligible importance, i.e., \( \frac{\partial \phi_i}{\partial N_j^V} \rightarrow 0; \; \frac{\partial \phi_j}{\partial N_i^V} \rightarrow 0 \), the matrix \([\Lambda]\) simplifies to yield

\[
\begin{bmatrix}
\Lambda_{11} & \Lambda_{12} \\
\Lambda_{21} & \Lambda_{22}
\end{bmatrix} = \begin{bmatrix}
1 & D_{1m}^V 0 \\
0 & 0 D_{2m}^V
\end{bmatrix}
\]

(7)

Strictly speaking, we should expect eq 7 to hold when the volume fractions of both penetrants in the membrane are negligibly small.

The parameters on the left-hand side of eq 2 may be expressed in terms of gradients in the volume fractions by introducing a \( 2 \times 2 \) dimensional matrix of thermodynamic correction factors \([\Gamma]\)

\[
\phi_i \frac{d\mu_i}{R T} = \phi_i \frac{d\ln a_i}{dz} = \sum_{j=1}^{2} \frac{d\phi_j}{\phi_j} \frac{d\ln a_j}{dz} \Gamma_{ij} = \frac{d\phi_i}{\phi_i} \frac{d\ln a_i}{dz}
\]

(8)

The four elements \( \Gamma_{ij} \) can be determined by the analytic differentiation of eq 1.

Combining eqs 2, 4, and 8, we derive an explicit expression for the volumetric fluxes as functions of the gradients in the volume fractions

\[
\begin{bmatrix}
N_1^V \\
N_2^V
\end{bmatrix} = \begin{bmatrix}
\Lambda_{11} & \Lambda_{12} \\
\Lambda_{21} & \Lambda_{22}
\end{bmatrix} \begin{bmatrix}
\frac{d\phi_1}{dz} \\
\frac{d\phi_2}{dz}
\end{bmatrix}
\]

(9)

Under steady-state conditions, and assuming that the volume fraction profiles for both penetrants across the membrane layer are linear, the permeation fluxes across a membrane of thickness \( \delta \) may be calculated explicitly as follows\(^ {17,18} \):

\[
\begin{bmatrix}
N_1^V \\
N_2^V
\end{bmatrix} = \begin{bmatrix}
\Lambda_{11} & \Lambda_{12} \\
\Lambda_{21} & \Lambda_{22}
\end{bmatrix} \begin{bmatrix}
\Gamma_{11} & \Gamma_{12} \\
\Gamma_{21} & \Gamma_{22}
\end{bmatrix} \begin{bmatrix}
\Delta \phi_1 \\
\Delta \phi_2
\end{bmatrix}
\]

(10)

In eq 10, \( \Delta \phi_i = \phi_{i0} - \phi_{i\delta} \) \( i = 1,2 \), where \( \phi_{i0} \) and \( \phi_{i\delta} \) are, respectively, the volume fractions at the upstream (subscript 0) and downstream (subscript \( \delta \)) faces of the membrane; the volume fractions are in equilibrium with the bulk fluid mixtures in the contiguous compartments, determined from solution of the F-H equations as detailed in the Supporting Information. In the linearized approach, the elements of each of the two matrices \([\Lambda]\) and \([\Gamma]\) are evaluated at the arithmetic averaged volume fractions \( \phi_{iav} = (\phi_{i0} + \phi_{i\delta})/2 \). The accuracy of the linearized eq 10 has been established in an earlier work.\(^ {18} \)

Except in the scenario in which the volume fractions of both penetrants are vanishingly small, i.e., \( \phi_i \to 0 \), each of the two square matrices \([\Lambda]\) and \([\Gamma]\) on the right-hand side of eq 10 will have significant off-diagonal elements; consequently, the flux of a penetrant is coupled to the driving force of its partner species. From eq 10, it is evident that there are two distinct and
separate contributions to coupled transports: (i) correlation effects, embodied in the off-diagonal elements of $[\Lambda]$ and (ii) thermodynamic coupling engendered by the off-diagonal elements of $[\Gamma]$. The significance of correlation effects has been highlighted in earlier published works. $^3,13,16$ The main focus of this article is on the significance of thermodynamic coupling effects in alcohol/water pervaporation.

As an illustration, Figure 1a presents calculations of $\Gamma_{ii}$ for the ternary mixture ethanol(1)/water(2)/PDMS(m) at 313 K also significantly influenced by the driving force for ethanol because $\Delta \phi_1 \gg \Delta \phi_2$ for hydrophobic PDMS. As an illustration of the strong influence of thermodynamic coupling, Figure 1b plots the ratio of driving forces $(\Gamma_{11} \Delta \phi_1 + \Gamma_{12} \Delta \phi_2) / (\Gamma_{21} \Delta \phi_1 + \Gamma_{22} \Delta \phi_2)$ as a function of $\omega_1^i$. Also plotted in Figure 1b is the corresponding ratio if thermodynamic coupling effects are ignored, $\Delta \phi_1 / \Delta \phi_2$. Neglect of thermodynamic coupling should be expected to have the effect of severely overestimating the ethanol/water permeation selectivity.

This article has threefold objectives. First, we aim to demonstrate that thermodynamic coupling effects are the root cause of mutual slowing-down effects that have been observed in the published experimental studies of Hietaharju et al.,$^3$ and Nasiri and Aroujalian$^4$ for ethanol/water pervaporation across PDMS membrane. The second objective is to show that the off-diagonal elements $\Gamma_{12}$ and $\Gamma_{21}$ also engender mutual slowing-down effects in hydrophilic (CA$^9$, polyimide$^{13}$ and PVA/PAN composite$^{11}$) membranes. The third objective is to offer deeper physicochemical insights into membrane permeation fluxes and selectivities by delineating the separate influences of diffusion and thermodynamic coupling for each of the case studies that are analyzed.

To meet the set objectives of this article, we analyze ethanol/water pervaporation across four different polymeric membranes: PDMS, CA, polyimide, and PVA/PAN composite. The Supporting Information accompanying this publication provides: (i) the F-H model parameters used in the phase equilibrium calculations and (ii) input data on the M-S diffusivities.

### RESULTS AND DISCUSSION

#### Analysis of Ethanol/Water/PDMS Permeation Data of Nasiri and Aroujalian

Nasiri and Aroujalian$^4$ report experimental data for pervaporation of ethanol(1)/water(2) mixtures across PDMS membrane, measured at three different temperatures: $T = 313$, 323, and 333 K. In eqs 19 and 20 of Nasiri and Aroujalian, used to model their own experiments, the M-S diffusivities are modified in the following manner to explicitly account for cluster formation leading to mutual slowing-down effects observed in their experiments:

$$D_{2m}^V = D_{2m}^V(0) \exp(e_{12}\phi_1) \exp(-b_{12}\phi_1^2 - b_{22}\phi_2^2)$$

$$D_{2m}^V = D_{2m}^V(0) \exp(e_{21}\phi_2) \exp(-b_{21}\phi_1^2 - b_{12}\phi_1\phi_2)$$ (11)

The set of plasticization, and clustering, coefficients, along with the zero-occupancy diffusivities are fitted for each of the three experiment sets; see Table 2 of their paper. Below, we adopt a different approach for modeling their three sets of experiments, using the linearized eq 10, invoking the Vignes interpolation formula $S$, along with eq 3 to describe the penetrant–membrane interactions. From sorption equilibrium, it is noted that the volume fractions of water, $\phi_2$, in the membrane are about 1–2 orders of magnitude lower than that of ethanol, $\phi_1$; therefore, the plasticization coefficients $e_{12}$, $e_{21}$ are taken as zero. We use the same set of plasticization coefficients for all three sets of experiments: $e_{12} = 5$; $e_{21} = 0$; $e_{12} = 12$; $e_{22} = 0$.

The fitted values of zero-occupancy M-S diffusivities are specified in Table S4 of the Supporting Information.

Two different scenarios A and B are used to model the Nasiri and Aroujalian experiments. The continuous solid lines in Figure 2a,b are obtained using scenario A, using eq 10, along with proper evaluation of $\Gamma_{ii}$ using the F-H eqs 1; there is good agreement...
agreement with experimental data (indicated by the symbols). The dashed lines in Figure 2a,b are model calculations using scenario B, also using eq 10, but ignoring thermodynamic coupling contributions by invoking the assumption $\Gamma_{ij} = \delta_{ij}$, the Kronecker delta. The use of scenario B leads to overestimation of both ethanol and water fluxes. This leads us to conclude that the mutual slowing-down effects are engendered by thermodynamic coupling effects.

Further insights into the influence of negative cross-coefficients $\Gamma_{12}$ and $\Gamma_{21}$ are obtained by comparing the ratio of the mass fluxes of ethanol to water (see Figure 3). Ignoring thermodynamic coupling (scenario B) overestimates the ethanol/water flux ratios at all three temperatures. The influence of negative values of $\Gamma_{12}$ and $\Gamma_{21}$ is to suppress the flux of ethanol to a greater extent than that of water, leading to lower ethanol/water separation selectivity.

To elucidate the contribution of the correlation effects, and also the plasticization coefficients, $\xi_{ij}$, we performed model calculations for scenario C in which (a) correlation effects are ignored, using eq 7, and (b) the influence of swelling is also ignored by setting $\xi_{ij} = 0$. In scenario C, the ratio of fluxes is described by

\[
\frac{N_{1}^{V}}{N_{2}^{V}} = \left( \frac{D_{12}^{\Delta}(0) (\Gamma_{11} \Delta \phi_{1} + \Gamma_{22} \Delta \phi_{2})}{D_{21}^{\Delta}(0) (\Gamma_{11} \Delta \phi_{1} + \Gamma_{22} \Delta \phi_{2})} \right) \quad \text{and} \quad \frac{N_{1}^{\text{mass}}}{N_{2}^{\text{mass}}} = \left( \frac{\rho_{1}^{L} N_{1}^{V} / V_{1}}{\rho_{2}^{L} N_{2}^{V} / V_{2}} \right) \frac{N_{1}^{\text{molar}}}{N_{2}^{\text{molar}}} = \frac{N_{1}^{V} / V_{1}}{N_{2}^{V} / V_{2}}
\]

Equation 12 is essentially the thermodynamically corrected driving flux ratio (cf. Figure 1b), multiplied by a constant factor. The dotted lines in Figure 3 represent model calculations of the ethanol/water mass flux ratios using eq 12. The agreement of scenario C with experiment is comparable to that of scenario A, which includes the effects

![Figure 2](image1.png)

**Figure 2.** (a, b) Experimental data (indicated by symbols) of Nasiri and Aroujalian for the mass pervaporation mass fluxes of penetrants ethanol (1) and water (2) across PDMS (m) at 313 K (red circles), 323 K (blue triangles), and 333 K (green squares), plotted as a function of the mass fraction of ethanol in the liquid feed mixture in the upstream compartment $\omega_{1}^{L}$. The continuous solid lines are M-S model calculations (scenario A) using eqs 3, 5, and 10. The dashed lines are flux calculations in which thermodynamic correction factors are ignored (scenario B), i.e., $\Gamma_{ij} = \delta_{ij}$. The input F-H and diffusivity data are provided in Tables S2 and S4 of the Supporting Information.

![Figure 3](image2.png)

**Figure 3.** Ratio of the mass flux of ethanol to that of water for ethanol/water pervaporation across PDMS at (a) 313 K, (b) 323 K, and (c) 333 K, plotted as a function of the mass fraction of ethanol in the liquid feed mixture in the upstream compartment $\omega_{1}^{L}$. Model calculations using three different scenarios A (continuous solid lines), B (dashed lines), and C (dotted lines) are compared to the experimental data (symbols) of Nasiri and Aroujalian. The input diffusivity data are provided in the Supporting Information.
of both correlations and plasticization. Two separate conclusions can be drawn. First, correlation effects are of negligible importance for ethanol/water/PDMS permeation. Second, swelling effects do not influence permeation selectivities in the three sets of Nasiri experiments in which the ethanol mass fraction in the upstream membrane compartment was restricted to \( \omega_{1L} < 0.7 \). Rather, swelling effects serve primarily to influence the magnitudes of the individual diffusivities \( D_{im} \) and fluxes \( N^i \).

**Analysis of Ethanol/Water/PDMS Permeation Data of Hietaharju.** Hietaharju et al.\(^3\) report experimental data on the mass fluxes of ethanol, \( \omega_{2L} \), in the bulk liquid mixture in the upstream compartment at temperatures \( T = 313 \) and 333 K. They\(^3\) also report experimental data for vapor permeation in which the ethanol/water vapor mixture, in equilibrium with an ethanol/water liquid-phase mixture at the corresponding dew point, is permeated across the membrane. The experimental data for the mass fluxes of ethanol and water are indicated by symbols in Figure 4a,b. The flux relations used by Hietaharju et al.\(^3\) to model their own experiments do not account for thermodynamic coupling effects (see eqs 28 and 29 of their paper). Consequently, the match of their model predictions with experiments is extremely poor, especially for ethanol (see Figure 7 of their paper). We demonstrate that the poor match between experimental data and model is wholly ascribable to thermodynamic coupling effects.

The continuous solid lines in Figure 4a,b are model calculations using scenario A, as detailed in the foregoing section; the agreement is very good for all three data sets. We also confirmed that neglecting correlation effects and using eq 7 to calculate \([\Lambda]\) lead to nearly identical values of permeation fluxes; this leads us to conclude that the coupling effects arise solely from thermodynamic influences and not from correlated motions of penetrants in the polymer matrix.

The dashed lines in Figure 4a,b represent model calculations for scenario B in which thermodynamic coupling effects are ignored; both the fluxes of ethanol and water are higher than the estimations using scenario A. The explanation for the decrease in both fluxes is traceable to the negative off-diagonal elements \( \Gamma_{i2} \) and \( \Gamma_{2i} \), as shown in Figure 1a.

Figure 5 plots the ratio of the mass fluxes of ethanol to water as a function of \( \omega_{1L} \) for the set of experiments at 313 K. The

![Figure 4](image-url)  
Figure 4. (a, b) Experimental data (indicated by symbols) of Hietaharju et al.\(^3\) for the pervaporation mass fluxes of penetrants ethanol (1) and water (2) across PDMS (m) at 313 K (red circles) and 333 K (green squares), and vapor permeation (blue triangles), plotted as a function of the mass fraction of ethanol in the liquid feed mixture in the upstream compartment \( \omega_{1L} \). The continuous solid lines are M-S model calculations (scenario A) using eqs 3, 5, and 10. The dashed lines are flux calculations in which thermodynamic correction factors are ignored (scenario B), i.e., \( \Gamma_{i2} = \delta_{i2} \). The input F-H and diffusivity data are provided in Tables S2 and S3 of the Supporting Information.

![Figure 5](image-url)  
Figure 5. Ratios of the mass fluxes of ethanol to water for ethanol/water pervaporation across PDMS at 313 K plotted as a function of the mass fraction of ethanol in the liquid feed mixture in the upstream compartment \( \omega_{1L} \). Model calculations using three different scenarios A (continuous solid lines), B (dashed lines), and C (dotted lines) are compared to experimental data (symbols) of Hietaharju et al.\(^3\). The input diffusivity data are provided in Tables S2 and S3 of the Supporting Information.

The influence of negative values of \( \Gamma_{i2} \) and \( \Gamma_{2i} \) is to suppress the flux of ethanol to a greater extent, leading to lower ethanol/water separation selectivity; consequently, the flux ratios calculated using scenario A (continuous solid lines) are significantly lower than those calculated using scenario B (dashed lines). Ignoring thermodynamic coupling (scenario B) overestimates the ethanol/water flux ratios at all three temperatures.

To gauge the importance of the influence of plasticization, the dotted lines in Figure 5 present calculations for scenario C, wherein eq 12 is used to determine the flux ratios. The estimations of scenario C are slightly poorer than those for scenario A, especially for the ethanol mass fractions in the upstream membrane compartment \( \omega_{1L} > 0.5 \). This suggests that plasticization influences the penetrant diffusivities to different extents; this influence manifests at higher penetrant occupancies in the membrane matrix.
Water/Ethanol Pervaporation across Hydrophilic Membranes. Figure 6a,b presents calculations of the ratios $\Gamma_{12}/\Gamma_{11}$ and $\Gamma_{21}/\Gamma_{22}$ for sorption equilibrium between bulk water(1)/ethanol(2) liquid mixtures and three different hydrophilic membranes: CA, polyimide, and PVA/PAN. For all three membranes, the two ratios are negative and we should anticipate that thermodynamic coupling would engender mutual slowing-down effects. For hydrophilic membranes, correlation effects should also be expected to be of significance because the more mobile penetrant, water, also has the higher permeation flux. These two anticipated results are tested below using three case studies.

We first performed pervaporation flux calculations for water(1)/ethanol(2)/CA (m) using the F-H and M-S diffusivity data provided by Mulder et al., who established that swelling effects are important and the experimental data could be adequately described by choosing $\varepsilon_{11} = \varepsilon_{12} = \varepsilon_{21} = \varepsilon_{22} = 7.3$.

The continuous solid lines in Figure 7a are flux calculations using scenario A. The negative off-diagonal elements $\Gamma_{12}$ and $\Gamma_{21}$ cause both water and ethanol fluxes to be reduced below the values anticipated by scenario B, i.e., $\Gamma_{ij} = \delta_{ij}$. The dashed line in Figure 7b represents water/ethanol flux ratios ignoring thermodynamic correction factors are ignored (scenario B). The assertion $\Gamma_{ij} = \delta_{ij}$ essentially implies the use of eq 7 for flux calculations. With increasing degrees of correlation, the water/ethanol flux ratio decreases, due to increasing retardation of the mobile penetrant water. The reasoning for this is that the magnitude of $\Gamma_{21}/\Gamma_{22}$ is larger than that of $\Gamma_{12}/\Gamma_{11}$. Consequently, we should expect thermodynamic coupling effects influence the ethanol flux to a greater extent than the water flux.

Figure 8a,b compares experimental data on the molar fluxes for pervaporation of water/ethanol mixtures across PVA/PAN composite membrane at 333 K, with calculations scenarios to estimate the degree of correlations, besides the Vignes interpolation formula 5: $\frac{B_{V2}}{\delta_{V1}} = 0$, $\frac{B_{V2}}{\delta_{V1}} = 5$, and $\frac{B_{V2}}{\delta_{V1}} = 20$. The assertion $\frac{B_{V2}}{\delta_{V1}} = 0$ essentially implies the use of eq 7 for flux calculations. With increasing degrees of correlation, the water/ethanol flux ratio decreases, due to increasing retardation of the mobile penetrant water. The dashed line in Figure 7b represents water/ethanol flux ratios ignoring thermodynamic coupling; this shows that the influence of the negative off-diagonal elements $\Gamma_{12}$ and $\Gamma_{21}$ is to reduce the flux of ethanol more than the flux of water. The reasoning for this is that the magnitude of $\Gamma_{21}/\Gamma_{22}$ is larger than that of $\Gamma_{12}/\Gamma_{11}$. Consequently, we should expect thermodynamic coupling effects influence the ethanol flux to a greater extent than the water flux.

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(indicated by the continuous solid lines) based on scenario A, in which the degree of correlations is quantified as $\frac{D_{21}^V}{D_{11}^V} = 3$, along with the choice $\varepsilon_{11} = \varepsilon_{12} = \varepsilon_{21} = \varepsilon_{22} = 5$. If thermodynamic coupling effects are ignored and $\Gamma_{ij} = \delta_{ij}$ (scenario B calculations shown by the dashed lines), the match with experiments is significantly worse, and both water and ethanol fluxes are overestimated to a significant extent.

In Figure 8c, the experimentally determined water/ethanol fluxes ratios are compared to M-S model flux calculations using three different degrees of correlations: $\frac{D_{21}^V}{D_{11}^V} = 0.2$, $\frac{D_{21}^V}{D_{11}^V} = 3$, and $\frac{D_{21}^V}{D_{11}^V} = 20$. The flux ratios reduce by more than 1 order of magnitude with increasing degree of correlations.

Figure 9a,b compares the experimental data\(^1\) on volumetric fluxes for pervaporation of water/ethanol mixtures across a polyimide membrane with model calculations based on scenarios A and B. There is good agreement between the experimental data and scenario A in which the degree of correlations is described by $\frac{D_{21}^V}{D_{11}^V} = 3$, along with $\varepsilon_{11} = \varepsilon_{12} = \varepsilon_{21} = \varepsilon_{22} = 2$. Use of scenario B, invoking $\Gamma_{ij} = \delta_{ij}$, leads to overestimation of both fluxes. To gauge the significance of correlations, Figure 9c compares the experimentally determined water/ethanol fluxes ratios with model calculations using scenario A to that of scenario C (using eq 12). Ignoring correlations has the effect of overestimating the water/ethanol selectivities by about an order of magnitude.

For all three cases studies on hydrophilic membranes analyzed above, the influence of swelling serves to enhance the diffusivities of either penetrant, but does not influence water/ethanol selectivities. On the other hand, the influence of thermodynamic coupling effects is to lower both water and ethanol fluxes, reducing the flux of ethanol more than the flux of water. In other words, the influence of swelling does not completely nullify the influence of thermodynamic coupling.

**General Applicability of the M-S Model for Describing Membrane Permeation.** In addition to the five different case studies discussed above, the applicability of the Maxwell–Stefan model eq 2 has been established for a number of other membrane permeation experimental studies.

For ethanol/water permeation across PDMS membrane, Aguilar-Valencia et al.\(^1\) use the M-S formulation to rationalize coupling between ethanol and water fluxes observed in their experiments. Experimental data on ethanol/water pervaporation across silicone rubber membranes are amenable to quantitative modeling with the M-S formulation.\(^25,26\) Ebneyamini et al.\(^3\) use the M-S formulation to model their experiments for dehydration of aqueous butanol solutions using hydrophobic membranes. However, thermodynamic coupling effects are not of significant importance because the experiments were conducted with dilute aqueous solutions for which both $\Gamma_{12} \approx 0$ and $\Gamma_{21} \approx 0$. Izgák et al.\(^27,28\) establish the applicability of the M-S formulation for a near-quantitative description of the pervaporation of 1-alcohol/toluene mixtures across low-density polyethylene membranes.

Mutual slowing-down effects are not restricted to pervaporation processes; they also manifest for permeation of gaseous $\text{CO}_2/\text{CH}_4$ across a cross-linked polyethylene oxide (XLPEO) membrane.\(^16,18\) The M-S model eq 2, with proper accounting of both thermodynamic coupling and correlation effects, is required for quantitative modeling of the experimental data; see Figures S14–S17 of the Supporting Information for details of analysis. Genduso et al.\(^29\) use an analogous approach to model coupling effects in $\text{CO}_2/\text{CH}_4$ permeation across the XLPEO membrane.

The M-S formulation is used to describe coupling effects during water/alcohol permeation across both hydrophilic and hydrophobic zeolite membranes,\(^30\) for which experimental
studies demonstrate the occurrence of mutual slowing-down effects.

**CONCLUSIONS**

Published experimental data for alcohol/water pervaporation across both hydrophobic (PDMS) and hydrophilic (CA, polyimide, PVA/PAN) membranes are modeled by combining the Flory–Huggins description of sorption equilibrium with the Maxwell–Stefan diffusion formulation. For steady-state permeation, this combination results in eq 10, in which the matrices $[\Lambda]$ and $[\Gamma]$ reflect, respectively, the diffusivity and thermodynamic contributions. In general, each of these matrices contains off-diagonal contributions; as a result, the fluxes of alcohol and water are coupled to each other. The following major conclusions emerge from our analysis.

1. For alcohol/water pervaporation across hydrophobic and hydrophilic membranes, the off-diagonal elements $\Gamma_{12}$ and $\Gamma_{21}$ are both negative in all of the cases examined. Consequently, the effective driving forces for penetrant transport are strongly influenced.

2. For both hydrophobic and hydrophilic membranes, the influence of thermodynamic coupling is to suppress the flux of both penetrants, leading to mutual slowing down. For hydrophobic membranes, the flux of ethanol is reduced to a greater extent, resulting in lower ethanol/water selectivity. On the other hand, for hydrophilic membranes, the water/ethanol selectivity is enhanced by the contribution of the negative off-diagonal elements $\Gamma_{12}$ and $\Gamma_{21}$.

3. For hydrophobic PDMS membranes, correlation effects appear to be of negligible importance because more mobile water is practically excluded from the polymer matrix. In sharp contrast, for hydrophilic membranes, correlation effects serve to reduce water/ethanol selectivities to a significant extent due to retardation of water transport.

4. While membrane swelling has the effect of influencing the magnitudes of the penetrant diffusivities, the corresponding influence on pervaporation selectivities is of minor importance for both hydrophobic and hydrophilic membranes.

5. The distinction between swelling effects and thermodynamic coupling effects can be summarized as follows: swelling influences diffusivities, whereas the off-diagonal elements of the matrix of thermodynamic correction factors influence the driving forces for transport of penetrants.

**ASSOCIATED CONTENT**

* Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02255.

Detailed derivation of the Maxwell–Stefan equations, the F-H model parameters used in the phase equilibrium calculations, and input data on the M-S diffusivities (PDF)

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NOMENCLATURE

Latin Alphabet

- $a_i$: activity of species $i$, dimensionless
- $D_{ij}^V$: modified M-S diffusivity for binary penetrant pair $i$-$j$, m$^2$/s
- $D_{ij}^M$: modified M-S diffusivity for penetrant $i$ in polymer $j$, m$^2$/s
- $M_i$: molar mass of species $i$, kg mol$^{-1}$
- $M$: mean molar mass of mixture, kg mol$^{-1}$
- $N_i$: molar flux of species $i$, mol m$^{-2}$ s$^{-1}$
- $N_{maxi}$: molar flux of species $i$, kg m$^{-2}$ s$^{-1}$
- $N_i^V$: volumetric flux of species $i$, m$^3$ m$^{-2}$ s$^{-1}$
- $R$: gas constant, 8.314 J mol$^{-1}$ K$^{-1}$
- $T$: absolute temperature, K
- $d_i$: distance coordinate along membrane thickness, m
- $\delta$: upstream face of membrane, $z = 0$
- $\delta_i$: upstream face of membrane, $z = \delta$
- $\epsilon_{ij}$: plasticization coefficient, dimensionless
- $[\Gamma]$: matrix of thermodynamic factors, dimensionless
- $\delta$ (Greek letter): thickness of membrane, m
- $\delta_{ij}$: Kronecker delta, dimensionless
- $\phi_i$: volume fraction of penetrant $i$ in polymer, dimensionless
- $\phi_{i0}$: volume fraction of penetrant $i$, dimensionless
- $\phi_{ij}$: volume fraction in bulk liquid mixture, dimensionless
- $\phi$: volume fraction of polymer, dimensionless
- $\phi_i$: volume fraction of component $i$, m$^3$ m$^{-3}$
- $\chi$: interaction parameter in Flory–Huggins model, dimensionless
- $\omega_i$: mass fraction of component $i$ in liquid-phase feed mixture, dimensionless
- $\bar{V}_{ij}$: partial molar volume of species $i$, m$^3$ mol$^{-1}$
- $\bar{V}_{ij}$: molar volume of mixture, m$^3$ mol$^{-1}$

Greek Alphabet

- $\Gamma$: thermodynamic factors, dimensionless
- $[\Gamma]$: matrix of thermodynamic factors, dimensionless
- $\delta$: thickness of membrane, m
- $\delta_{ij}$: Kronecker delta, dimensionless
- $\epsilon_{ij}$: plasticization coefficient, dimensionless
- $[\Lambda]$: matrix of Maxwell–Stefan diffusivities, m$^2$/s
- $\mu$: molar chemical potential, J mol$^{-1}$
- $\phi_i$: volume fraction of penetrant $i$ in polymer, dimensionless
- $\phi_{i0}$: volume fraction of penetrant $i$, dimensionless
- $\phi_{ij}$: volume fraction in bulk liquid mixture, dimensionless
- $\rho_i$: mass density of component $i$, kg m$^{-3}$
- $\chi$: interaction parameter in Flory–Huggins model, dimensionless
- $\omega_i$: mass fraction of component $i$ in liquid-phase feed mixture, dimensionless

Subscripts

- $i$: referring to penetrant $i$
- $m$: referring to membrane
- $0$: upstream face of membrane, $z = 0$
- $\delta$: upstream face of membrane, $z = \delta$

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