Practical Friction-Based Approach to Modeling Multicomponent Diffusion

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Although most industrial drying and separation technologies are based on transport of multiple components, a convenient and practical means of describing multicomponent diffusion over wide temperature and concentration ranges has not been developed for polymer solutions or even for simple liquid mixtures. We have been able to demonstrate that all of the diffusion coefficients required to describe molecular transport in multicomponent systems can be easily predicted from self-diffusion coefficients and thermodynamic information when the mass flux with respect to the mass-average velocity is expressed in terms of the frictional force experienced by a molecule as it undergoes Brownian motion. This approach enables the flux equations for any combination of materials to be written in terms of experimentally measurable quantities. The model was tested by: (1) predicting literature data for principal diffusion coefficients in a ternary system; (2) applying the diffusion model to predict the drying behavior of three ternary systems; (3) predicting experimental values of the principal and cross coefficients for a ternary organic solvent mixture from self-diffusion data measured by PFG-NMR and available thermodynamic data; and (4) examining whether the limiting cases in this model are physically realistic. The applicability of the model to gas transport and polymer interdiffusion is also briefly examined.

Introduction

In the analysis of molecular transport, a diffusion coefficient is generally experimentally evaluated from the proportionality of the flux and the compositional gradient of a particular species (Fick, 1855). For a binary system, a unique diffusion coefficient D describes molecular transport at a particular temperature, pressure, and composition. When three or more components are present in the system, the diffusion coefficients determined in this manner are simply effective, pseudo-binary values (Cussler, 1976). A rigorous analysis of multicomponent diffusion considers how the flux of one component is influenced by not only its own concentration gradient but by the concentration gradients of every other component in the system (Onsager, 1931; DeGroot and Mazur, 1962; Cussler, 1976). Thus, an array of diffusion coefficients is required to completely describe the various fluxes.

The number of diffusion coefficients D_{ij} employed to describe transport within a system of n components is equal to $(n-1)^2$. The diagonal terms of the array (D_{ii}) are called the main or principal diffusion coefficients, while the off-diagonal terms (D_{ij}, where $i \neq j$) are termed the cross-coefficients. The principal coefficients reflect the effect that a concentration gradient of component i has on the flux of component i, while the cross-coefficients indicate the effect that a concentration gradient of component j has on the flux of component i ($i \neq j$). On the basis of the Onsager reciprocal relations (Onsager, 1931), however, these coefficients are subject to certain restraints that reduce the number of independent diffusion coefficients in an n-component system to $n(n-1)/2$.

Two mathematical frameworks developed to elucidate multicomponent diffusion include the generalized Stefan-Maxwell and Onsager formalisms (Cussler, 1976). The Stefan-Maxwell approach (Stefan, 1872; Maxwell, 1867; Lightfoot et al., 1962) describes the multicomponent diffusion process in terms of the mutual diffusion coefficients of the

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individual binary pairs within the system. The second, developed by Onsager (1931), suggests that a generalization of Fick's law can be used to explain transport in dense systems. In this case, one component must arbitrarily be designated as a *solvent*. The flux of the *solute* molecules can then be written in terms of concentration gradients in all of the solute molecules in the system. The Stefan-Maxwell model, particularly the generalized form suggested by Lightfoot et al. (1962), has gained popular acceptance in examining gas transport and diffusion in porous media (Krishna and Wesselingh, 1997; Krishna, 1993), since all of the coefficients can be estimated from the kinetic theory of gases (Curtiss and Hirschfelder, 1949). The applicability of either of these theories to simple liquid or polymeric systems, however, is limited since the Stefan-Maxwell diffusivities are not the same as the binary diffusivities for these systems (Curtiss and Bird, 1996, 1997) and the D_{ij} for the Onsager formalism tend to be strong functions of concentration (Cussler, 1976).

By expressing the chemical potential gradient in terms of the mass average velocity and the frictional force experienced by a molecule relative to its rate of Brownian motion, we propose in this work a method of accurately predicting the main and cross diffusion coefficients for the Onsager model from self-diffusion and thermodynamic data. Although some researchers use the term self-diffusion to represent the rate of Brownian motion of a molecule when surrounded by identical molecules (Reid et al., 1977), the self-diffusion coefficient of a molecule is often considered to be a proportionality factor relating its mean-squared displacement with time as it undergoes a random walk in *any* homogeneous medium (such as Bearman, 1961; Vrentas and Duda, 1977a; Blum, 1986). Consequently, this coefficient exhibits dependences on temperature, pressure, and concentration. We have adopted the latter definition of self-diffusion for use in this article.

The model has been tested by: (1) predicting literature D_{ij} data for a ternary organic solvent mixture consisting of acetone, benzene, and methanol from self-diffusion data measured by PFG-NMR and from available thermodynamic data; (2) predicting diffusion behavior in a system consisting of methanol, toluene, and poly(vinyl acetate), using free-volume predictions of ternary self-diffusion behavior along with the Flory-Huggins model for polymer-solvent interaction; (3) applying the model to predict the drying behavior of three solvent-coated polymer films containing (i) polystyrene/toluene/ethylbenzene, (ii) polystyrene/toluene/benzene, and (iii) polystyrene/toluene/tetrahydrofuran; and (4) examining whether the limiting cases in the model are physically realistic. The applicability of the model to multicomponent gas transport in porous media and polymer interdiffusion is also briefly examined.

Theory

The Bearman (1961) statistical mechanical theory contends that shortly after a concentration gradient is established in an isothermal, isobaric system, a quasi-stationary regime is reached in which the driving force for diffusion, that is, the negative of the chemical potential gradient, equals the opposing frictional force. Thus, the chemical potential gradient for component 1 in the system can be expressed as

$$\Delta\mu_1 = -\frac{\rho_2 N_A^2 \zeta_{12}(v_1 - v_2)}{M_2} - \frac{\rho_3 N_A^2 \zeta_{13}(v_1 - v_3)}{M_3} - \cdots \quad (1)$$

Here, μ_1 is the chemical potential of component 1 with units of energy per mole, ζ_{ij} are the coefficients that describe the frictional force between molecules i and j, while ρ_i and M_i denote the mass density and molecular weight of component i, respectively. In addition, N_A is Avogadro's number (mol^{-1}), and v_i is the species velocity of component i (cm/s). In this relationship, the frictional force between molecules i and j, ζ_{ij}, is inherently assumed to be identical to that between molecules j and i, ζ_{ji} (Bearman and Kirkwood, 1958; Bearman, 1961; Hess et al., 1990). This assumption implies the validity of the Onsager reciprocal relations for the case of diffusion in isothermal systems (Bearman and Kirkwood, 1958). Although the coefficients are different, the Bearman model is comparable to the Stefan-Maxwell model since the chemical potential gradient in both models is related to relative velocities through drag or friction coefficients.

Although diffusion flux expressions (j_i) can be written in terms of these friction coefficients (Vrentas et al., 1985a), the practical application of these equations in liquid or polymeric systems is inevitably accomplished by assuming that (i) the cross-coefficients $(D_{ij},\ i \neq j)$ are equal to zero and (ii) the principal diffusion coefficients (D_{ii}) are approximately equal to the self-diffusion coefficients (D_i) in the dilute concentration range (Vrentas et al., 1985a).

The task of evaluating ζ_{ij} $(i \neq j)$ becomes particularly difficult when one realizes that these coefficients are strongly dependent on temperature and concentration and that the number of coefficients to be evaluated in an n-component mixture, assuming symmetry, is $n(n-1)/2$. Since a straightforward means of evaluating or predicting these coefficients unambiguously is currently unavailable, an alternate approach to modeling multicomponent diffusion is expected to be valuable in many commercial processes.

Description of multicomponent diffusion can be dramatically simplified if one considers the frictional force a molecule experiences *on average* within a system, rather than evaluates the individual frictional forces between a molecule and every other molecule in the system, as is typically done (Krishna, 1993, 1997). To this end, we write a force balance between the chemical potential gradient and the average resistive force (Hanley, 1985), namely

$$\nabla\mu_i = -f_i M_i (v_i - v) \quad (2)$$

Here, f_i corresponds to the friction that component i experiences on average in the multicomponent mixture, v_i is the species velocity of component i, and v denotes the mass-average velocity (cm/s). The mass-average velocity is selected since this is the reference frame in which force balances apply.

Defined in this way, only $n-1$ friction coefficients must be evaluated in an n-component system, representing a significant reduction from Bearman's formalism. Equation 2 can be obtained directly from the Bearman model by imposing a direct proportionality between ζ_{ij} and M_j (see Appendix A).

Model Development

Consider the definition (Bird et al., 1960) of the mass flux relative to the mass average velocity j_i (g/cm$^2\cdot$s)

$$j_i = \rho_i(v_i - v) \tag{3}$$

On the basis of Eq. 2, j_i may also be expressed as

$$j_i = -\frac{\rho_i \nabla \mu_i}{f_i M_i} \tag{4}$$

Furthermore, since the summation of the individual component mass fluxes must equal zero, then it immediately follows that

$$\sum_{i=1}^{n} j_i = \sum_{i=1}^{n} \frac{\rho_i \nabla \mu_i}{f_i M_i} = 0 \tag{5}$$

To apply Onsager's flux equations (Onsager, 1931), we relate the mass flux of component i with respect to the volume-average velocity $j_i^{\neq}$ to the mass flux of component i with respect to the mass-average velocity through

$$j_i^{\neq} = j_i - \rho_i \sum_{i=1}^{n} \hat{V}_i j_i \tag{6}$$

where $\hat{V}_i$ is the partial specific volume of component i (cm^3/g). Since Eq. 6 is an uncommon way of expressing the flux, we relate this equation to the familiar expression for $j_i^{\neq}$ in terms of the volume-average velocity (Bird et al., 1960) in Appendix B. For the sake of brevity and applicability to the data reported here, we hereafter develop the expressions for diffusion in a ternary system. Application of the model to higher-order multicomponent systems is straightforward and is left to the interested reader.

For a ternary system, the flux of component 1 from Eq. 6 is

$$j_1^{\neq} = j_1 - \rho_1\left[\hat{V}_1 j_1 + \hat{V}_2 j_2 + \hat{V}_3 j_3\right] \tag{7}$$

Substitution of Eq. 4 into Eq. 7 yields

$$j_1^{\neq} = \frac{-\rho_1 \nabla \mu_1}{f_1 M_1} - \rho_1\left[\hat{V}_1\left(\frac{-\rho_1 \nabla \mu_1}{f_1 M_1}\right) + \hat{V}_2\left(\frac{-\rho_2 \nabla \mu_2}{f_2 M_2}\right) + \hat{V}_3\left(\frac{-\rho_3 \nabla \mu_3}{f_3 M_3}\right)\right] \tag{8}$$

Application of Eq. 5 permits Eq. 8 to be rewritten as

$$j_1^{\neq} = \frac{\rho_1 \nabla \mu_1}{f_1 M_1}\left[-1 + \rho_1 \hat{V}_1 - \rho_1 \hat{V}_3\right] + \frac{\rho_1 \rho_2 \nabla \mu_2}{f_2 M_2}\left[\hat{V}_2 - \hat{V}_3\right] \tag{9}$$

A similar analysis for $j_2^{\neq}$ yields

$$j_2^{\neq} = \frac{\rho_2 \nabla \mu_2}{f_2 M_2}\left[-1 + \rho_2 \hat{V}_2 - \rho_2 \hat{V}_3\right] + \frac{\rho_2 \rho_1 \nabla \mu_1}{f_1 M_1}\left[\hat{V}_1 - \hat{V}_3\right] \tag{10}$$

According to Onsager (1931), the flux of a solute molecule (relative to the volume-average velocity) is caused by concentration gradients in all of the solutes. Expressed in this fashion, one component in the system is arbitrarily designated as the solvent. Thus, for a ternary system this amounts to (Cussler, 1976)

$$j_1^{\neq} = -D_{11}\nabla\rho_1 - D_{12}\nabla\rho_2 \tag{11}$$

$$j_2^{\neq} = -D_{21}\nabla\rho_1 - D_{22}\nabla\rho_2 \tag{12}$$

According to the phase rule, for a homogeneous ternary system in which temperature (T) (K) and pressure (P) (mm Hg) are fixed, the concentration of only two components may be specified. Consequently, we find that

$$\nabla\mu_i = \left(\frac{\partial \mu_i}{\partial \rho_1}\right)_{T,P,\rho_2}\nabla\rho_1 + \left(\frac{\partial \mu_i}{\partial \rho_2}\right)_{T,P,\rho_1}\nabla\rho_2 \tag{13}$$

Substitution of Eq. 13 into Eqs. 9 and 10 followed by a comparison of the results with Eqs. 11 and 12 yields the following relationships for the ternary diffusion coefficient array in terms of the friction coefficients that are forced to satisfy the Gibbs-Duhem relation of thermodynamics

$$D_{11} = \frac{\rho_1}{M_1 f_1}\left[1 - \rho_1 \hat{V}_1 + \rho_1 \hat{V}_3\right]\left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,P,\rho_2} + \frac{\rho_1 \rho_2}{M_2 f_2}\left[\hat{V}_3 - \hat{V}_2\right]\left(\frac{\partial \mu_2}{\partial \rho_1}\right)_{T,P,\rho_2} \tag{14}$$

$$D_{12} = \frac{\rho_1}{M_1 f_1}\left[1 - \rho_1 \hat{V}_1 + \rho_1 \hat{V}_3\right]\left(\frac{\partial \mu_1}{\partial \rho_2}\right)_{T,P,\rho_1} + \frac{\rho_1 \rho_2}{M_2 f_2}\left[\hat{V}_3 - \hat{V}_2\right]\left(\frac{\partial \mu_2}{\partial \rho_2}\right)_{T,P,\rho_1} \tag{15}$$

$$D_{21} = \frac{\rho_1 \rho_2}{M_1 f_1}\left[\hat{V}_3 - \hat{V}_1\right]\left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,P,\rho_2} + \frac{\rho_2}{M_2 f_2}\left[1 - \rho_2 \hat{V}_2 + \rho_2 \hat{V}_3\right]\left(\frac{\partial \mu_2}{\partial \rho_1}\right)_{T,P,\rho_2} \tag{16}$$

$$D_{22} = \frac{\rho_1 \rho_2}{M_1 f_1}\left[\hat{V}_3 - \hat{V}_1\right]\left(\frac{\partial \mu_1}{\partial \rho_2}\right)_{T,P,\rho_1} + \frac{\rho_2}{M_2 f_2}\left[1 - \rho_2 \hat{V}_2 + \rho_2 \hat{V}_3\right]\left(\frac{\partial \mu_2}{\partial \rho_2}\right)_{T,P,\rho_1} \tag{17}$$

Although somewhat simpler in form than the coefficients derived from Bearman's theory (1961), these expressions still cannot be applied practically since the temperature and concentration dependence of the f_i remain unknown. To circumvent this problem, we consider that the friction a molecule experiences in a mixture is related to its rate of Brownian motion through the classic relation derived by Einstein (1906), namely,

$$D_i = \frac{RT}{M_i f_i} \tag{18}$$

In this equation D_i is the self-diffusion coefficient of component i ($\mathrm{cm^2/s}$) in the multicomponent mixture and R is the gas constant (1.9872 cal/mol·K). Although D_i exhibits concentration and temperature dependence (Bearman, 1961; Vrentas and Duda, 1977a), these coefficients can be measured experimentally by analytical techniques such as pulsed field gradient nuclear magnetic resonance (Blum, 1986), isotopic exchange (Bueche et al., 1952), or forced Rayleigh scattering (Sillescu and Ehlich, 1990). Furthermore, D_i can often be evaluated for liquid and polymer systems by application of free-volume theory (Cohen and Turnbull, 1959; Fujita, 1961; Vrentas and Duda, 1977a,b).

Substituting Eq. 18 into Eqs. 14 to 17 provides a functional form of the coefficients required to describe diffusion in a ternary mixture, since the self-diffusion coefficients can be measured experimentally (or predicted theoretically) and the chemical potential gradients can be estimated from equilibrium data

$$D_{11} = \frac{D_1 \rho_1}{RT}\left[1 - \rho_1 \hat{V}_1 + \rho_1 \hat{V}_3\right]\left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,P,\rho_2} + \frac{D_2 \rho_1 \rho_2}{RT}\left[\hat{V}_3 - \hat{V}_2\right]\left(\frac{\partial \mu_2}{\partial \rho_1}\right)_{T,P,\rho_2} \tag{19}$$

$$D_{12} = \frac{D_1 \rho_1}{RT}\left[1 - \rho_1 \hat{V}_1 + \rho_1 \hat{V}_3\right]\left(\frac{\partial \mu_1}{\partial \rho_2}\right)_{T,P,\rho_1} + \frac{D_2 \rho_1 \rho_2}{RT}\left[\hat{V}_3 - \hat{V}_2\right]\left(\frac{\partial \mu_2}{\partial \rho_2}\right)_{T,P,\rho_1} \tag{20}$$

$$D_{21} = \frac{D_1 \rho_1 \rho_2}{RT}\left[\hat{V}_3 - \hat{V}_1\right]\left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,P,\rho_2} + \frac{D_2 \rho_2}{RT}\left[1 - \rho_2 \hat{V}_2 + \rho_2 \hat{V}_3\right]\left(\frac{\partial \mu_2}{\partial \rho_1}\right)_{T,P,\rho_2} \tag{21}$$

$$D_{22} = \frac{D_1 \rho_1 \rho_2}{RT}\left[\hat{V}_3 - \hat{V}_1\right]\left(\frac{\partial \mu_1}{\partial \rho_2}\right)_{T,P,\rho_1} + \frac{D_2 \rho_2}{RT}\left[1 - \rho_2 \hat{V}_2 + \rho_2 \hat{V}_3\right]\left(\frac{\partial \mu_2}{\partial \rho_2}\right)_{T,P,\rho_1} \tag{22}$$

The diffusion equations presented in Eqs. 11, 12, and 19 to 22 do not specify the constituents of the ternary mixture, that is, the system could consist of three gases, three liquids, three polymers, or any combination thereof. In the following sections, we examine limiting behavior of the proposed model and compare predictions from these equations to experimental data.

Experimental Studies

Self-diffusion coefficients of acetone, benzene, and methanol were measured at a variety of compositions by pulsed field gradient nuclear magnetic resonance (PFG-NMR). This work was done on a Bruker AMX-360 at a ^{1}H resonance frequency of 360 MHz using a 5-mm inverse probe equipped with z-gradients. The Hahn echo experiments with pre-gradient pulses were performed at 25°C using an observation time of 3.6 ms. The gradient strength was varied between 0 and 308 G/cm during the course of an individual experiment.

Results and Discussion

Limiting cases

In a binary system, the mutual diffusion coefficient D is equal to the self-diffusion coefficient of component 1 in the concentration limit of pure 2, that is, $D(\rho_1 \to 0) = D_1(\rho_1 \to 0)$. If one of the components is a polymer or a solid, D can be estimated over the rest of the concentration interval from the product of the self-diffusion coefficient of the more mobile species and a thermodynamic term (Duda et al., 1979; Vrentas and Vrentas, 1993). The ternary equations presented in Eqs. 19 to 22 conform to these limiting cases if $\rho_2 = 0$, so that the ternary system collapses to a binary system composed of components 1 and 3.

When $\rho_2 = 0$ and $\rho_1 \to 0$, the principal diffusion coefficient describing the flux of component 1, D_{11}, is given by D_1, the self-diffusion coefficient of component 1, while the cross-diffusion coefficient, D_{12}, is zero. At finite concentrations of component 1, D_{11} is predicted to equal the product of D_1 and a thermodynamic term related to the chemical potential gradient of component 1 in a manner analogous to established theoretical formalisms (Duda et al., 1979; Vrentas and Vrentas, 1993). Analogous results are achieved if ρ_1 is set equal to zero and a binary system of components 2 and 3 ensues.

If we consider the case when the mobility of the two diffusing species in a binary mixture is comparable (such as for polymer interdiffusion), the resulting expression from our model (see Eq. 19) is reminiscent of those expressions developed by Kramer et al. (1984) and Sillescu (1984) for fast-mode polymer-polymer diffusion. The fast-model diffusion theory is currently considered the best representation of transport in polymer-polymer systems. We conclude, therefore, that in the infinitely dilute limit of each of the components, Eqs. 19 to 22 correctly match the diffusion behavior expected for binary systems.

Ternary system (2 solvents, 1 polymer)

Capillary column inverse gas chromatography (CCIGC) has gained tremendous popularity (Pawlisch et al., 1987; Hadj Romhane et al., 1995; Surana et al., 1997) as an expedient and reliable technique to measure diffusion and partition coefficients in polymer/solvent systems in the pure polymer limit. Recent advances (Tihminlioglu et al., 1997) have extended the applicability of CCIGC into the range of finite solvent concentrations so that (i) binary mutual diffusion coefficients can be measured over broad ranges of temperature and concentration, and (ii) limited transport and equilibrium information can be ascertained for multicomponent systems.

A ternary system consisting of methanol (1), toluene (2), and poly(vinyl acetate) (PVAc) (3) constitutes the subject of one such recent investigation (Surana et al., 1998). In that study, the effect of toluene on the transport rate of methanol (and vice versa) within the ternary mixture was assessed. Since trace amounts of penetrant were employed in all the CCIGC experiments, the diffusion coefficients measured are presumed to be the principal coefficients.

In order to apply the present model (Eqs. 19 to 22) to predict diffusion behavior in this ternary system, estimates for the solvent self-diffusion coefficients in the ternary system are needed. Although experimental data are not available for this ternary system, data for the binary pairs methanol-PVAc (Kishimoto, 1964) and toluene-PVAc (Vrentas et al., 1985b) are available. By correlating these data with the binary form of the free-volume theory of diffusion (Vrentas and Duda, 1977a,b) for a binary polymer-solvent system, one can predict the self-diffusion behavior of the two penetrants in a polymer-solvent-solvent system (Vrentas et al., 1984) D_1 and D_2, from

$$D_1 = D_{o1}\exp\left(\frac{-\gamma\left(\omega_1\hat{V}_1^* + \omega_2\frac{\xi_{13}}{\xi_{23}}\hat{V}_2^* + \omega_3\hat{V}_3^*\xi_{13}\right)}{\hat{V}_{FH}}\right) \tag{23}$$

$$D_2 = D_{o2}\exp\left(\frac{-\gamma\left(\omega_1\hat{V}_1^*\frac{\xi_{23}}{\xi_{13}} + \omega_2\hat{V}_2^* + \omega_3\hat{V}_3^*\xi_{23}\right)}{\hat{V}_{FH}}\right) \tag{24}$$

where

$$\frac{\hat{V}_{FH}}{\gamma} = \sum_{i=1}^{3}\omega_i\frac{K_{1i}}{\gamma}\left(K_{2i} - T_{gi} + T\right) \tag{25}$$

All of the parameters comprising Eqs. 23 to 25 can be determined from pure-component physical property data and from analysis of binary mutual-diffusion data (Duda and Zielinski, 1996). These parameters are listed in Table 1, and the binary diffusion data correlations employed here are presented in Figures 1 and 2 for methanol-PVAc and toluene-PVAc, respectively.

Methanol and toluene self-diffusion coefficients predicted from Eqs. 23 to 25, as well as estimates of chemical potential gradients from the Flory-Huggins theory (Flory, 1942; Huggins, 1942), have been substituted into Eqs. 19 to 22 to estimate the principal and cross-diffusion coefficients of the

Table 1. Parameters for Ternary Free-Volume Model (Eqs. 23–25)

D_{o1}	1.41×10^{-3} cm^2/s
D_{o2}	1.89×10^{-4} cm^2/s
$\hat{V}_1^*$	0.959 cm^3/g
$\hat{V}_2^*$	0.917 cm^3/g
$\hat{V}_3^*$	0.728 cm^3/g
K_{11}/γ	9.73×10^{-4} cm^3/g·K
$K_{21} - T_{g1}$	−38.09 K
K_{12}/γ	1.57×10^{-3} cm^3/g·K
$K_{22} - T_{g2}$	−90.5 K
K_{13}/γ	4.33×10^{-4} cm^3/g·K
$K_{23} - T_{g3}$	−256.4 K
ξ_{13}	0.53
ξ_{23}	0.67

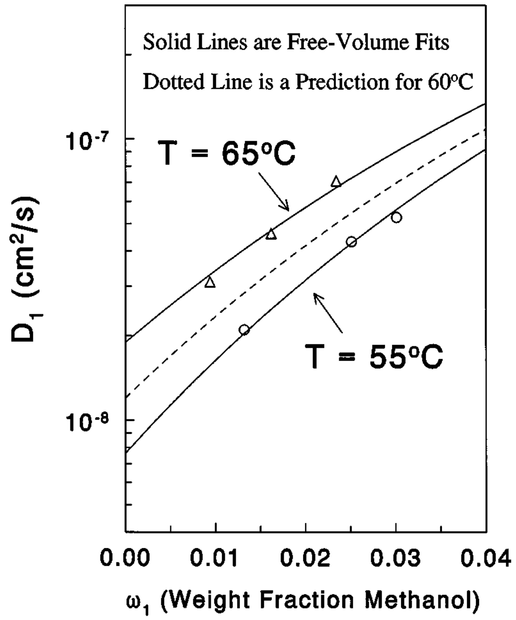

Figure 1. Experimental data (Kishimoto, 1964) and free-volume theory correlation (——) for methanol/PVAC self-diffusion coefficients at 55 and 65°C.

FV prediction of the diffusion behavior expected at 60°C is also indicated (– – –).

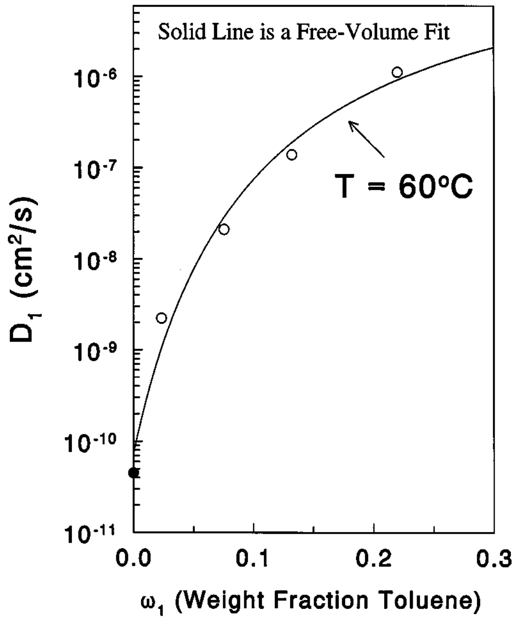

Figure 2. Experimental data and free-volume theory correlation (——) for toluene/PVAC mutual diffusion at 60°C.

(○) represent literature data (Vrentas et al., 1985b), while (●) is a datum obtained in this study by capillary column inverse gas chromatography.

methanol-toluene-PVAc ternary system. The values of χ_{12}, χ_{13}, and χ_{23} used in these calculations are 1.00, 1.19, and 0.78, respectively, and the partial specific volumes $\hat{V}_1$, $\hat{V}_2$, and $\hat{V}_3$ are assumed to be independent of concentration and equal to 1.326, 1.203, and 0.861 cm^3/g, respectively.

Model predictions for the principal diffusion coefficients are presented in Figures 3 and 4 along with available experimental data collected by CCIGC (Surana et al., 1998). Considering that the results from our model are based on predictions of ternary self-diffusion behavior from binary diffusion data correlations, the model predictions are considered to be in good agreement with the experimental data. For completeness, we present the effect of concentration on all of the diffusion coefficients in this ternary system in a series of contour plots in Figures 5a and 5b. Figures 5a and 5b clearly illustrate that our model predicts the cross-coefficients are of comparable magnitude with the principal coefficients under certain conditions.

Drying predictions: ternary system (2 solvents, 1 polymer)

Among the ultimate envisioned usages of the proposed model (Eqs. 19 to 22) are the modeling of devolatilization and the drying of solvent-coated polymer films. Drying of polymer solutions impacts the manufacture of photographic films, synthetic fibers, adhesives, and a variety of other polymeric products. Appropriately accounting for the momentum, heat, and mass transfer aspects during the formation of a polymer film by removal of a single solvent from a polymer solution has been the focus of several recent publications (Yapel, 1988; Vrentas and Vrentas, 1994; Alsoy and Duda, 1996). The principles evoked in these studies have been recently extended (Alsoy and Duda, 1998) and applied to examine the drying of multicomponent polymer solutions both through experimentation and simulation.

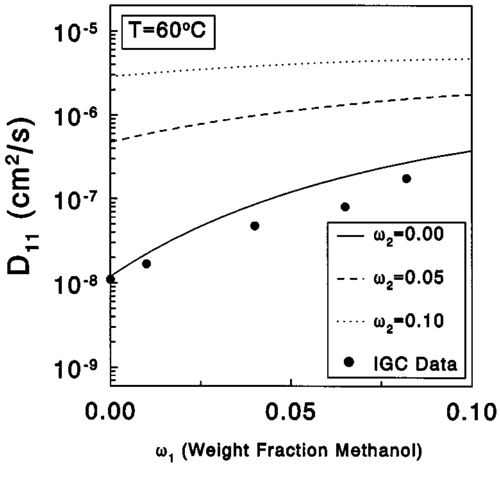

Figure 3. Experimental data (Surana et al., 1998) vs. theoretical predictions from Eqs. 19 to 22 for the principal diffusion coefficient D_{11} in a ternary system consisting of methanol (1), toluene (2), and poly(vinyl acetate) (3) at 60°C and various concentrations.

The predicted effect of toluene concentration from Eq. 19 is also indicated as dotted lines.

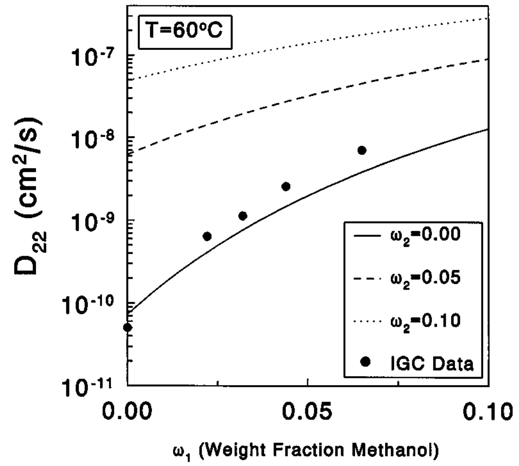

Figure 4. Experimental data (Surana et al., 1998) vs. theoretical predictions from Eqs. 19 to 22 for the principal diffusion coefficient D_{22} in a ternary system consisting of methanol (1), toluene (2), and poly(vinyl acetate) (3) at 60°C and various concentrations.

The predicted effect of toluene concentration from Eq. 22 is also indicated as dotted lines.

By inserting our diffusion model (Eqs. 19 to 22) into the multicomponent drying analysis developed by Alsoy and Duda (1998), we are able to examine the rate of total solvent removal as a function of time for three systems for which literature data exist: (i) polystyrene/toluene/ethylbenzene (Alsoy and Duda, 1998), (ii) polystyrene/toluene/benzene (Alsoy and Duda, 1998), and (iii) polystyrene/toluene/tetrahydrofuran (Drake and Wang, 1989). The concentration and temperature dependence of the solvent self-diffusion coefficients was represented by Eqs. 23 to 25 with the appropriate free-volume parameters. Comparison of the predicted and experimentally measured drying behavior for these systems is presented in Figures 6 to 8. The predictions are in good agreement with the experimental data in all cases.

Ternary system (three organic liquids)

Although multicomponent diffusion processes are relatively common, evaluation of both the principal and cross-diffusion coefficients is seldom performed. In one study by Alimadadian and Colver (1976), however, all of the diffusion coefficients were determined in a mixture consisting of acetone, benzene, and methanol at 25°C. Thermodynamic data available for this ternary system have been analyzed through the use of a modified version of the Peng-Robinson equation of state. The derivatives required in Eqs. 19 to 22 have been estimated by performing a finite difference analysis, that is, the composition was incrementally decreased until no noticeable change was observed in the chemical potential gradient.

The self-diffusion coefficients of acetone, benzene, and methanol in ternary mixtures of varied composition were

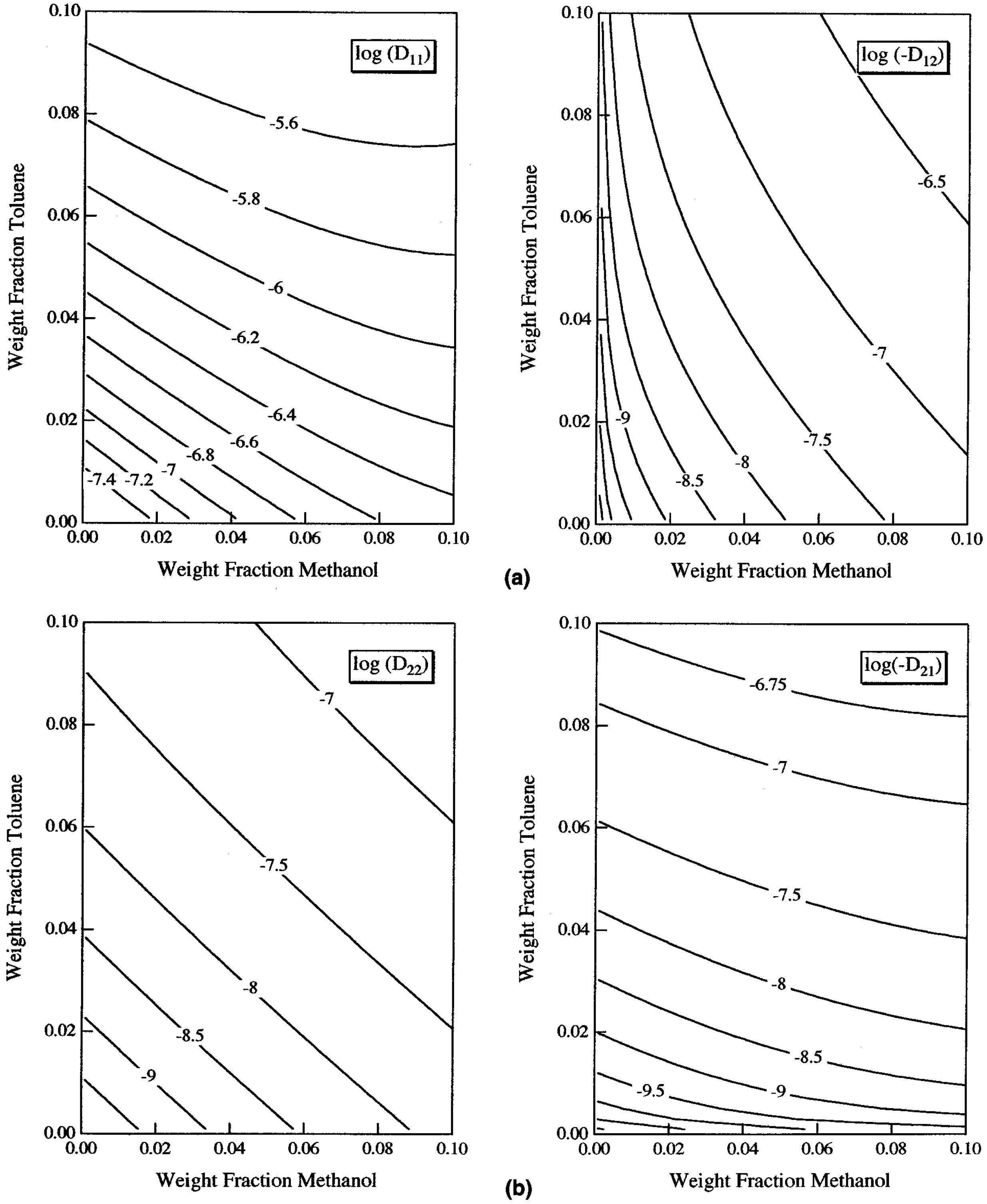

Figure 5. Contour plots highlighting the predicted effect of toluene and methanol concentration from Eqs. 19 to 22, on the principal and cross-diffusion coefficients: (a) D_{11} and D_{12}; (b) D_{22} and D_{21}, in a ternary mixture composed of methanol (1), toluene (2), and poly(vinyl acetate) at 60°C.

measured by PFG-NMR at 25°C. The compositions evaluated were chosen to match the multicomponent data available in the literature (see Table 2). By using these data, as well as the chemical potential gradients and partial specific volumes determined from a modified Peng-Robinson equation of state, we could predict the principal and cross-coefficients for this system. These predictions are presented in Figures 9 to 12 in the form of parity plots.

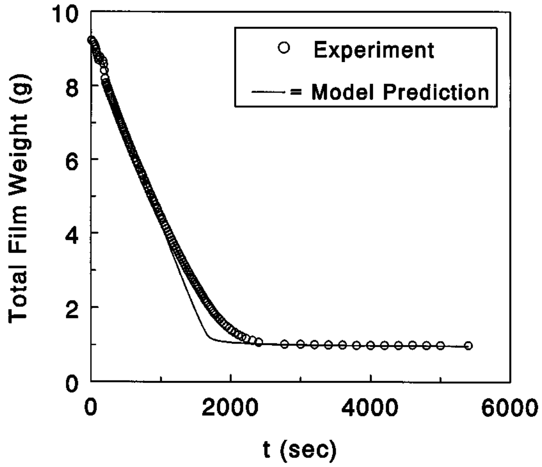

Figure 6. Predicted vs. experimental drying behavior of a multicomponent polymer solution composed of polystyrene, toluene, and ethylbenzene.

Predictions were performed by inserting the proposed diffusion model (Eqs. 19 to 22) into the multicomponent drying analysis developed by Alsoy and Duda (1998).

The flux of component 1 is dictated by D_{11} and D_{12}, whereas the flux of component 2 is governed by D_{21} and D_{22} (see Eqs. 11 to 12). The predicted diffusion coefficients appear to miss the experimental data in a consistent manner, that is, if the principal coefficient overpredicted then the cross-coefficient underpredicted. Given the experimental uncertainty of the NMR self-diffusion data (ca. 10%) and the inherent inaccuracy of estimating chemical potential *gradients* from experimental equilibria data, we consider the accuracy of these predictions to be reasonably good.

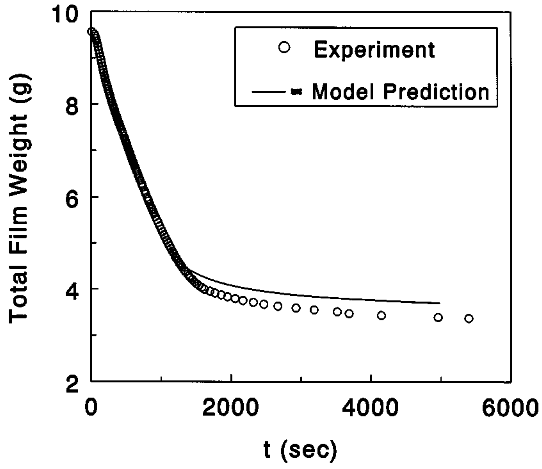

Figure 7. Predicted vs. experimental drying behavior of a multicomponent polymer solution composed of polystyrene, toluene, and benzene.

Predictions were performed by inserting the proposed diffusion model (Eqs. 19 to 22) into the multicomponent drying analysis developed by Alsoy and Duda (1998).

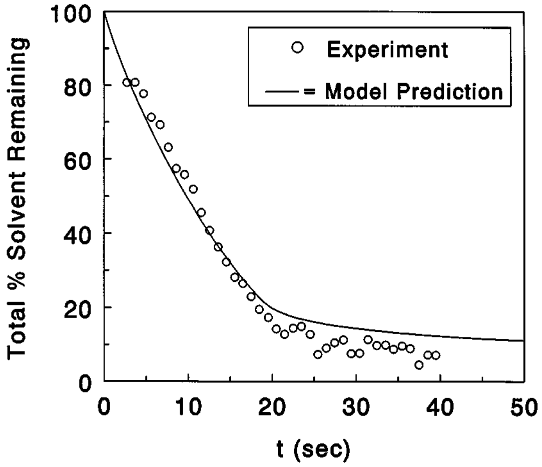

Figure 8. Predicted vs. experimental (Drake and Wang, 1989) drying behavior of a multicomponent polymer solution composed of polystyrene, toluene, and tetrahydrofuran.

Predictions were performed by inserting the proposed diffusion model (Eqs. 19 to 22) into the multicomponent drying analysis developed by Alsoy and Duda (1998).

Gas mixtures

If an ideal gas mixture is considered, then the chemical potential gradients can be explicitly evaluated from

$$\mu_i - \mu_i^o \approx RT \ln\left(\frac{P_i}{P_i^o}\right) = RT \ln\left(\frac{\rho_i RT}{M_i P_i^o}\right) \qquad (26)$$

where μ_i^o is the chemical potential as standard state conditions (cal/mol), P_i is the partial pressure of component i (mm Hg), and P_i^o is the saturation vapor pressure of component i (mm Hg). Furthermore, the partial specific volumes ($\hat{V}_i$) can be determined from

$$\hat{V}_i \equiv \left(\frac{\partial V}{\partial m_i}\right)_{T,P,m_j} \qquad (27)$$

in which case

Table 2. Self-Diffusion Coefficient Data from Ternary Mixtures of Acetone (1), Benzene (2), and Methanol (3) at 25°C

X_1	X_2	X_3	$D_1 \times 10^5$ (cm²/s)	$D_2 \times 10^5$ (cm²/s)	$D_3 \times 10^5$ (cm²/s)
0.350	0.302	0.348	4.2	3.8	3.8
0.766	0.114	0.120	5.1	4.6	4.7
0.553	0.190	0.257	4.8	4.3	4.7
0.400	0.500	0.100	4.0	3.6	3.9
0.299	0.150	0.551	4.1	4.0	3.6
0.206	0.548	0.246	3.7	3.3	3.4
0.102	0.795	0.103	3.3	2.9	3.3
0.120	0.132	0.748	3.6	3.4	3.1
0.150	0.298	0.552	3.4	3.2	2.9

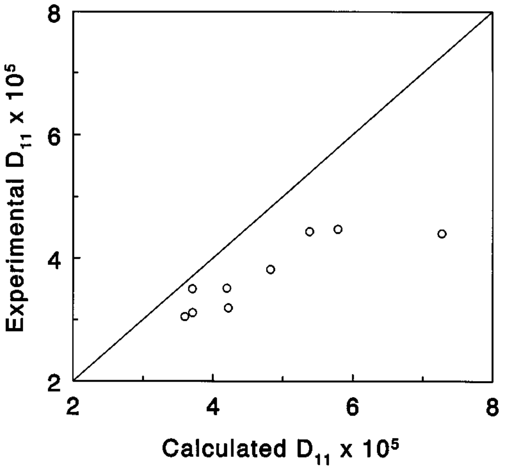

Figure 9. Experimental data (Alimadadian and Colver, 1976) vs. theoretical predictions from Eqs. 19 to 22 for the principal diffusion coefficient D_{11} in a ternary system consisting of acetone (1), benzene (2), and methanol (3) at 25°C and various concentrations.

$$V = \left[\frac{m_1}{M_1} + \frac{m_2}{M_2} + \frac{m_3}{M_3} \right] \left[\frac{RT}{P} \right] \tag{28}$$

where m_i is the mass of component i (g). All of the terms required in Eqs. 19 and 22, therefore, can be evaluated from Eqs. 26 to 28.

The proposed model suggests, therefore, that even for mixtures of ideal gases both principal and cross-diffusion coefficients exist and are given by

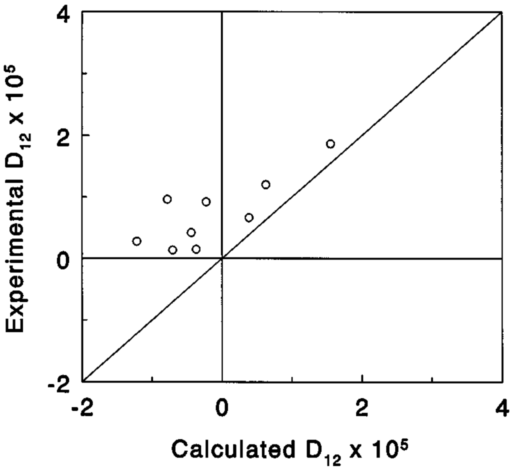

Figure 10. Experimental data (Alimadadian and Colver, 1976) vs. theoretical predictions from Eqs. 19 to 22 for the cross-diffusion coefficient D_{12} in a ternary system consisting of acetone (1), benzene (2), and methanol (3) at 25°C and various concentrations.

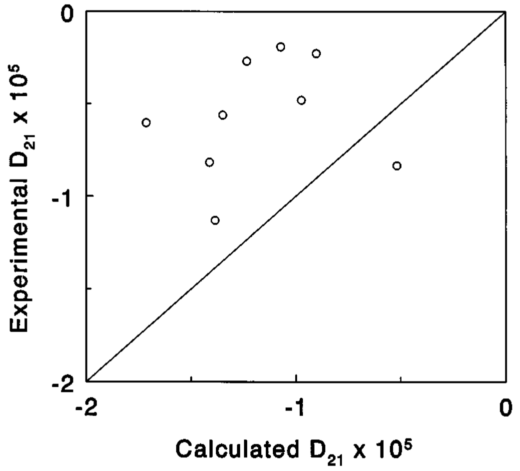

Figure 11. Experimental data (Alimadadian and Colver, 1976) vs. theoretical predictions from Eqs. 19 to 22 for the cross-diffusion coefficient D_{21} in a ternary system consisting of acetone (1), benzene (2), and methanol (3) at 25°C and various concentrations.

$$D_{11} = D_1 \left[1 - \rho_1 \hat{V}_1 + \rho_1 \hat{V}_3 \right] \tag{29}$$

$$D_{12} = D_2\, \rho_1 \left[\hat{V}_3 - \hat{V}_2 \right] \tag{30}$$

$$D_{21} = D_1\, \rho_2 \left[\hat{V}_3 - \hat{V}_1 \right] \tag{31}$$

$$D_{22} = D_2 \left[1 - \rho_2 \hat{V}_2 + \rho_2 \hat{V}_3 \right] \tag{32}$$

If we now consider a binary gas mixture consisting of components 1 and 2, substitute the results of Eqs. 19 to 22, and

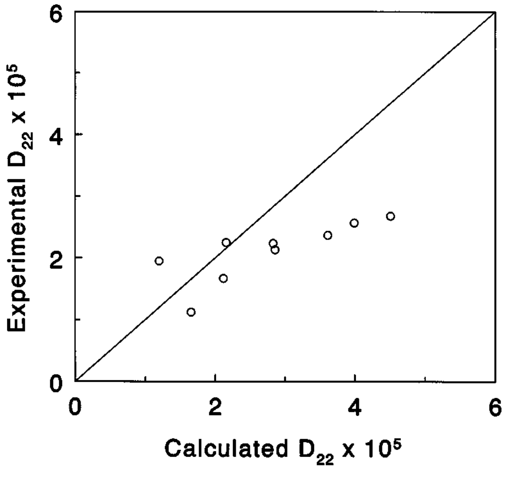

Figure 12. Experimental data (Alimadadian and Colver, 1976) vs. theoretical predictions from Eqs. 19 to 22 for the principal diffusion coefficient D_{22} in a ternary system consisting of acetone (1), benzene (2), and methanol (3) at 25°C and various concentrations.

Eqs. 26 to 28 into Eqs. 11 and 12, and apply the common experimental constraint (Evans et al., 1961) that the total pressure is uniform, that is, $\nabla\rho_1 = -\nabla\rho_2$, then it immediately follows that

$$\frac{j_1^{\neq}}{j_2^{\neq}} = -\frac{M_2}{M_1} \tag{33}$$

This result is identical to the definitions of flux presented by Bird et al. (1960) (see Appendix C).

Ternary system (2 gases with solid)

Molecule-wall interactions may become as important as molecule–molecule interactions in the diffusion of a binary gas mixture into a porous media. Consequently, the solid must be considered as a component and the system treated as a ternary mixture. Since the solid is stationary ($\upsilon_3 = 0$) and its molecular weight is essentially infinite, the mass average velocity of this system can be set equal to zero. Substituting this result into Eq. 2, employing Eq. 26 for an estimate of the chemical potential gradient, applying the constraint $\nabla P_1 = -\nabla P_2$, and assuming Knudsen diffusion yields a result commonly observed for transport within porous media.

$$\frac{j_1^{\neq}}{j_2^{\neq}} = \frac{D_1}{D_2} \propto -\sqrt{\frac{M_2}{M_1}} \tag{34}$$

Although the initial experiments by Graham were based on a quite different experimental design, this scaling relationship is colloquially referred to as Graham's law of effusion (1850).

Macropore diffusion

Since the mass-average velocity of a dilute gas system within a high molecular weight solid is approximately equal to zero, the chemical potential gradient of component i can be simply expressed from a combination of Eqs. 2 and 18 as

$$\nabla\mu_i = -\frac{RT\upsilon_i}{D_i} \tag{35}$$

Inclusion of the definition of the molar flux with respect to a stationary coordinate system and the chemical potential for an isothermal, ideal gas, that is,

$$N_i \equiv c_i\upsilon_i \approx \frac{P_i\upsilon_i}{RT} \tag{36}$$

and

$$\nabla\mu_i = RT\,\nabla \ln P_i \tag{37}$$

yields the well-known partial pressure driving force model (Krishna, 1993) commonly used to describe macropore diffusion

$$N_i = -\frac{D_i\nabla P_i}{RT} \tag{38}$$

Conclusions

In this work, we have developed a novel diffusion model that enables the principal and cross-diffusion coefficients to be easily determined for multicomponent systems from readily accessible thermodynamic and self-diffusion data. Since the proposed model is general, that is, the state of each component in the multicomponent system is not specified, we have tested the model by accurately predicting principal and cross-diffusion coefficients in ternary systems consisting of three organic liquids (acetone, benzene, and methanol) and two organic liquids and a polymer (methanol, toluene, and poly(vinyl acetate)). We have also successfully applied the model to predict the drying behavior of three ternary (2 solvents/1 polymer) solvent-coated polymer films composed of: (i) polystyrene/toluene/ethylbenzene; (ii) polystyrene/toluene/benzene; and (iii) polystyrene/toluene/tetrahydrofuran.

The limiting cases of the proposed model correctly match the diffusion behavior that is characteristic of all binary systems and suggests a functional form for polymer-polymer interdiffusion that is reminiscent of the fast-mode transport theory. Lastly, application of the model to examine multicomponent gas transport provides relationships that have been established in describing diffusion in porous media.

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Notation

c_i = molar concentration of component i in mixture, mol/cm^3
D_{oi} = pre-exponential factor in free-volume model, cm^2/s
D_{ii} = principal diffusion coefficient of component i in a multicomponent mixture, reflecting effect of component i on the flux of component i, cm^2/s
D_{ij} = cross-diffusion coefficient of component i in a multicomponent mixture, reflecting effect of component j on the flux of component i, cm^2/s
J_i = molar flux of component i relative to mass-average velocity, mol/cm$^2\cdot$s
K_{1j} = free-volume parameter of component j, cm^3/g$\cdot$K
K_{2j} = free-volume parameter of component j, K
M_i = molecular weight of component i, g/mol
N_i = molar flux of component i relative to stationary axes, mol/cm$^2\cdot$s
T_{gi} = glass transition temperature of component i, K
$\upsilon^{\neq}$ = volume-average velocity, cm/s
V = volume, cm^3
$\hat{V}_{FH}$ = specific hole free volume for free-volume model, cm^3/g
$\hat{V}_i^*$ = specific critical hole free volume for free-volume model, cm^3/g

Greek letters

γ = overlap factor which accounts for shared free-volume
μ_i = chemical potential of component i, cal/mol
ξ_{ij} = ratio of jumping units of components i and j in free-volume model
ρ_i = mass concentration of component i in mixture, g/cm^3
ϕ_i = volume fraction of component i
χ_{ij} = Flory-Huggins parameter indicating strength of interactions between components i and j

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Appendix A

The chemical potential gradient for component 1 in a ternary system expressed in terms of the Bearman model (Eq. 1) is

$$\nabla\mu_1 = -\frac{\rho_2 N_A^2 \zeta_{12}(v_1 - v_2)}{M_2} - \frac{\rho_3 N_A^2 \zeta_{13}(v_1 - v_3)}{M_3} \quad \text{(A1)}$$

After substituting the definition of the mass-average velocity into Eq. 2, the analogous expression for the chemical potential gradient from the model proposed in this work is

$$\nabla\mu_1 = -f_1 M_1 [\omega_2(v_1 - v_2) + \omega_3(v_1 - v_3)] \quad \text{(A2)}$$

where ω_i is the weight fraction of component i.

By equating the factors before the velocity difference terms, one discovers that

$$f_1 M_1 = \frac{\rho_2 N_A^2 \zeta_{12}}{\omega_2 M_2} = \frac{\rho_3 N_A^2 \zeta_{13}}{\omega_3 M_3} \tag{A3}$$

Through rearrangement Eq. A3 and substitution of the relationship between weight fraction and mass concentration one obtains

$$\frac{\zeta_{12}}{\zeta_{13}} = \frac{\omega_2 \rho_3 M_2}{\omega_3 \rho_2 M_3} = \frac{\omega_2 \omega_3 \rho M_2}{\omega_2 \omega_3 \rho M_3} \tag{A4}$$

where ρ is the mass density of the solution (g/cm^3).

Thus, the proposed model is identical to the Bearman relationship if a direct proportionality between ζ_{ij} and M_j is imposed, that is

$$\frac{\zeta_{12}}{\zeta_{13}} = \frac{M_2}{M_3} \tag{A5}$$

Appendix B

Substitution of Eq. 3 into Eq. 6 yields

$$j_i^{\neq} = j_i - \rho_i \sum_{i=1}^{n} \hat{V}_i \rho_i (v_i - v) \tag{B1}$$

Multiplying through by ρ_i and substituting the definition for the mass flux of species i with respect to stationary axes, that is, $n_i = \rho_i v_i$ (Bird et al., 1960) one obtains

$$j_i^{\neq} = j_i - \rho_i \sum_{i=1}^{n} \hat{V}_i (n_i - \rho_i v) \tag{B2}$$

Expanding Eq. B2, taking v out of the summation, and recognizing that $\Sigma \hat{V}_i \rho_i = 1$, since this represents the summation of the volume fractions of the system, that is, $\Sigma \phi_i = 1$, results in

$$j_i^{\neq} = j_i - \rho_i \sum_{i=1}^{n} \hat{V}_i n_i + \rho_i v \tag{B3}$$

Substitution of Eq. 3 into Eq. B3 yields

$$j_i^{\neq} = \rho_i v_i - \rho_i v - \rho_i \sum_{i=1}^{n} \hat{V}_i n_i + \rho_i v \tag{B4}$$

which may be simplified to

$$j_i^{\neq} = \rho_i v_i - \rho_i \sum_{i=1}^{n} \hat{V}_i n_i = \rho_i v_i - \rho_i \sum_{i=1}^{n} \hat{V}_i \rho_i v_i \tag{B5}$$

Since $\hat{V}_i \rho_i$ is the volume fraction of component i in the system, that is, $\phi_i = \hat{V}_i \rho_i$ and the volume-average velocity is defined as (Bird et al., 1960)

$$v^{\neq} = \sum_{i=1}^{n} \phi_i v_i \tag{B6}$$

then the mass flux relative to the volume-average velocity can be written in the familiar form given by Bird et al. (1960), namely

$$j_i^{\neq} = \rho_i (v_i - v^{\neq}) \tag{B7}$$

Appendix C

The mass (j_i) and molar fluxes (J_i) with respect to the mass average velocity (v) of two components in a binary system $(i = 1$ and $2)$ can be expressed as

$$\frac{j_1}{\rho_1} = \frac{J_1}{c_1} = v_1 - v \tag{C1}$$

$$\frac{j_2}{\rho_2} = \frac{J_2}{c_2} = v_2 - v \tag{C2}$$

where ρ_i, c_i, and v_i are the mass and molar concentrations and species velocities of component i, respectively.

Dividing Eq. C1 by Eq. C2 yields

$$\frac{J_1}{J_2} = \frac{j_1 \rho_2 c_1}{j_2 \rho_1 c_2} \tag{C3}$$

By substituting the relationship between the mass and molar concentrations

$$\rho_i = c_i M_i \tag{C4}$$

and the result that the summation of the individual component mass fluxes with respect to the mass average velocity equals zero, that is,

$$j_1 + j_2 = 0 \tag{C5}$$

one obtains the relationship between the molar fluxes with respect to the mass average velocity that must be satisfied for a binary system, namely

$$\frac{J_1}{J_2} = -\frac{M_2}{M_1} \tag{C6}$$

This result is different than that commonly expressed for a system consisting of two gases and a solid (see Eq. 34), and suggests that such systems should be considered *ternary*, since molecule-wall interactions are as important as molecule-molecule interactions.

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