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Molecular-Dynamics Simulation of Mutual Diffusion in Nonideal Liquid Mixtures

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The mutual-diffusion coefficients, D_{12}, of *n*-hexane, *n*-heptane, and *n*-octane in chloroform were modeled using equilibrium molecular-dynamics (MD) simulations of simple Lennard-Jones (LJ) fluids. Pure-component LJ parameters were obtained by comparison of simulations to experimental self-diffusion coefficients. While values of "effective" LJ parameters are not expected to simulate accurately diverse thermophysical properties over a wide range of conditions, it was recently shown that effective parameters obtained from pure self-diffusion coefficients can accurately model mutual diffusion in ideal, liquid mixtures. In this work, similar simulations are used to model diffusion in nonideal mixtures. The same combining rules used in the previous study for the cross-interaction parameters were found to be adequate to represent the composition dependence of D_{12}. The effect of alkane chain length on D_{12} is also correctly predicted by the simulations. A commonly used assumption in empirical correlations of D_{12}, that its kinetic portion is a simple, compositional average of the intradiffusion coefficients, is inconsistent with the simulation results. In fact, the value of the kinetic portion of D_{12} was often outside the range of values bracketed by the two intradiffusion coefficients for the nonideal system modeled here.

KEY WORDS: liquid mixtures, molecular dynamics, mutual diffusion, nonideal mixtures.

1. INTRODUCTION

The composition dependence of transport properties in liquid mixtures has been difficult to quantify because of its strong connection to unlike molecular interactions. Nevertheless, productive estimation techniques have

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been developed for liquid mixture viscosity and thermal conductivity. These correlations are generally based on a compositional average of pure-component values plus a nonideal correction term. However, prediction of mutual-diffusion coefficients, D_{12}, in liquid mixtures is greatly complicated by the absence of corresponding pure-component properties. Unlike thermal conductivity and viscosity, the mutual-diffusion coefficient does not approach the self-diffusion coefficient in the pure-component limit. Mutual diffusion is a collective property of the mixture itself, dependent upon the relative velocities of the two components. Figure 1 provides a convenient definition of the various diffusion coefficients used in this work. It also illustrates that intradiffusion coefficients, D_i, are single-component properties which in the pure-component limit become self-diffusion coefficients, D_i^0. The mutual-diffusion coefficient, on the other hand, bears no explicit relationship to the self-diffusion coefficients but does become equal to the intradiffusion coefficient at infinite dilution, D_i^∞.

Recently Stoker and Rowley [1], hereafter referred to as SR, proposed calculating D_{12} via equilibrium MD simulations using effective Lennard–Jones (LJ) parameters obtained from self-diffusion coefficients. Previously, empirical correlations of the concentration dependence of D_{12} have generally been based on infinite dilution values of the mutual-diffusion

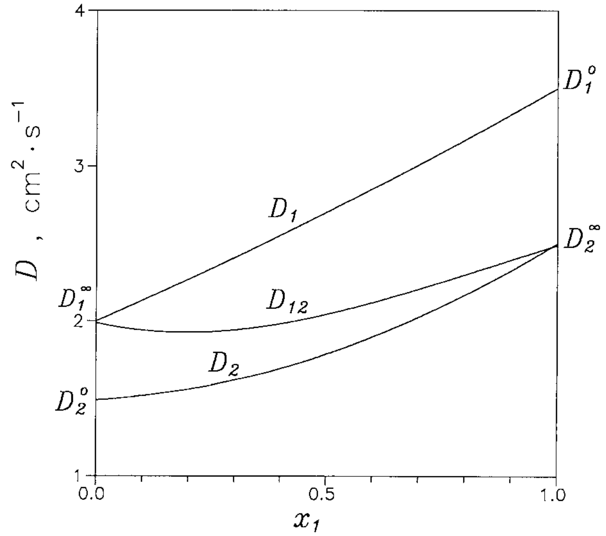

Fig. 1. Generalized composition dependence of mutual-diffusion, D_{12}, and intradiffusion, D_i, coefficients. Limits of D_i are the self-diffusion coefficient, D_i^0, and the infinite-dilution value, D_i^∞.

coefficient or values of the intradiffusion coefficients at the mixture composition. For example, Darken [2] proposed that

$$\bar{D}_{12} = x_1 D_2 + x_2 D_1 \tag{1}$$

where $\bar{D}_{12}$ is the kinetic portion of the diffusion coefficient related to D_{12} by

$$D_{12} = \bar{D}_{12} Q \tag{2}$$

The thermodynamic factor Q is defined as

$$Q \equiv 1 + \left(\frac{\partial \ln \gamma_1}{\partial \ln x_1}\right)_{\mathrm{T,P}} \tag{3}$$

x_1 is the mole fraction of component 1, and γ_1 is the activity coefficient based on the pure-component standard state. This form of Darken's equation is seldom used because of the unavailability of intradiffusion coefficients. Instead, D_i are usually replaced with infinite dilution values because there are estimation methods [3] for D_i^∞. The modified form is

$$\bar{D}_{12} = x_1 D_2^\infty + x_2 D_1^\infty \tag{4}$$

Another *ad hoc* correlation for D_{12} in terms of infinite dilution coefficients is [4]

$$D_{12} = (D_1^\infty)^{x_2} (D_2^\infty)^{x_1} Q \tag{5}$$

This equation has been found to fit experimental data quite well for ideal or nearly ideal mixtures. Unfortunately, neither of these equations works consistently for nonideal liquid mixtures. It has been suggested [3] that the thermodynamic factor Q tends to overcorrect for the mixture nonidealities.

MD simulations of D_{12} in LJ fluids can be used to check the validity of Eq. (1). The work by SR indicated that simulated D_{12} could also be used to predict values for real mixtures if the pure-component, "effective" LJ parameters were obtained from self-diffusion coefficient data. SR were able to use the Lorentz–Berthelot (LB) combining rule for ε_{12} but were forced to use a weighted combining rule for σ_{12} in order to obtain agreement with experiment. The same combining rule was used for all of the systems which they studied. Because the alkane + carbon tetrachloride mixtures studied by SR were nearly ideal, it seems appropriate to extend their work to the substantially nonideal mixtures of alkanes + chloroform. In so doing, the objectives of the study are (1) an evaluation of Eq. (1) from MD simulations, (2) a study of the interrelationship of the various diffusion coefficients, and (3) a test of the SR method for prediction of real D_{12} in nonideal mixtures from LJ simulations.

2. MD SIMULATIONS OF D_{12}

MD simulations of thermophysical properties are becoming more routine. Although used in the past primarily as "experimental" data against which theories based on the same interaction model could be tested, simulations today are being used more and more to model real systems, either by using "effective" parameters over a limited range of conditions or by using more realistic site–site models assumed applicable over a wider range of conditions. Increasing computer availability and speed along with more efficient simulation algorithms are making such calculations more practical for thermophysical property estimation.

However, MD simulations of mutual-diffusion coefficients are still rare. This paucity is due primarily to the collective nature of D_{12}, essentially the same problem which has inhibited development of accurate empirical correlations. Collective properties are inherently harder to calculate and have poorer statistics than single-species or one-particle properties. The reason for these larger uncertainties is seen in the equilibrium MD formulations. The problems inherent in the calculation are the same for both mean-square-displacement and time-correlation function formulations, so we discuss only the latter, as it is the method used in our simulations. The intradiffusion coefficient can be calculated from [5–8]

$$D_i = \frac{1}{3} \int_0^\infty \langle \mathbf{v}_{i\alpha}(t_0) \cdot \mathbf{v}_{i\alpha}(t_0 + t) \rangle \, dt \tag{6}$$

where $\mathbf{v}_{i\alpha}$ is the velocity vector of particle α of component i. The angle braces in this case indicate not only a time average but also a particle average because each molecule of a particular component may be used to obtain a replicate of the time correlation function. The corresponding equation for mutual-diffusion coefficients is [9–11]

$$D_{ij} = \frac{Q}{3Nc_i c_j} \int_0^\infty \langle \mathbf{J}_{ij}(t_0) \cdot \mathbf{J}_{ij}(t_0 + t) \rangle \, dt \tag{7}$$

where

$$\mathbf{J}_{ij}(t) = c_j \sum_{\alpha=1}^{N_i} \mathbf{v}_{i\alpha}(t) - c_i \sum_{\beta=1}^{N_j} \mathbf{v}_{j\beta}(t) \tag{8}$$

c_i is the number density of i and N_i is the number of i particles such that $\sum N_i = N$. The mutual diffusion coefficient defined in Eq. (8) corresponds to the commonly measured coefficient based on the fixed volume reference frame [10, 11]. It directly corresponds to the diffusion coefficient commonly measured in the laboratory. The coefficient D_{12} can be related to the mutual-diffusion coefficient based on the center-of-mass reference frame, D_{12}^{m}, the mass density, ρ, and the partial specific volume of species 2, $\bar{V}_2$, by [10]

$$D_{12} = \rho D_{12}^{\mathrm{m}} \bar{V}_2 \tag{9}$$

The latter diffusion coefficient is defined in terms of the mass flux of component 1 relative to the center of mass, $\mathbf{j}_1$, by Fick's law,

$$-\mathbf{j}_1 = \rho D_{12}^{\mathrm{m}} \nabla w_1 \tag{10}$$

where w_1 is the mass fraction of component 1.

Because of the collective nature of D_{ij} apparent in Eq. (8), only one value of J_{ij} can be calculated per time step during the simulation, as opposed to the N_i values per time step that can be obtained and averaged to obtain intradiffusion coefficients from Eq. (6). While simulations of intradiffusion coefficients accurate to 2 or 3% can be made with relatively short simulations on a small number of particles, comparable statistics for mutual-diffusion coefficients would require simulations longer by at least a factor of N. This is not the only problem, however. Mutual-diffusion simulations [11] (i) have a number dependence for smaller systems, (ii) require at least 2000–2500 independent time origins in phase space, and (iii) may require longer integrations to include the long-time correlation tail. As a result, long simulations involving many independent time averages for $\bar{D}_{12}$ were utilized.

Mutual-diffusion coefficients in this work were calculated from NVE simulations on 343 particles and the Green–Kubo formalism of Eq. (7). A small number correction deduced from the work of Schoen and Hoheisel [11] was applied. All simulations were run at 30°C and at densities corresponding to literature experimental data [12] to permit direct comparisons of simulated and experimental D_{12} values. The code and simulation procedures are the same as previously used by SR for the alkane + carbon tetrachloride system, and details of the simulations have been reported previously by SR. The only differences between the code used in this work and that of SR is the current ability to spread out the origins of the correlation functions to gain more efficiency. Both methods were used in this work and found to agree within the precision of the simulations. As before, at least 3000 independent time origins were included in the runs necessitating run lengths of between 90,000 and 120,000 time steps (900–1200 ps). Correlation information for each time origin was collected for 6 ps (600 time steps), which was found to be adequate for loss of correlation and decay of the long-time tail. Values of the diffusion coefficient were determined from the average value of the correlation function integral in the range 3 to 6 ps. The expected uncertainty in simulated D_i values is about 2%, while $\bar{D}_{12}$ values are expected to be accurate to about 6%.

3. PURE-COMPONENT LJ PARAMETERS

It is well known that several equally valid sets of σ and ε parameters may result when the parameters are regressed from experimental data. Generally, any one set is adequate for calculating properties similar to those from which the parameters were regressed. However, much poorer results are obtained when parameters regressed from one property are used to predict another. Multiproperty regression can be used to decouple σ and ε and obtain unique values, but this is at the expense of the accuracy of the individual properties. Much of this problem is presumed to be the inadequacy of the spherical LJ potential model for nonspherical, real molecules. The inadequacies of the model are absorbed into the "effective" LJ parameters, but this spherical averaging will not have the same effect on different properties. A better procedure is to use site–site potentials because the geometrical influence of the potential around each site should be much more spherical than that of the molecule. This introduces considerable complexity into the problem but is essential for multiproperty simulations. In this work, effective molecular LJ parameters obtained from self-diffusion coefficients are used to calculate mutual-diffusion coefficients. We justify the use of effective LJ parameters here on the basis of its desired simplicity and the assumption that the effective potential should affect D_i^0 and D_{12} similarly.

As by SR, values of ε/k were obtained from the literature [3] as regressed from viscosity data. Values of σ_i were adjusted from literature values to obtain agreement between simulated and experimental D_i^0 values. SR showed that D_i^0 is considerably more sensitive to σ than ε. Fitting σ and retaining the literature value of ε therefore eliminate the problem of coupled parameters and provide values closest to those obtained from viscosity data. In practice, multiple simulations of D_i^0 were performed with different values of σ until the simulated values bracketed the experimental point. One or two more simulations were then made at σ values suggested by a linear interpolation between the bracketed values. The closest simulated values including at least one on either side of the experimental value were then used to obtain the final value of σ using quadratic inter-

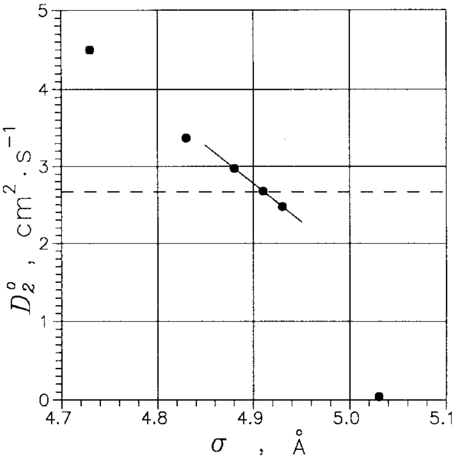

Fig. 2. Evaluation of σ by matching simulated (points) and experimental (dashed line) D_i^0 values.

polation. Results of this procedure for chloroform are shown in Fig. 2. Each simulation point in Fig. 2 is actually an average of four to six replicate simulations containing 10,000 time steps each. Values of D_i^0 from the literature and the LJ parameters obtained from this procedure are shown in Table I. Where the literature D_i^0 values were not reported at 30°C, a temperature adjustment was made based on the temperature dependence of the pure-component viscosity, η, using [13]

$$D^0(T_2) = D^0(T_1)\left[\frac{\eta(T_1)}{\eta(T_2)}\right]^{2/3}\left(\frac{T_2}{T_1}\right)^{1.7805} \tag{11}$$

Table I. Values of σ Obtained by Comparing Simulated Self-Diffusion Coefficients to the Experimental Values Shown here at 30°C[a]

Component	m (10^{-22} g)	D_i (10^{-5} cm$^2\cdot$s^{-1})	σ (Å)	ε/k (K)[b]
Chloroform	1.982	2.67[c]	4.911	327.0
n-Hexane	1.431	4.37[d]	5.645	413.0
n-Heptane	1.664	3.20[e]	5.955	429.0
n-Octane	1.897	2.42[e]	6.323	320.0

[a] Values for ε/k regressed from viscosity data were used directly from the literature.
[b] Source: Ref. 3.
[c] Source: Ref. 17.
[d] Source: Ref. 18.
[e] Source: Ref. 13.

For mixtures, the LJ cross interactions must also be defined. Again, because of the lower sensitivity of $\bar{D}_{12}$ to it, ε_{12} was obtained from the Lorentz–Berthelot (LB) combining rule:

$$\varepsilon_{12}=\sqrt{\varepsilon_1 \varepsilon_2} \tag{12}$$

The σ_{12} combining rule used by SR for *n*-alkane (1) + carbon tetrachloride (2) mixtures,

$$\sigma_{12}=0.75\sigma_1+0.25\sigma_2, \tag{13}$$

was utilized for the mixtures studied here, with 2 referring to chloroform. The required heavier weighting of the alkane contribution to σ_{12} compared to that of the LB combining rule is probably due to the larger effective spherical volume swept out by the rotating cigar-shaped alkane molecules as they interact with the more spherical CCl_4 or $CHCl_3$ molecules.

4. SIMULATION RESULTS

A direct comparison of MD results to experimental data requires values of the thermodynamic factor Q. Although some attempt has been made to obtain Q from the simulation itself [10], it is difficult to obtain good statistics for the chemical potential [6] from simulations of dense fluids; the statistics for simulated Q, which depends upon the derivative of the chemical potential with respect to composition, are quite poor. The uncertainty in Q has been larger than the value of Q itself in previous simulations [10]. The appropriately differentiated NRTL activity coefficient model with parameters recommended by Gmehling et al. [14] was used to obtain Q in this work for *n*-hexane and *n*-heptane mixtures with chloroform. No data were found for *n*-octane + chloroform mixtures so the modified UNIFAC [15] group contribution method was used for this system. The resultant excess free energy, g^E, was fitted to a three-term Redlich–Kister expansion,

$$\frac{g^E}{RT}=x_1x_2[B+C(x_1-x_2)+D(x_1-x_2)^2] \tag{14}$$

from which analytical derivatives with respect to composition could be obtained. The equation for Q derived from Eq. (14) is

$$\begin{aligned} Q=1+x_1x_2\{&4x_2[C+2D(2x_1-x_2)] \\ &-2[B+C(3x_1-x_2)+D(x_1-x_2)(5x_1-x_2)]\} \end{aligned} \tag{15}$$

Table II. Redlich–Kister Constants for Q in Chloroform Mixtures at 30°C from Modified UNIFAC

Solute	B	C	D
n-Hexane	0.5254	−0.0635	0.00801
n-Heptane	0.5261	−0.1018	0.0196
n-Octane	0.5194	−0.1369	0.0346

Table II contains the values of the Redlich–Kister parameters obtained from this procedure for all of the mixtures studied. Because final values of D_{12} are strongly dependent upon the accuracy of Q in accordance with Eq. (2), it is interesting to compare values of Q obtained from the NRTL and Wilson equations with values from Eq. (15) for the two mixtures for which experimental data are available. From the comparison shown in Table III, it seems that uncertainties in Q may be as large as 7%, though they are probably smaller in most cases. The uncertainty in Q combined with that inherent in the simulations of $\bar{D}_{12}$ implies an expected uncertainty in D_{12} of about 10–12%.

Simulated values of D_i, $\bar{D}_{12}$, and D_{12} for chloroform mixtures are shown in Table IV. A comparison of simulated and experimental [12] values of D_{12} is presented in Fig. 3. Within the above-stated uncertainty, the combining rule used by SR appears also to represent adequately D_{12} in the nonideal chloroform mixtures, although the simulations are distinctly

Table III. Comparison of Q Values Obtained from NRTL, Wilson, and UNIFAC Equations

x_1	NRTL	Wilson	Eq. (15)
n-Hexane + $CHCl_3$			
0.1	0.844	0.835	0.874
0.3	0.738	0.709	0.748
0.5	0.775	0.725	0.742
0.7	0.865	0.811	0.811
0.9	0.959	0.932	0.929
n-Heptane + $CHCl_3$			
0.1	0.921	0.885	0.851
0.3	0.817	0.782	0.728
0.5	0.785	0.783	0.747
0.7	0.821	0.845	0.831
0.9	0.924	0.942	0.939

Table IV. Results of MD Simulations in Chloroform Mixtures at 30°C

x_1 (1 = alkane)	D_1 ($10^{-5}\mathrm{cm}^2\cdot\mathrm{s}^{-1}$)	D_2 ($10^{-5}\mathrm{cm}^2\cdot\mathrm{s}^{-1}$)	$\bar{D}_{12}$ ($10^{-5}\mathrm{cm}^2\cdot\mathrm{s}^{-1}$)	Q	D_{12} ($10^{-5}\mathrm{cm}^2\cdot\mathrm{s}^{-1}$)
n-Hexane					
0.1	2.01	2.62	2.70	0.844	2.28
0.3	2.14	2.74	3.01	0.738	2.22
0.5	2.49	3.03	3.56	0.775	2.76
0.7	3.19	3.76	4.08	0.865	3.53
0.9	3.77	4.36	4.17	0.959	4.00
n-Heptane					
0.1	1.71	2.57	2.28	0.921	2.10
0.3	1.55	2.27	2.52	0.817	2.06
0.5	1.73	2.33	2.96	0.785	2.32
0.7	2.13	2.79	3.54	0.821	2.91
0.9	2.82	3.54	3.70	0.924	3.42
n-Octane					
0.1	1.38	2.22	2.22	0.830	1.84
0.3	1.26	1.95	2.54	0.713	1.81
0.5	1.34	1.98	2.97	0.758	2.25
0.7	1.67	2.27	3.09	0.851	2.63
0.9	2.27	2.81	3.42	0.924	3.16

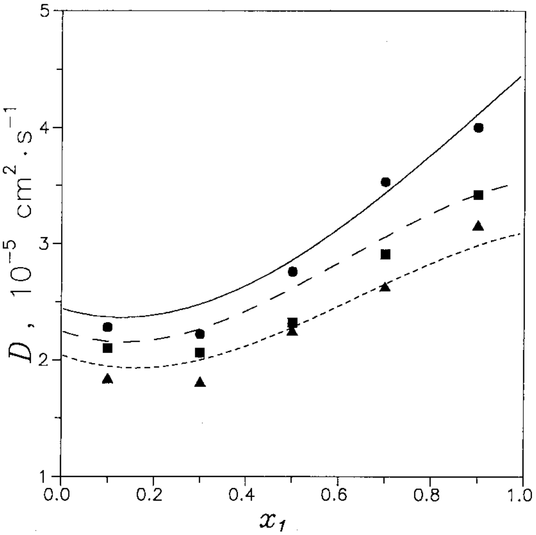

Fig. 3. Simulated (points) and smoothed experimental (lines) diffusion coefficients for mixtures of *n*-hexane (●, ——), *n*-heptane (■, — — —), and *n*-octane (▲, - - - -) in chloroform.

low in the region $0.2 < x_1 < 0.6$. This could be due to either the combining rule or a systematic deviation in Q. Interestingly, this is the compositional region where Q has its smallest values or largest deviations from unity.

5. DISCUSSION OF RESULTS

The assumptions inherent in the Darken equation, Eq. (1), become apparent when Eq. (7) is rearranged as [16]

$$\bar{D}_{12} = x_2 D_1 + x_1 D_2 + kT\left(\frac{x_2}{m_1} + \frac{x_1}{m_2}\right) \int_0^\infty \Upsilon(t)\, dt \tag{16}$$

where $\Upsilon(t)$ is a sum of all cross-correlations of the type $\langle \mathbf{v}_i(0) \cdot \mathbf{v}_j(t) \rangle$ with $i \neq j$. Comparison with Eq. (1) shows that Darken's relation holds when the cross-correlations are small relative to the direct correlations. This should be exact only in infinitely dilute solutions. For those cases in which $\Upsilon(t)$ is small, $\bar{D}_{ij}$ could be conveniently computed from Eq. (1) and molecular-dynamics simulations of D_i rather than from direct simulations of $\bar{D}_{12}$. Unfortunately, it appears that such a computational convenience is seldom possible, and the basis of Eq. (1) is generally invalid. This is seen in Table V, where a comparison of Eq. (1) and a compositional average of

Table V. Test of Correlations Between Intradiffusion Coefficients and $\bar{D}_{ij}$

x_1 (1 = alkane)	$\bar{D}_{12}$ [Eq. (1)] ($10^{-5}\,\mathrm{cm^2 \cdot s^{-1}}$)	$\bar{D}_{12}$ (ave.) ($10^{-5}\,\mathrm{cm^2 \cdot s^{-1}}$)	$\bar{D}_{12}$ (MD) ($10^{-5}\,\mathrm{cm^2 \cdot s^{-1}}$)
n-Hexane + $CHCl_3$			
0.1	2.07	2.56	2.70
0.3	2.32	2.56	3.01
0.5	2.76	2.76	3.56
0.7	3.59	3.36	4.08
0.9	4.30	3.83	4.17
n-Heptane + $CHCl_3$			
0.1	1.80	2.48	2.28
0.3	1.77	2.05	2.52
0.5	2.03	2.03	2.96
0.7	2.59	2.33	3.54
0.9	3.47	2.89	3.70
n-Octane + $CHCl_3$			
0.1	1.46	2.14	2.22
0.3	1.47	1.74	2.54
0.5	1.66	1.66	2.97
0.7	2.09	1.85	3.09
0.9	2.76	2.32	3.42

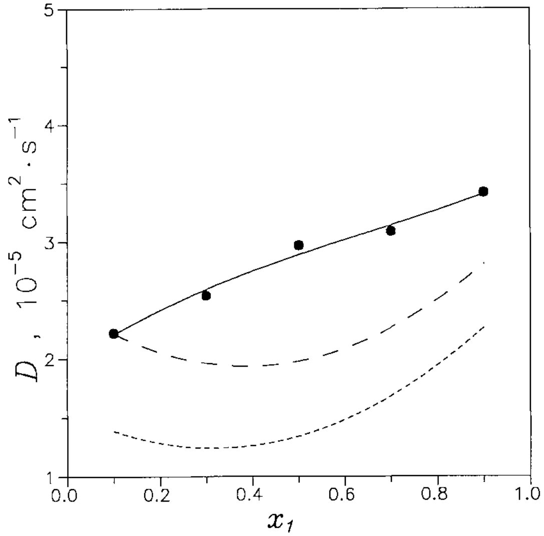

Fig. 4. Simulated values of D_1 (- - - - -), D_2 (— — —), and $\bar{D}_{12}$ (●, ——) in *n*-octane + chloroform mixtures.

D_i values are compared with the simulated value $\bar{D}_{12}$. It is not just Q that is affected by mixture nonidealities, but the cross-correlation terms in Eq. (16) also become quite substantial, causing large deviations from convenient compositional averages of D_i. This is apparent in Fig. 4, where the composition dependence of $\bar{D}_{12}$ is seen to bear little relationship to that of the intradiffusion coefficients. In these nonideal mixtures, the value of $\bar{D}_{12}$ obtained from simulations often lies outside the range of values bracketed by the simulated D_i values.

6. CONCLUSIONS

It is particularly difficult to estimate the mutual-diffusion coefficient as a function of composition because there is no corresponding pure-component property. Empirical correlations often use either intradiffusion coefficients or infinite-dilution diffusion coefficients in the correlation, but these often do not work well for nonideal mixtures. The MD simulations performed here indicate that except for very ideal mixtures, the cross time-correlation function contributes significantly to $\bar{D}_{12}$, calling into question the basis for correlations in terms of D_i. Unfortunately, this also means that simulation of D_i cannot be used as an alternative to the inherently more difficult and less accurate simulations of $\bar{D}_{12}$.

Reasonably good agreement with experimental data was obtained from LJ simulations of D_{12} in nonideal chloroform mixtures when parameters regressed from pure-component self-diffusion data were used with the same combining rules found by SR to be effective for ideal carbon tetrachloride mixtures. It appears that this simulation method may be a useful predictive method. It is not expected that the same combining rule used here holds for other mixtures, but extension of the method to site–site interaction potentials for which the standard LB combining rules are expected to apply would probably eliminate this problem. Additionally, using site–site interactions may make the model sufficiently realistic that properties other than the self-diffusion coefficient can be used to obtain the pure-component interaction parameters. Ultimately, this may lead to a simulation prediction method in which tabulated group or site interaction parameters can be used to calculate the mutual-diffusion coefficient at any desired composition for most liquid mixtures. Perhaps the greatest advantage of this method would then be its logical extension to multicomponent mixtures for which there are several independent diffusion coefficients. We are currently planning diffusion simulations using site–site potentials and simulations in multicomponent mixtures to test the feasibility of these ideas.

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