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Detailed Molecular Simulations to Investigate Multicomponent Diffusion Models

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The theoretical treatment of multicomponent diffusion is complicated by the generally unknown dependence of diffusivities on the local concentration of species. As pointed out by Nauman and Savoca in 2001, the standard treatment uses an n-*1 by* n-*1 matrix of diffusion coefficients for an* n-*component system and can give anomalous and non-physical results when there is no dominant component and when the various components have significantly different diffusivities. Although theoretically resolved by postulating diffusivities with suitable concentration dependence, there has been no practical resolution of this problem short of unrealistic, exhaustive experimentation. Nauman and Savoca proposed two models for multicomponent diffusion that produce only physically possible results, but they were unable to suggest which model was better. This article reports on molecular dynamic experiments that were designed to differentiate between the models. Specifically studied were ternary, liquid mixtures of ethane, octane, and hexadecane. It was found that the proportional flux model agrees with the molecular simulations. No cross-diffusion was observed in agreement with this model and in contrast to the alternative, pair-wise flux model. The proportional flux model is easy to implement and requires a minimum of data, although detailed, compositional dependent diffusion coefficients can be incorporated into the model when such data are available.* © 2005 American Institute of Chemical Engineers *AIChE J,* 52: 1304–1307, 2006

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Introduction

Transport properties of alkanes are of considerable interest in processes like petroleum refining (cracking, reforming) and separation. Diffusion is a molecular mixing process, with the diffusion coefficient being a tensor quantity expressible in matrix form. Existing theories and experiments to predict multicomponent diffusivities are limited to very specific systems.[1,2]

Numerical solutions of standard diffusion equations sometimes lead to artifacts. For multi-component mixtures in which the diffusivities of major constituents differ significantly, interesting and occasionally non-physical phenomena may be predicted. Standard theories of multicomponent diffusion predict cross-diffusion, and numerical solutions of diffusion equations with reasonable but constant values of diffusivities can lead to negative local concentrations of a minor component or to concentrations that sum to more than the molar density of the system.[3] Consider a system with two components (50/50 by volume) where one component is much heavier than the other. The heavier and hence slower component will slow down migration of the lighter component, thus reducing its diffusivity to a value that is much lower than its bulk diffusivity. Diffusivity of the heavy component may or may not be affected by the presence of the lighter and more mobile component. Add a third, uniformly distributed, minor component to the system. Is cross-diffusion induced? Theoretical treatments and their underlying problems in solving multicomponent diffusion problems have been summarized in a recent article.[4] Here, we validate a straightforward method to account for the cross diffusion coefficient.

Liquid diffusivity can be measured experimentally using several techniques. These methods have been applied to oli-

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Table 1. *n*-Alkane Systems Simulated in this Work

Components (Volume %)	Number of Molecules
n-octane (100%)	384
n-hexadecane (100%)	192
n-hexadecane + ethane − infinite dilution (<1% C2)	192 + 6
n-octane + ethane − infinite dilution (<1% C2)	384 + 6
n-hexadecane + *n*-octane (50%)	90 + 180
infinite dilution (<1% C16)	1 + 384
infinite dilution (<1% C8)	192 + 1
n-hexadecane (45%) + *n*-octane (45%) + ethane (10%)	256 + 512 + 456

gomer and polymer melts and solutions to measure diffusivities with and without concentration gradients. These techniques have evolved from the use of the diaphragm cell technique[5,6] and Gouy interferometry[7] to pulsed-gradient spin-echo (PGSE) nuclear magnetic resonance (NMR).[8] Lately, PGSE-NMR has proved a very useful and relatively simple method to measure self-diffusivities of liquid mixture, but its application to alkane mixtures requires components with diffusivities separated by an order of magnitude.[9]

It is difficult to use physical experiments to determine the extent of cross-diffusion induced in a minor component by the diffusion of major components. The goal of this article is to distinguish between diffusion models[3] that allow use of binary diffusion data to predict ternary behavior. These models may or may not predict interesting behavior such as cross-diffusion, but they always give physically plausible results. In lieu of physical experiments, molecular dynamics (MD) simulations with a united atom model of alkane mixtures were used to estimate the binary diffusion coefficients and to test the model predictions for a ternary mixture. Comparisons of the molecular simulations with numerical solutions of the diffusion equation allow the better model to be chosen.

MD simulations of single component and binary systems of *n*-alkanes were run to validate the MD parameters and simulation technique by comparison with experimental results. Then a slab geometry was simulated to test predictions of the continuum models reported earlier.[3]

Details of Numerical Simulations

MD simulations of the pure component and multicomponent systems listed in Table 1 were performed at constant temperature (300 K) and pressure (1 atm) using the GROMACS code.[10] Alkane molecules were represented explicitly using bond length and angle, and torsion parameters provided by Mondello et al.[11] Berendsen's coupling algorithms were used to maintain constant temperature and pressure.[12] Periodic boundary conditions were applied in all three directions. The simulations were run with a time step of 2 fs. All the simulations listed in Table 1 include at least 500 ps (up to 1 ns) of equilibration time, and the results reported here are calculated from a trajectory of 2 ns for some simple systems and up to 10 ns for larger or more complex multicomponent systems. The reported diffusivities are calculated from Einstein's equation for diffusion in 3D by averaging over all N molecules of that component. The total momentum (center-of-mass motion) of the whole system was nullified at every time step to avoid any convection. The number of molecules in these simulations is large enough that the error in the measured self-diffusion coefficient, due to conservation of momentum in the simulation box, is negligible.

Results and Discussion

We first explored finite size effects on the diffusion coefficient of *n*-dodecane molecules. Figure 1 shows the rate of change of the mean square displacements (MSD) of the center of masses of all molecules. The diffusion coefficient increases slightly with increases in system size up to 1024 molecules. Similar observations have been documented in the literature.[13,14] The extrapolated diffusion coefficient in an infinite domain is reasonably close to that determined using 256 molecules of *n*-dodecane. The pure binary and multicomponent systems shown in Table 1 have system sizes large enough to give a good estimate of diffusion coefficient.

Binary mixtures of alkanes

Single component self diffusivities and tracer diffusion coefficients in liquid alkane mixtures have been calculated using similar molecular dynamics simulations[15-17] and have been confirmed by experimental studies.[8] Experimental techniques have difficulties in measuring tracer diffusion coefficients of components with low concentrations,[9] but computer simulations can avoid this problem.

All concentrations mentioned in this work are in terms of volume fraction or volume percentage. Infinite dilution (<1% concentration) corresponds to the diffusion observed for just one molecule of the component in a box filled by the second component. In the case of ethane, six molecules were used to measure its diffusion rate at infinite dilution in octane and hexadecane. In this work, we have run pure component simulations of two alkanes (octane and hexadecane). 50% and <1% (infinitely dilute) binary mixtures were also simulated. As the concentration of a component decreases, longer simulation trajectories are required to obtain smooth MSD behavior. The MSD plots, averaged with the trajectories of all molecules belonging to each component in the system, were cumulated at various time intervals, and the diffusion coefficients were calculated using the time period during which the MSD curves converged while showing displacements that were at least about two times the molecular size of that component. Figure 2 shows MSD plots for octane and hexadecane molecules from

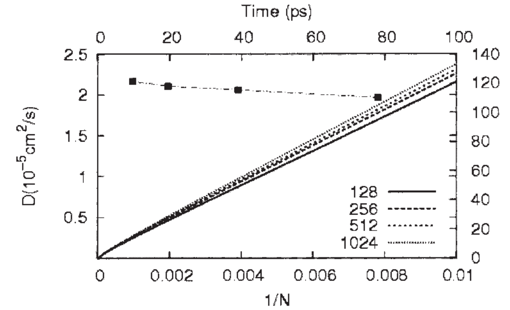

Figure 1. Behavior of the diffusion coefficient for n-dodecane(C12) at 350K and 1 atm with increasing system size.

The righthand axis is the mean square displacement.

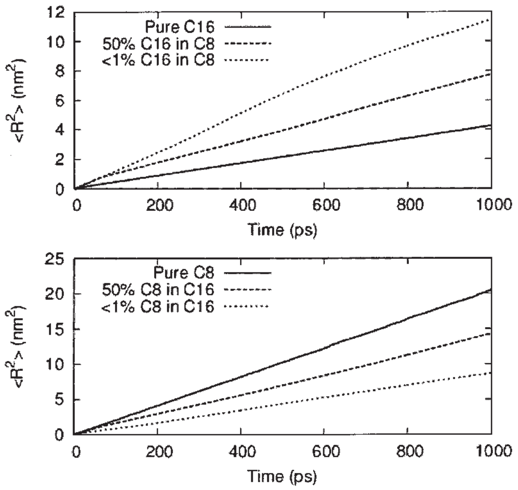

Figure 2. Mean square displacements for octane-hexadecane binary systems at various concentrations (v%).

simulations at three different concentrations of each component.

Table 2 shows the diffusion coefficient as a function of alkane concentration (v%) calculated from simulations. Monotonic dependence of diffusivity on concentration for binary systems composed of short n-alkane molecules has been reported earlier in the literature.[9,16,18] The diffusion coefficients of ethane at infinite dilution in bulk octane and bulk hexadecane using molecular dynamics simulations were found to be 6.1052(± 1.77) $\times$ 10^{-5} cm^2/s and 2.5244(± 1.46) $\times$ 10^{-5} cm^2/s, respectively.

The pure component diffusivities measured from the united atom simulations is in good agreement with experimental results.[8] The MD simulations provide a good measure of concentration dependent tracer diffusivities for binary systems and set the stage for investigation of more complicated multicomponent systems.

Special ternary system with alkane slabs

Figure 3 shows the snapshot of a ternary alkane system having slabs of octane and hexadecane with ethane molecules distributed uniformly over the entire simulation box. The slabs are formed in the direction normal to the z-axis in the simulation space. Additional partial forces were imposed on the octane and hexadecane molecules to create these slabs during the equilibration period of the simulation. The slab geometry for the major components replicated the initial condition used in the original description of the competing diffusion models.[3] The results from the MD detailed simulations can thus be compared to the continuum mechanical solutions for the macroscopic models. Once the slabs were formed, the slab forming forces were applied for an additional 1 ns to create several random configurations of the slab geometry. We chose four configurations from the 1 ns long trajectory as starting points for the production runs. During the production run in these four simulations, we observed the slabs diffusing into one another as time passed. Within 2.5 ns all the concentrations profiles flatten out, i.e., the octane and hexadecane molecules have formed a homogeneous system.

Figure 4 shows density profiles calculated using the three continuum models discussed by Nauman and Savoca[3]: the standard model, the pair-wise flux model, and the proportional flux model. The diffusion coefficients used in these macroscopic models are the self-diffusion coefficients obtained from the united atom simulations of pure components normalized by

Table 2. Diffusion Coefficient $\times$ 10^{-5} cm^2/s for Octane-Hexadecane Binary Systems

Concentration (v%)	Octane	Hexadecane
Experimental (100%)	2.818	0.4466
100%	3.4027 (±0.152)	0.7036 (±0.039)
50%	2.3311 (±0.392)	1.2545 (±0.131)
<1%	1.4578 (±0.834)	2.1651 (±0.676)

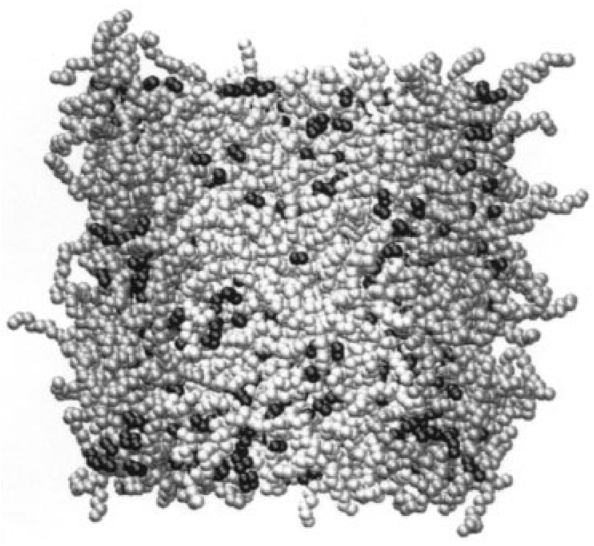

Figure 3. Snapshot of molecular dynamics simulation of the initial condition with octane (white) and hexadecane slabs (gray) and uniformly distributed ethane (black) molecules.

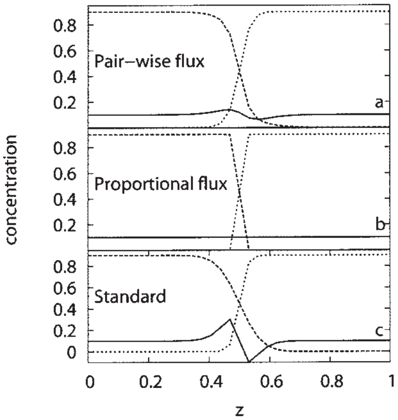

Figure 4. Volume fractions predicted from continuum models for the slab geometry and using relative diffusion coefficients as obtained by MD.

The solid lines represent the component that is uniformly distributed, ethane.

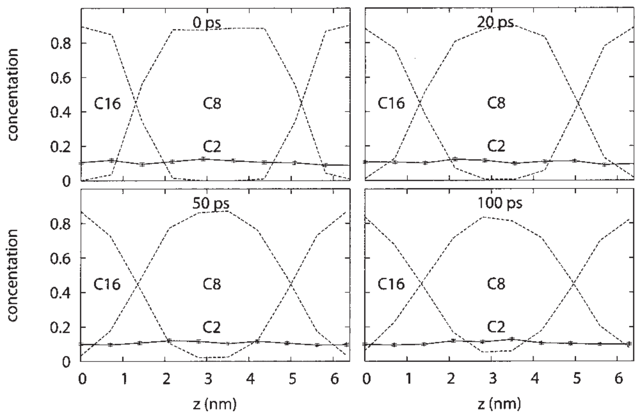

Figure 5. Evolution of volume fractions from MD simulations for diffusion in the test geometry.

Ethane is uniformly distributed across octane and hexadecane slabs, initially and throughout the simulation.

the ethane self-diffusion coefficient. The self-diffusion coefficients are good representation of the mobility of alkanes provided the entire system is composed of a mixture of similar alkane molecules. Considering the composition of our system (linear alkanes), we approximate the Fickian diffusion coefficients used in the models by the self-diffusion coefficients obtained from the MD simulations. The macroscopic models are non-dimensional in space, time, and concentrations. The y-axis in Figure 4 shows the volume fraction for the various components; the linear dimension of the simulation box scales the x-axis, and the time in the plots is adjusted to show the maximum predicted deviation from uniformity of the minor component. Note that this minor component is initially uniform and becomes uniform at long times. The standard model predicts extensive cross diffusion, to the point that the ethane concentration becomes negative. The pair-wise flux method also predicts cross diffusion, with concentration fluctuations of about 50% of the average concentration range for the minor, initially uniform component (ethane), but the predicted ethane concentration always remains positive. The proportional flux model predicts no cross diffusion. The existence of cross diffusion was used to discriminate between the two physically realistic models.

Figure 5 shows the average concentrations as volume fractions of the three components from pooled data from the four different simulation runs. The large bin size, 8 Å, reduces the noise in the density profiles and convincingly shows an absence of cross diffusion. Clearly, the ethane concentration is uniform throughout the system at various time intervals in the simulation. Ethane was replaced with a slower component, dodecane, whose diffusivity is intermediate between that of octane and hexadecane. The concentration profile for dodecane (not shown here) also remained uniform in the system at all times.

Conclusions

The tracer diffusivities at different concentrations of binary mixtures can be determined from molecular dynamics simulations. For the small, linear n-alkanes considered in this work, the tracer diffusivities are a linear function of concentration. MD is also suitable for studying more complex systems, such as the ternary slab geometries used here to test various continuum models.[3] A key finding for the system of octane and hexadecane with ethane as a uniformly distributed minor component was the absence of cross diffusion. This result is consistent with the proportional flux model[3] and is substantially different from the standard model of multicomponent diffusion that predicts extensive and even nonphysical levels of cross diffusion.

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