Molecular Simulations and NMR Measurements of Binary Diffusion in Zeolites

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The first comparison is made of molecular dynamics (MD) simulation and experimental self-diffusivities for a binary mixture adsorbed inside a zeolite. MD results for methane/tetrafluoromethane mixtures in silicalite agree well with self-diffusion coefficients from pulsed field gradient NMR. At constant total loading, the diffusivities of both components decrease as the fraction of the larger, less-mobile CF_4 in the system is increased. Singlet and pair distribution functions were also calculated. The simulations predict preferential adsorption of CF_4 in the straight channels and methane in the zigzag channels.

Introduction

Zeolites are inorganic, microporous, crystalline solids widely used as catalysts, adsorbents, and ion exchangers.[1] The high selectivities that are possible make zeolites attractive materials for new environmentally friendly industrial processes. However, our ability to choose and tailor zeolites for specific processes is limited by a lack of understanding of the molecular-level interactions and their influence on macroscopic phenomena. In many catalytic and adsorption processes using zeolites, the rate of diffusion of adsorbed molecules inside the zeolite pore system plays an important, sometimes critical, role in determining the overall observed performance.[2,3] The strong constant interactions between the adsorbed species and the zeolite lattice give rise to a diffusion regime referred to as configurational diffusion. This regime is poorly understood due to the sensitivity of zeolite diffusivities on subtle differences in adsorbate and pore geometry, as well as on energetic interactions such as those between adsorbates and zeolitic cations. In particular, binary or multicomponent diffusion has not received nearly as much attention as single-component diffusion in zeolites, although it is, of course, such multicomponent behavior that is of interest in practical applications of zeolites.[4−6]

Molecular simulations have proven extremely useful in elucidating the role of molecular-level interactions in zeolite diffusion. Employing atomistically-detailed models and the principles of statistical mechanics, such simulations can predict diffusivities of various sorbates in different zeolites in generally good agreement with experimental values. Theodorou et al.[7] have recently reviewed work in this area. The most popular simulation technique used to date has been, by far, molecular dynamics (MD) simulation, in which the Newtonian equations of motion are integrated forward in time and the self-diffusivity is calculated from the molecules' mean-squared displacement.[8] In addition to the self-diffusivities, MD simulations also provide information on modes of sorbate motion, siting in different regions of the zeolite, and the heats of sorption. Despite MD's success for single-component diffusion in zeolites, there have been no MD simulations reported for binary diffusion of realistic sorbates, although Chitra and Yashonath[9] have reported MD simulations of binary mixtures of Lennard-Jones spheres having identical mass in NaY zeolite. One reason for this has been

the general lack of mixture experimental self-diffusivity data for systems amenable to MD simulation. In addition problems of generating an equilibrated initial configuration for the simulation are exacerbated for multicomponent systems.

In this work we have used molecular dynamics simulation to investigate the self-diffusion of binary mixtures of methane and tetrafluoromethane (CF_4) in the zeolite silicalite. To provide verification of the simulation results, we also performed pulsed field gradient (PFG) nuclear magnetic resonance (NMR) self-diffusion measurements[2,10] for the same systems. Total loading was held constant at 12 molecules per unit cell, while the composition was varied from pure methane to pure CF_4.

Experimental Section

Self-diffusion coefficients for methane and CF_4 were measured by ^1H and ^{19}F PFG NMR, respectively, on a home-built spectrometer, FEGRIS, operating at a proton resonance frequency of 60 MHz. Measurements were made with the Hahn spin-echo sequence with typical observation times for diffusion of 2 ms. Large-crystal silicalite samples, synthesized by the method of Müller and Unger,[11] were supplied by S. Ernst and J. Weitkamp of the University of Stuttgart. Samples for the diffusion measurements were prepared as described previously.[12]

Simulations

Methane and CF_4 molecules were modeled as single interaction sites. Sorbates were assumed to interact with one another and with the zeolite by a pairwise-additive Lennard-Jones potential between interaction sites. As in much of the previous work in this field, interactions with the zeolite silicon atoms were neglected.[13−16] The oxygen atoms of the zeolite lattice were assumed to be fixed at the crystallographic coordinates determined from X-ray diffraction studies of the orthorhombic phase.[17] Silicalite has two sets of interconnected pores about 5.5 Å in diameter. A set of straight channels is directed along the *y* crystallographic axis, while a set of zigzag channels is directed along the *x* axis. These channels meet in a somewhat larger channel intersection. Methane/methane and methane/oxygen Lennard-Jones parameters were identical to those used by others.[14,15] CF_4/CF_4 parameters were taken from the literature.[18] Using the silicalite oxygen parameters of June et al.,[13] Lorentz-Berthelot combining rules were used to obtain

TABLE 1: Potential Parameters for the MD Simulations

	ϵ/k (K)	σ (Å)
CH_4-CH_4	147.95	3.73
CF_4-CF_4	134.0	4.662
CH_4-CF_4	140.80	4.196
CH_4-O	133.3	3.214
CF_4-O	109.57	3.734

parameters for the CF_4/oxygen interactions.[8] The potential parameters are summarized in Table 1.

The MD simulations were carried out with a Fortran code derived from the single-component code of June et al.[19] A Gear predictor−corrector algorithm was used to integrate the equations of motion in the microcanonical (NVE) ensemble with a time step of 5 fs. The number of sorbate molecules was usually set to either 192 or 256. Using half as many or twice as many molecules revealed no system size effects in the results. Initial configurations were generated by randomly placing the sorbates in the zeolite pores. The configurations were equilibrated by performing 10 000 Monte Carlo cycles in which trial moves were accepted according to a Boltzmann weighting (NVT ensemble). For a system of N molecules, each Monte Carlo cycle consisted of N trial molecular displacements and, for mixtures, $\approx 0.1N$ identity changes. An identity change move consisted of randomly choosing a molecule of each species and attempting to interchange their positions (or equivalently their chemical identities). It has been observed in the past[20] that, while MD can simulate such systems over the relevant time scales, it is not very efficient at *generating* an equilibrium configuration. This problem is even worse for mixtures, but such a Monte Carlo scheme, because of the identity change moves, allows for a much more efficient equilibration of the system. Initial velocities were assigned from a Maxwell−Boltzmann distribution, and the equations of motion were integrated for 100 ps with velocity rescaling to achieve the desired temperature. Then the production runs (with no velocity rescaling) were carried out for lengths of 1000 ps (methane) or 2500 ps (CF_4 or mixtures). Runs of 2500 ps took about 100 min on a DEC AlphaStation.

Results and Discussion

Before trying to simulate diffusion of methane/CF_4 mixtures, it was necessary to verify that our molecular model was capable of reproducing single-component behavior for these species. Our methane parameters had been used in the past by other authors[14,15] and shown to yield self-diffusivities in good agreement with PFG NMR measurements. Our results (not shown) are virtually identical to those in the literature as expected since we are using the same potential parameters. Calculated and measured self-diffusivities for CF_4 in silicalite at 200 and 300 K are shown as a function of sorbate loading in Figure 1. At four and eight molecules per unit cell there is excellent agreement between the calculated and measured values. The agreement at 12 molecules per unit cell is not as good. This is possibly due to limitations of our molecular model. In another test of the model, Heuchel et al.[21] have shown, using grand canonical Monte Carlo simulations, that this model predicts adsorption isotherms in very good agreement with their experimental isotherms at low pressures but that it underpredicts the amount adsorbed at higher pressures. Heuchel et al. find experimentally that the saturation loading for CF_4 in silicalite is around 12−13 molecules per unit cell, the loading at which we notice the discrepancy in the diffusivities. For methane the saturation loading is close to 15.[24]
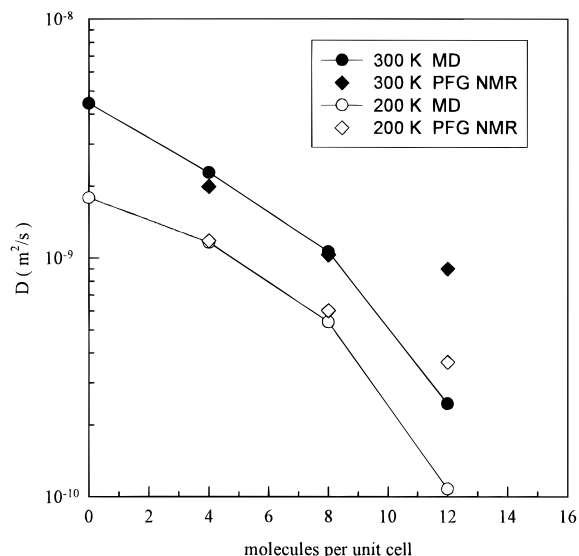

Figure 1. Single-component self-diffusivities of CF_4 in silicalite as measured by PFG NMR and predicted by MD simulations.
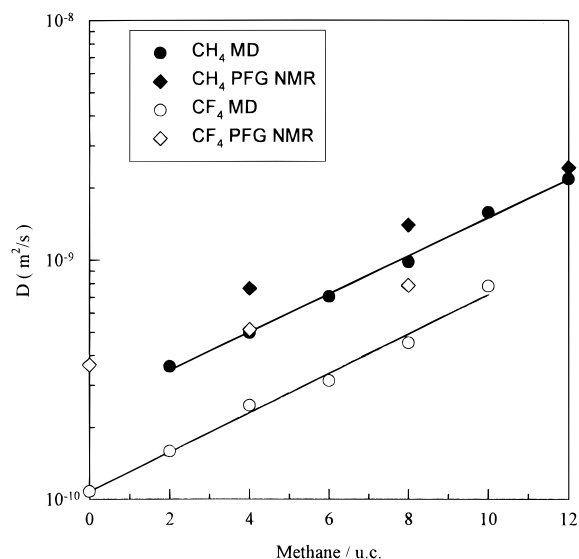

Figure 2. Self-diffusivities of methane/CF_4 mixtures in silicalite, ranging from pure methane to pure CF_4. The total loading in all cases is 12 molecules per unit cell, and the temperature is 200 K. The lines through the MD results are linear regressions, although there is no reason to expect a linear relationship. Error bars (not shown) are about $\pm 20\%$ for both the MD simulations and the PFG NMR measurements.

Mixture results are presented in Figure 2 for a series of compositions ranging from pure methane to pure CF_4. In all cases the total loading was kept constant at 12 molecules per unit cell, and the temperature was 200 K. The agreement between the simulation results and the experimental values is good. The MD predictions are consistently lower due to the discrepancy noted above for pure CF_4 at this loading. It can be seen from both the MD and the PFG NMR results that as the fraction of CF_4 in the system increases (the less mobile species), the mobilities of *both* species decrease. Because CF_4 is larger than methane, the free volume available decreases as the amount of CF_4 increases, holding the total number loading constant. The trend in the diffusivities seems reasonable. It should be noted, however, that such behavior is not universally observed. For example, using PFG NMR Hong et al.[22] observed that in a mixture of ethane and ethene in NaX zeolite the diffusivity of ethene was unchanged from its single-component value at the same (total) loading. The diffusivity of the more
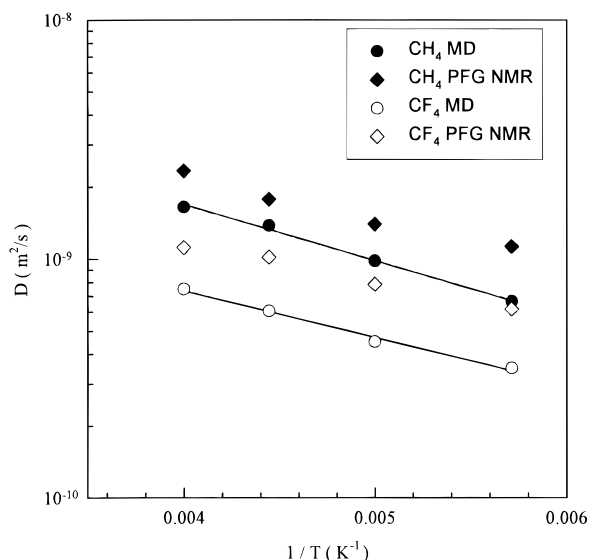
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Figure 3. Arrhenius plot for self-diffusion coefficients of methane and CF_4 in silicalite at a loading of eight methane and four CF_4 per unit cell. Results are shown from PFG NMR and MD simulation.

TABLE 2: Distribution of Species among the Different Zeolite Channel Types for Various Adsorbed Phase Compositions[a]

methane/u.c.	CH_4 in I	CH_4 in S	CH_4 in Z	CF_4 in I	CF_4 in S	CF_4 in Z
12	1.3	4.4	6.3			
10	1.2	3.5	5.3	0.2	0.9	0.9
8	1.0	2.6	4.4	0.5	1.8	1.8
6	0.8	2.0	3.2	0.7	2.5	2.8
4	0.6	1.2	2.2	1.0	3.2	3.8
2	0.3	0.5	1.2	1.3	3.9	4.8
0				1.6	4.4	6.0

[a] All results are for a total loading of 12 molecules per unit cell at 200 K. The table lists the average loading of methane and CF_4 molecules in the channel intersections (I), straight channels (S), and zigzig channels (Z). (Each row adds up to 12, the total loading in all cases.)

mobile ethane, on the other hand, was reduced considerably in the mixture in comparison to its single-component diffusion coefficient. Similarly for methane/ethene in NaY and ethane/ethene in silicalite, Nivarthi and McCormick[23] also observed that slowly-diffusing sorbates reduce the mobility of otherwise mobile coadsorbed species but are themselves relatively unaffected. That different qualitative trends are seen in different systems is not unexpected in light of the differing molecular-level interactions (e.g. presence of cations). One common trend, however, is that in our work and these two other studies the difference in mobility of the two species is less for mixtures than for the pure components.

The effect of temperature on the diffusivities is shown in Figure 3 for a loading of eight methane and four CF_4 per unit cell. Simulation and experiment both give activation energies for diffusion of 3−5 kJ/mol for both species in the mixture. We observed similar activation energies in our PFG NMR measurements for pure CF_4 at various loadings, and similar activation energies have been reported in the past for methane.[2,13]

Diffusivities of 10^{-10} m^2/s as shown in Figures 1 and 2 are toward the lower end of the range that can be predicted reliably by molecular dynamics simulation in a reasonable amount of computer time with current computer hardware. For such low diffusivities we simulated 2500 ps, which gives root-mean displacements of at least 12 Å. A few longer runs with root-mean displacements of 17 Å (almost a unit cell edge length) confirmed that our simulations of 2500 ps were long enough for this system.

In addition to the diffusivities, the simulations also provide information on thermodynamic and structural properties of these systems. The average potential energy experienced by the molecules is related to the heat of adsorption. This energy can be conveniently considered as arising from two sources: sorbate/sorbate and zeolite/sorbate interactions, both of which vary slightly with loading for single-component adsorption.[24] Interestingly, for the mixtures of Figure 2, the zeolite/sorbate interactions for methane and CF_4 are remarkably constant with varying composition, taking values of −15.8 and −23.0 kJ/mol for methane and CF_4, respectively. This is somewhat surprising, since as we discuss next, the molecules are segregated into different portions of the zeolite at different compositions and the different channels are known to have different adsorption

energies.[13] We are currently investigating further the connection between sorbate siting and energetics.[21]

For purposes of calculating where the molecules adsorb within the silicalite pore system, we divided the intracrystalline space into intersection (I), straight (S), and zigzag (Z) regions as described by June et al.[25] using the methane/silicalite potential energy surface. The three regions have relative sizes of 14.2, 38.4, and 47.4%, respectively. For the pure components, the molecules avoid the energetically less favorable channel intersections, especially at low loading or low temperature. At higher loadings and temperatures, the molecules in single-component systems are distributed more and more according to the distribution dictated simply by the relative volumes of the three regions.[25] Mixture siting results for various compositions are presented in Table 2 for constant total loading of 12 molecules per unit cell at 200 K. When both components are present, CF_4 is seen to adsorb preferentially in the straight channels while methane adsorbs more in the zigzag channels. Thus at a composition of 6 methane and 6 CF_4 per unit cell there are on average 2.5 CF_4 in the S sites but only 2.0 methane molecules, while the Z sites contain 3.2 methane and only 2.8 CF_4 molecules. Or, if we concentrate on the local composition within a particular region we see, for example, that at a composition of four methane and eight CF_4 per unit cell the composition within the S regions is 26% methane and 74% CF_4, the composition in the Z regions is 37% methane and 63% CF_4, and the overall composition is 33% methane and 67% CF_4.

In addition to investigating where the adsorbates are located with respect to the zeolite, we also investigated their locations with respect to one another by calculating pair distribution functions $g(r)$ from the configurations generated by the MD simulations. Figure 4 compares the pure component pair distribution functions of methane and CF_4 at 200 K and a loading of 12 molecules per unit cell (u.c.). Nearest-neighbor peaks at about 4.0 and 4.9 Å for methane and CF_4, respectively, are clearly seen. The longer-range structure in $g(r)$ is largely produced by the periodic arrangement of the zeolite pores.[24] In Figure 5 pair distribution functions are shown for a mixture of six methane/u.c. and six CF_4/u.c. at 200 K. Results are presented separately for methane/methane pairs, CF_4/CF_4 pairs, and methane/CF_4 pairs. In all cases results are normalized appropriately so that $g(r)$ approaches unity at large distances. By integrating the pair distribution function to its first minimum, the number of nearest neighbors within a distance r can be determined[25]

$$n(r) = 4\pi\rho \int_0^r g(\xi)\xi^2 \, d\xi$$

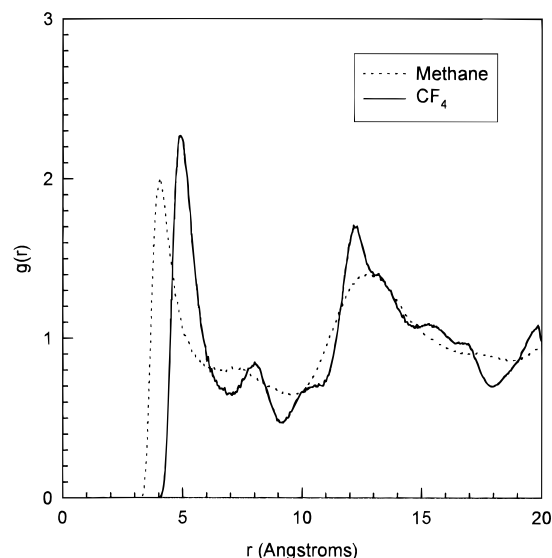where ρ is the density of the species in question. We performed

Figure 4. Pure-component pair distribution functions for methane and CF$_4$ at 200 K and 12 molecules per unit cell.
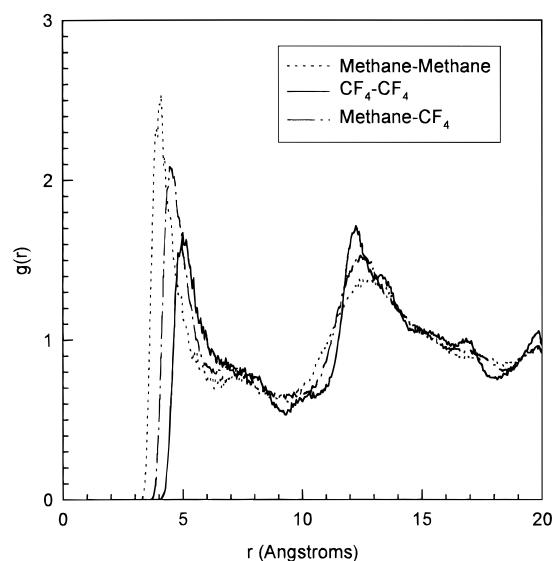

Figure 5. Pair distribution functions for a mixture of six methane/u.c. and six CF$_4$/u.c. at 200 K. Separate results are shown for methane/methane pairs, CF$_4$/CF$_4$ pairs, and methane/CF$_4$ pairs.

this integration out to 6.5 Å for the five curves shown in Figures 4 and 5. For pure methane we found 2.30 neighbors within 6.5 Å. For CF$_4$ we found 2.34. For the 50−50 mixture the numbers of neighbors were 1.23, 0.99, and 1.17 for methane/methane, CF$_4$/CF$_4$, and methane/CF$_4$ pairs, respectively. Thus at this composition, most molecules have on average about two neighboring molecules within 6.5 Å—one methane neighbor and one CF$_4$ neighbor.

It has been observed both experimentally[26−28] and by MD simulation[13,14,19,20] that diffusion in silicalite is anisotropic. Preferential adsorption of methane and CF$_4$ in the zigzag and straight channels, respectively, clearly could affect the components of the diffusion tensor in this system. As we increase the fraction of CF$_4$ holding total loading constant in Figure 2 and Table 2, the overall diffusivities decrease, but we might expect that diffusivity in the direction of the straight channels, D_y, might decrease more than diffusivity in the direction of the zigzag channels, D_x, due to the preference of the slower CF$_4$ to reside in the straight channels. In Table 3 it can be seen that this is indeed seen in the MD simulations, as the ratio D_y/D_x falls with increasing CF$_4$ content. Preferential diffusion of

TABLE 3: Diffusion Anisotropy for CF$_4$[a]

methane/u.c.	D_x (m^2/s)	D_y (m^2/s)	D_y/D_x
10	4.1×10^{-10}	18×10^{-10}	4.4
8	3.4×10^{-10}	6.7×10^{-10}	2.0
6	3.6×10^{-10}	4.8×10^{-10}	1.3
4	3.0×10^{-10}	3.2×10^{-10}	1.1
2	2.1×10^{-10}	2.2×10^{-10}	1.0
0	1.3×10^{-10}	1.3×10^{-10}	1.0

[a] All data are for a total loading of 12 molecules per unit cell at 200 K. The x and y components of the diffusivity tensor for CF$_4$ are given along with their ratio.

certain reactants or products along separate channel systems has been hypothesized by Derouane and co-workers as a possible mechanism in zeolite catalysis and referred to as "molecular traffic control".[29,30] Derouane suggested that if reactants diffuse in by one set of channels and products diffuse out by another set of channels, counter diffusion effects might be minimized and overall catalytic activity enhanced. Derouane's model applies to a steady-state catalytic system in which concentration gradients exist, while our simulations are for a nonreacting system at equilibrium and thus without concentration gradients or fluxes. Nevertheless, the essential element of the molecular traffic control hypothesis is observed in our simulations: preferential adsorption (and mobility) of different species in a mixture in different channel systems of the zeolite pore network.

Conclusions

This work has demonstrated the potential of molecular dynamics simulations for predicting diffusion properties of binary mixtures in zeolites. Given the complexities of single-component diffusion in zeolites,[1−3,7] we feel that such simulations will play a key role in understanding multicomponent diffusion, where answering fundamental theoretical questions such as the relation between equilibrium and nonequilibrium behavior will be even more demanding than for single-component adsorption systems. For the simple system of methane and tetrafluoromethane in silicalite, we have presented an atomistic model that yields single-component self-diffusivities in reasonable agreement with experiment. The same model also yields self-diffusivities for the mixtures that agree well with results of our pulsed field gradient NMR diffusion measurements. The mixture investigations were carried out for a series of samples all with a loading of 12 molecules per unit cell, varying the composition from pure methane to pure CF$_4$. Both simulation and experiment show that as the fraction of the larger, less-mobile CF$_4$ is increased (at constant total loading) the diffusivities of both components decrease.

The simulations also predict that when both methane and CF$_4$ are present there is a tendency for CF$_4$ to adsorb preferentially in the straight channels while methane adsorbs preferentially in the zigzag channels. This segregation gives rise to changes in diffusion anisotropy as a function of composition. The experimental verification of this presents an interesting challenge for future research. This kind of segregation is also the key feature of the molecular traffic control idea hypothesized by Derouane and co-workers.[29,30] Our simulations provide tentative evidence of such an effect. The system investigated consists of two rather similar species, where one would expect the smallest driving force for segregation. That we see segregation even for this system suggests that the phenomena might be very common.

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