Diffusion of a Mixture of Methane and Xenon in Silicalite: A Molecular Dynamics Study and Pulsed Field Gradient Nuclear Magnetic Resonance Experiments

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The diffusion of a mixture of methane and xenon in the zeolite silicalite is studied by use of molecular dynamics (MD) simulations and pulsed field gradient (PFG) nuclear magnetic resonance (NMR). For a fixed total number of guest molecules, the ratio of xenon to methane is varied in order to examine the special properties of diffusion in a mixture. High xenon concentrations were found to slow the methane diffusivity in the mixture, while the diffusion of xenon is nearly unaffected by high methane concentrations. The reason for the dominance of xenon is the larger local heat of adsorption of xenon and the larger mass of xenon compared to methane in combination with channel size and topology in silicalite. Simulated and experimental data are in very good agreement with each other. Diffusion anisotropy as resulting from the MD simulations is discussed in terms of the correlation rule for diffusion in the interconnected pore system of ZSM-5 (Kärger, J. *J. Phys. Chem.* **1991**, *98*, 5558).

1. Introduction

Zeolites have become an attractive model system for molecular diffusivities in porous media. The numerous technical applications in chemical industries as, e.g., molecular sieves, catalysts, or ion exchangers² are of practical interest, while from the theoretical point of view their well-defined crystal structure makes them very interesting.³

MD simulations have proven to be a helpful tool in understanding diffusion phenomena.^{4,5} The MD simulations are able to monitor the local process of molecular migration, being unaccessible by any experimental technique, and allow parameter variation over wide ranges with very little costs. This makes MD simulations a useful supplement to experiments.

2. Lattice of Silicalite

Silicalite is the aluminum-free and therefore cation-free variant of the zeolite ZSM-5. The symmetry group of silicalite is *Pnma* with cell parameters a = 20.07 Å, b = 19.92 Å, and c = 13.42 Å.⁶ In silicalite there is a three-dimensional channel network, which consists of only two kinds of channels (Figure 1). One type, called straight channel, is parallel to the ydirection. The other one, called zigzag channel, follows the xdirection with its main component but has an oscillating component parallel to the z direction. These two kinds of channels are connected to each other at intersections which enable displacements in z direction to follow the path z1, s, z2in Figure 1. The two channels have a similiar size, the straight channels with a slightly elliptical cross section of 5.3×5.6 $Å^2$, and the zigzag channels, $5.1 \times 5.5 Å^2$. As the diffusants considered in this study are smaller than the channel diameters, anomal diffusion, which was observed for channel sizes aproximately equal to the size of the diffusants,7 should not occur. Contrary to A zeolites the system is therefore not very sensitive to small changes either in the structure or in the interaction parameters. Accordingly we used a rigid framework



Figure 1. Schematic view of the channel system within one unit cell of silicalite.

because previous studies in silicalite with rigid/flexible framework led to similar results with regard to the diffusion coefficient.⁸⁻¹¹

3. MD Simulations

All interactions are modeled by 12–6 Lennard-Jones (LJ) pair potentials using the form

$$U_{ij} = 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$
(1)

where i,j indicate the interacting particles with the distance r_{ij} , ϵ is the minimum of the potential, and $U(\sigma) = 0$. As in silicalite there are no cations, no electrical charges occur, and we neglect any electrostatic interactions. Methane is approximated by a one-center LJ potential, because this spherical potential has been shown to be a good approximation to a five-center LJ potential¹² and it makes the simulation less time-consuming. The LJ parameters used are given in Table 1. The LJ parameters for silicon–guest lead to a substantially weaker interaction than those for oxygen–guest. Furthermore, this interaction is screened by the oxygen atoms, so we neglected the influence of the silicon atoms, as is usually done in MD simulations of zeolites.

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TABLE 1: Lennard-Jones Interaction Parameters

CH_4-O	$CH_4 - CH_4$	CH ₄ -Xe	Xe-Xe	Xe-O
3.214	3.730	3.897	4.064	3.296
1.108	1.230	1.517	1.870	1.679

The LJ parameters are taken from the literature wherever possible. For Xe–Xe and Xe–O they are taken from ref 13. For CH₄–CH₄ and CH₄–O there is a wide variety of parameters in the literature.¹⁴ Since there is no convincing argument for one special set of parameters, we choose an intermediate set introduced by Goodbody et al.,¹⁰ which was also used by Maginn et al.¹⁵ In contrast to the case of the cation-free LTA zeolite,¹⁴ the diffusion of the considered guest molecules in silicalite should not be very sensitive to the choice of the parameter set because there are no narrow sites in the lattice like the windows between different cages in the LTA zeolite. To get consistent values for parameters of the interaction between xenon and CH₄, we calculated them using the rule of Lorentz–Berthelot:¹⁶

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{2}$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \tag{3}$$

3.1. Technical Details. The simulations were done using the velocity Verlet algorithm¹⁷ with a time step of 10 fs. Each run contained a thermalization part of 10 000 steps (100 ps) and an evaluation part of 500 000 steps (5 ns). The size of the MD box was varied in such a way that it accommodated 128 guest molecules for a loading of 4, 8, and 16 molecules per unit cell and 144 guest molecules for a loading of 12 molecules per unit cell. The simulations were carried out for temperatures of 300 and 150 K. The constance of temperature was ensured by a weak coupling to an external bath according to ref 18. In that work, this algorithm was shown to leave the velocity autocorrelation function unchanged even for much stronger couplings than implemented in this work. As the diffusion coefficient can be calculated by integrating the velocity autocorrelation function, it is not influenced by this algorithm. The MD program (Fortran) runs on a Cray M94 and on a Cray J90 of the HLRZ at the Forschungszentrum Jülich. We calculated the diffusion coefficients for the three main directions x, y, and z and a mean diffusion coefficient $D = \frac{1}{3}(D_x + D_y + D_z)$ using the first four moments of displacement according to ref 19.

3.2. Results of the Simulations. The simulations were carried out at two temperatures. For T = 300 K, we calculated the whole range of loadings mentioned in section 3.1. At T = 150 K, we calculated runs for a loading of 8 molecules per unit cell to be able to compare the simulations with the experiments. These results are given in section 4.2. Unless otherwise quoted, in this section we refer to the simulations at room temperature. Some of the results at T = 300 K were previously published in ref 20.

3.2.1. Pure Adsorbents. Figures 2 and 3 show the dependence of the diffusion coefficient of pure methane and pure xenon on the loading. In both cases there is the same qualitative behavior. The diffusion coefficient decreases with increasing loading. This behavior may be easily referred to more frequent changes in the direction of molecular motion because of more frequent collisions. As to be expected, in all cases the time dependence of the investigated moments follows normal diffusion. Due to the anisotropy of the channel system, the different directions show different diffusion coefficients. The



Concentration / particles per unit cell

Figure 2. Mean elements of the diffusion tensor and the mean diffusivity for pure methane for different loadings.



Figure 3. Mean elements of the diffusion tensor and the mean diffusivity for pure xenon for different loadings.

fastest diffusion takes place in the *y* direction, about one-third smaller is the diffusivity in the *x* direction, and much slower is the diffusion in *z* direction (more details are given in section 3.4). These results are in good agreement with literature data of computer simulations^{10,13} and are presented here to verify the computational model.

3.2.2. Diffusion in the Mixture. The results of the simulation of the binary mixture are shown in Figures 4-8. In all cases under study the methane diffusion is slowed dramatically due to the presence of xenon atoms, while the xenon diffusion depends mainly on the total number of guest molecules and shows only a slight dependence on the composition of the mixture. In the mixture, xenon diffusion shows a clear decrease with increasing xenon concentration at constant overall concentration only at the highest loading.

At all loadings, the methane diffusion slows down with increasing xenon content; at first more or less linear up to at a xenon loading between 8 and 10 atoms per unit cell, the methane diffusion is not significantly faster than the xenon diffusion. For the rest of the plot, the diffusion coefficient of methane follows that of xenon. In fact, by blocking the channel system, the xenon atoms may be considered to terminate the movement of the methane. This behavior is qualitatively identical for all loadings and all directions. The occurring differences in the shape of the plot are mainly of a quantitative nature due to the dependence of the diffusion coefficient on the total loading.



Xenon concentration / particles per unit cell

Figure 4. The single-component diffusion coefficients at T = 293 K for different mixtures of xenon and methane with a constant overall loading of 4 particles per unit cell (arithmetic mean of the diffusivities in *x*, *y* and *z* directions).



Xenon concentration / particles per unit cell

Figure 5. Single-component diffusion coefficients at T = 293 K for different mixtures of xenon and methane with a constant overall loading of 8 particles per unit cell (arithmetic mean of the diffusivities in *x*, *y*, and *z* directions).



Xenon concentration / particles per unit cell

Figure 6. Single-component diffusion coefficients at T = 293 K for different mixtures of xenon and methane with a constant overall loading of 12 particles per unit cell (arithmetic mean of the diffusivities in *x*, *y*, and *z* directions).

Altogether the behavior of the two components in the mixture is not of the same kind. The binary diffusion is clearly dominated by xenon, because xenon is nearly unaffected by the



Figure 7. Single-component diffusion coefficients at T = 293 K for different mixtures of xenon and methane with a constant overall loading of 16 particles per unit cell (arithmetic mean of the diffusivities in *x*, *y*, and *z* directions).

presence of methane, while methane is very strongly influenced by xenon. This result is in contrast to the behavior of the quite similar system of methane/tetrafluoromethane in silicalite.²¹ In that system both components exhibit similar behavior. Although CF₄ is less mobile than CH₄, the diffusivities of both components are found to depend on each other in a similar manner.

3.3. Variation of the Computational Parameters. The slower diffusion of xenon in comparison to methane has two reasons. On one hand xenon atoms are heavier than methane molecules (mass ratio 131:16), which leads to a lower mean velocity at the same temperature. On the other hand the interaction with oxygen is much stronger. The ϵ parameter of the Xe–O interaction is about 50% larger than that of the CH₄-O interaction, while the σ parameters are nearly identical (Table 1). This leads to a larger local heat of adsorption and therefore to less frequent crossings of the local energy barriers. To discriminate the relative importance of these two possible reasons, we took advantage of the possibility of MD simulations, to vary either of these influences separately from the other. We carried out simulations with binary mixtures of methane and two artificial species, which we called pseudo-xenon1 and 2. Pseudo-xenon1 has the same mass as xenon but the LJ parameters of methane, while pseudo-xenon2 has the LJ parameters of xenon but the mass of methane. If one of the reasons is dominating, both simulation series should show different habits. Both reasons turned out to be of similar importance. Figures 9 and 10 show that in both cases the plots are qualitatively similar to that in Figure 13; only the diffusion of the two pseudo-xenons is faster than the diffusion of real xenon, because one of the two reasons slowing down diffusion is eliminated.

3.4. Anisotropy of Diffusion. Due to the special channel system, the diffusion in silicalite is anisotropic. The ratio of the different diffusion coefficients D_x , D_y , and D_z is not independent of the physical situation. D_y is always bigger than D_x and the mean value of the ratio is $D_x/D_y \approx 0.66$ for most physical situations. Only for the highest loading (16 guest molecules per unit cell) did we find a significantly lower value of $D_x/D_y \approx 0.22$ for xenon at all compositions of the mixture and for methane in the mixtures with high xenon content, i.e., in the xenon-dominated mixtures. As diffusion in the *z* direction is composed of diffusion steps in the other two directions, the main elements of the diffusion tensor cannot be independent



Xenon concentration / particles per unit cell

Figure 8. Mean elements of the single-component diffusion tensor at T = 293 K for different mixtures of xenon and methane with a constant overall loading of 16 particles per unit cell.

from each other. Under the assumption that the propagation of the particles from channel intersection to channel intersection is independent of their previous diffusion path (Markovian process), one obtains the correlation rule¹

$$\frac{a^2}{D_x} + \frac{b^2}{D_y} = \frac{c^2}{D_z}$$
(4)

where *a,b,c* are the unit cell lengths.



Concentration of pseudo-xenon1 / particles per unit cell

Figure 9. Mean diffusion coefficients of methane and pseudo-xenon1 for a total concentration of 8 particles per unit cell at T = 150 K.



Concentration of pseudo-xenon2 / particles per unit cell

Figure 10. Mean diffusion coefficients of methane and pseudo-xenon2 for a total concentration of 8 particles per unit cell at T = 150 K.

For a quantification of deviations from the correlation rule, we use the parameter

$$\beta = \frac{c^2 / D_z}{(a^2 / D_y) + (b^2 / D_y)}$$
(5)

as introduced in ref 22. $\beta = 1$ would mean that the basic assumption of the correlation rule is fulfilled, i.e., that molecules passing an intersection continue their diffusion path independent of how they got to this intersection. $\beta > 1$ has to be interpreted as a preferential continuation of the diffusion path in one and the same channel type, while $\beta < 1$ indicates that the molecules prefer to switch from one channel type to the other.

We calculated β separately for the components of the mixture for all the simulation runs (Figure 11). We plotted the values for different physical situations in one histogram, since there was no perceptible trend in the β values with either temperature or loading, so we have accumulated the results in order to improve the statistics. Only for the highest loading (16 guest particles per unit cell) are there some hints that the distribution of β gets closer to 1, but this is difficult to isolate because each value for β represents a different model situation so that fluctuations in β are not surprising. Figure 11 shows that the values for β are spread over a relatively wide range of values with the mean value situated at $\beta = 1.2$ for xenon and at $\beta =$ 1.3 for methane. This indicates that there is a slightly enhanced probability that the molecules continue their diffusion path



Figure 11. Probability distribution of the parameter $\beta = (c^2/D_z)/[(a^2/D_x) + (b^2/D_y)]$ as resulting from the MD simulations.

through the same channel type, though eq 5) may still be considered to provide a good order-of-magnitude estimate.

4. Experimental Section

4.1. Methods. Pulsed field gradient (PFG) NMR^{3,23} has proven to be an effective tool to study intracrystalline zeolitic diffusion.^{3,24,25} PFG NMR directly monitors molecular displacements within adsorbate—adsorbent systems. The most favorable conditions for this method are provided by ¹H NMR. In the past few years PFG NMR has also been performed using ¹⁹F NMR,²⁶ whose sensitivity is similar to that of ¹H NMR, as well as ¹³C NMR,^{27 15}N NMR²⁸ and ¹²⁹Xe NMR.²⁹

Measurement of molecular diffusion by use of PFG NMR is based on the observation of the NMR signal attenuation Ψ after an appropriate sequence of radiofrequency pulses and inhomogeneous magnetic field (field gradient) pulses. In an isotropic system the echo attenuation obeys the relation^{3,23}

$$\Psi = \exp\left[-\gamma^2 \delta^2 g^2 D\left(\Delta - \frac{\delta}{3}\right)\right] \tag{6}$$

where δ , g, and Δ denote the width, intensity, and separation of the field gradient pulses and γ is the gyromagnetic ratio of the nuclei. D is the self-diffusivity of the molecules under study, which may easily be determined from the slope of the semilogarithmic plot of the spin—echo attenuation Ψ versus $(\delta g)^2$. From the self-diffusivity D the mean square displacement $\langle r^2 \rangle$ of the diffusing molecules can be obtained by the Einstein equation:

$$\langle r^2 \rangle = 6Dt \tag{7}$$

An unambiguous observation of intracrystalline diffusion by PFG NMR is only possible if the mean molecular displacement during the observation time is much smaller than the mean crystallite radius.

PFG NMR diffusion studies with ¹²⁹Xe NMR are complicated by the small gyromagnetic ratio (γ [¹²⁹Xe] = 7.4 × 10⁷ T⁻¹ s⁻¹) with respect to that of hydrogen (γ [¹H] = 2.675 × 10⁸ T⁻¹ s⁻¹). This results in a signal reduction by a factor of 2.12 × 10⁻² compared to hydrogen. The natural abundance of ¹²⁹Xe is only 26.44%, which leads to a further proportional reduction of the signal intensity. Altogether there is a reduction in sensitivity of the NMR signal by a factor of 5.6 × 10⁻³ in comparison to hydrogen. To compensate this disadvantage it is inevitable to accumulate the signal for a large number of single measurements. In the present study, for one single point of the spin–echo signal attenuation plot, using ¹²⁹Xe NMR, up to 1000 scans were necessary to achieve a sufficient signal-tonoise ratio at *T* = 152 K, while at *T* = 293 K the xenon signal

was insufficient even with such efforts. The necessary adjustment and the stability of the PFG NMR signal have been guaranteed by the home-built PFG NMR spectrometer FEGRIS 400.³⁰ This spectrometer is working at a proton resonance frequency of 400 MHz with a maximum field gradient amplitude of 24 T/m. In our experiments we applied the Hahn echo sequence with observation times Δ between $\Delta_{\min} = 0.8$ ms and $\Delta_{\text{max}} = 1.2$ ms and signal widths between $\delta_{\text{min}} = 0.1$ ms and $\delta_{\text{max}} = 0.46$ ms. Equation 6 implies isotropy of the system with respect to the direction of the applied magnetic field gradient and homogeneity; i.e., the mobility of all molecules within the sample is equal. In powder samples of crystallites with anisotropic structure, such as silicalite, the molecular mobility in the direction of the field gradient will be different in different crystallites, caused by the different orientation with respect to the magnetic field gradient. Thus, the NMR signal attenuation may be understood as a superposition of the diffusivities in all possible directions³¹

$$\Psi(\theta,\phi) = \frac{1}{4\pi} \int_0^{2\pi} \int_{-1}^{+1} \exp\{-\gamma^2 \delta^2 g^2 \Delta [D_{xx} \cos^2 \theta + D_{yy} \sin^2 \theta \cos^2 \phi + D_{zz} \sin^2 \theta \sin^2 \phi]\} \, \mathrm{d}\phi \, \mathrm{d}(\cos \theta) \tag{8}$$

where x, y, and z have been assumed to be the main tensor axes, which are identical with the common crystallographic axes in case of ZSM-5. Quantitative analysis shows that a deviation from the simple exponential curve of isotropic diffusion can only be measured if the spin-echo attenuation is followed over at least 1 order of magnitude. Therefore, a zeolite specimen with large crystallites is required to make those deviations from the ideal shape of signal attenuation negligibly small, which are due to interference effects at the crystallite boundaries or due to the intercrystalline space, i.e., due to notable contributions from restricted and long-range diffusion to the signal decay. Only if these conditions are fulfilled with a very high degree of accuracy can all three main diffusion tensor elements be calculated by eq 8. The silicalite crystallites in this study have typical dimensions of more than 20 μ m in the smallest direction, which is in fact parallel to the straight channels and therefore the decisive length. The mean absolute displacement during one scan can be calculated from the one-dimensional propagator. We assume that the propagator is Gaussian³

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$
(9)

so the mean absolute displacement

$$\langle |x| \rangle = \int_{-\infty}^{\infty} |x| P(x,t) \, \mathrm{d}x \tag{10}$$

is

$$\langle |x|\rangle = \frac{2}{\sqrt{\pi}}\sqrt{Dt} \tag{11}$$

The maximum measured diffusion coefficient here is $D_{\text{max}} = 5 \times 10^{-9} \text{ m}^2/\text{s}$ and a typical duration of the measurement is $\Delta = 1 \text{ ms}$. By the use of eq 11 we obtain an upper limit of the mean absolute displacement of

$$\langle |x| \rangle \leq 2.5 \times 10^{-6} \,\mathrm{m}$$

These displacements are small enough to allow the determination of the mean value $\frac{1}{3}(D_x + D_y + D_z)$ of intracrystalline diffusion. Furthermore, we extracted some information on anisotropic



Xenon concentration / particles per unit cell

Figure 12. Experimental and simulated data for the mean diffusion coefficient of methane and xenon in different compositions at T = 293 K (experiments) and T = 300 K (simulations) for a total loading of 8 particles per unit cell.



Xenon concentraton / particles per unit cell

Figure 13. Experimental and simulated data for the mean diffusion coefficients of methane and xenon in different compositions at T = 152 K (experiments) and T = 150 K (simulations) for a total loading of 8 particles per unit cell.

diffusion, but we were not able to determine all the three tensor elements with sufficient accuracy(see below).

The samples for the PFG NMR experiments were prepared by heating 12 mm high layers of zeolites in a contracted sample tube³² to ensure mechanical stability. The temperature was increased at a rate of 10 K/h under vacuum. After maintenance the samples at 673 K and a pressure lower than 0.01 Pa for 24 h, the samples were loaded with a known amount of the adsorbant and sealed off.

4.2. Results and Comparison with Simulations. The results of the experiments are in very good agreement with the results of the simulations. At room temperature (T = 293 K for the experiments, T = 300 K for the simulations; Figure 12) the diffusion coefficients for methane are a bit lower than the simulated values, but they are already within the error bars (not shown), which are about 20% in experiment and 10% in the simulations. As mentioned above, xenon diffusion was not measurable at room temperature. More important than the agreement of the total values is the similarity of the shape of the plots. Methane shows the predicted behavior; the diffusion in the mixture slows down with increasing xenon content.

At low temperatures (T = 152 K for the experiments, T=150 K for the simulations; Figure 13) methane shows the same behavior, but at this temperature it was also possible to measure

xenon diffusion. The measured absolute values of the xenon diffusivities are higher than the ones from simulation (up to twice the value), but the habit of the plot corresponds to the results of the simulations. The xenon diffusivity is nearly unaffected by the composition of the mixture.

As mentioned above, both the limited range of the observable spin-echo attenuation and the finite contribution of long-range and/or restricted diffusion prohibited a determination of the three principal values of the diffusion tensor. The message on anisotropy contained in the experimental data may, however, be deduced by including simplifying assumptions on the relative magnitudes of the principal elements. It is well-known from the MD simulations and previous PFG NMR measurements of diffusion anisotropy in silicalite/ZSM-5³³ that the diffusivity in the *z* direction is much smaller than in the *xy* plane. The shape of the NMR spin-echo attenuation is therefore mainly determined by the diffusivity in the z direction (D_z) and the mean value of the diffusivity in the xy plane, while differences between D_x and D_y are of minor influence only. In fact, simulations with magnitudes of D_x and D_y varying in the range predicted by the MD simulations have led to perceptable changes in the spin-echo attenuation only beyond the experimentally accessible range between 1 and 0.1. For the sake of simplicity, we have therefore analyzed the spin-echo attenuation by fitting eq 8) to the experimental data with the secondary condition D_x $= D_{\rm v}$. In this way, from the PFG NMR measurements the diffusivity in the z direction results to be 20% ($\pm 5\%$) of the mean value of the diffusivity in the xy plane. This result is in perfect agreement with the prediction of the correlation rule (eq 4) as well as with the MD simulations.

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