

On the diffusion mechanism of methane in a cation-free zeolite of type ZK4

S. Fritzsche ^{a,b}, R. Haberlandt ^{a,b}, J. Kärger ^b, H. Pfeifer ^b and K. Heinzinger ^c

^a *Research Group Statistical Theory of Non-Equilibrium Processes, WIP, KAI e.V., Permoserstrasse 15, O-7050 Leipzig, Germany*

^b *Department of Physics, Leipzig University, Linnéstrasse 5, O-7010 Leipzig, Germany*

^c *Max Planck Institute for Chemistry, Saarstrasse 23, W-6500 Mainz, Germany*

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Molecular dynamics (MD) simulations were performed in order to examine the mechanism of diffusion of guest molecules in a cation-free zeolite of type ZK4. The peculiarities of molecular motion are illustrated by the probability distribution of the residence times in the large cavities and by the velocity autocorrelation functions in combination with trajectory studies. Depending on the potential parameters used the diffusivities may increase or decrease with increasing concentration. The diffusion coefficients are found to follow an Arrhenius law which is examined for different loadings.

1. Introduction

Monte Carlo (MC) simulations and molecular statistical calculations of molecules adsorbed in zeolites have been performed since many years (e.g. [1]). However, molecular dynamics (MD) simulations – although applied to many fields of statistical physics [2] – have been used to determine transport behaviour in zeolites only since a couple of years, starting with a paper by Yashonath, Demontis and Klein [3]. In the meantime diffusion coefficients for different types of zeolites have been obtained from various MD simulations (e.g. [4–14]). The present paper is concerned with details of the diffusion mechanism including an analysis of the influence of the potential parameters on the transport properties as reflected, e.g., by the distribution function for the residence time of the molecules in the large cavities or the concentration dependence of the diffusion coefficients. In particular, the paper is intended to explain the different patterns of concentration dependence as observed experimentally [15–17] and to predict their occurrence on the basis of microdynamical considerations.

2. Model

We have considered the diffusion of methane molecules in a silicon rich model zeolite without cations which is similar to the really existing zeolites of the type ZK4 for a high silicon-to-aluminium ratio. This model is especially appropriate for computer simulations because of its cubic symmetry and the lack of cations. The structure of ZK4 is plotted schematically in fig. 1. At the edges one finds eight cubooctahedra formed by the silicon atoms which are connected through oxygen bridges. In the center the so-called large cavity can be seen which is connected by so-called windows to the six neighbouring cavities. The absence of cations and the vanishing dipole moment of the methane molecule allow us to take into account only short range intermolecular forces. Because of the nearly spherical shape of the methane molecule, the Lennard-Jones (LJ) (12,6) potential

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

can be used to describe the methane-methane interaction [18]. For the interaction of methane with the lattice atoms we also use LJ potentials as has been done in most MD papers dealing with molecular dif-

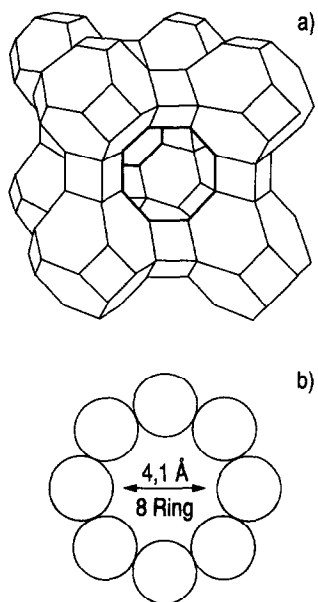


Fig. 1. (a) Structure of the zeolite ZK4: the silicon atoms are located at each vertex and the connecting oxygen atoms are at the center of each line. The window in front of the picture as well as the visible part of the window in the background are indicated by heavy lines. (b) Cross section through the oxygen atoms of a window between adjacent cavities.

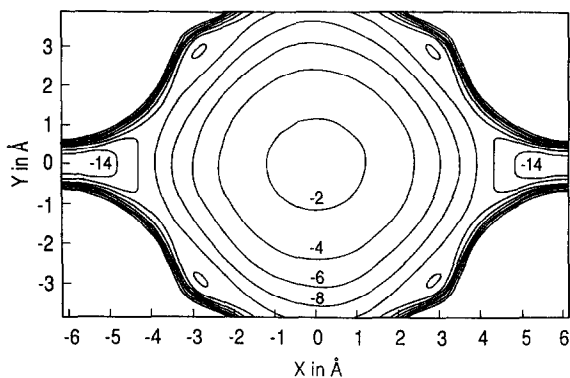


Fig. 2. Isopotential lines for a single methane molecule in a large cavity of the zeolite ZK4 calculated with the potential parameter set A (potential energy in kJ/mol). The energy difference between adjacent lines is 2 kJ/mol.

fusion in zeolites (see e.g. refs. [1,5–9,12,19,20]).

Figs. 2 and 3 show isopotential lines for a single methane molecule in a plane (cut through the center of the large cavity and four windows) of the zeolite ZK4. The calculations have been performed for two

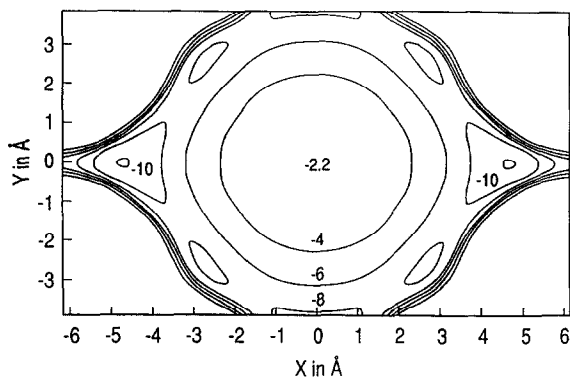


Fig. 3. Same as fig. 2 but calculated with the parameter set B.

different potential models. They are based on the following sets of parameters: Model A: [$\text{CH}_4\text{-CH}_4$: $\sigma=3.817$ Å, $\epsilon=1.232$ kJ/mol; $\text{CH}_4\text{-O}$: $\sigma=3.14$ Å, $\epsilon=1.5$ kJ/mol; $\text{CH}_4\text{-Si}$: $\sigma=2.14$ Å, $\epsilon=0.29$ kJ/mol] from refs. [1,21]. Model B: [as model A but with $\text{CH}_4\text{-O}$ changed to $\sigma=3.46$ Å, $\epsilon=0.81$ kJ/mol]. The latter values for the $\text{CH}_4\text{-O}$ interaction were used in ref. [19] and with a small modification also in refs. [5–8] while in ref. [12] interaction parameters very similar to those of model A were used. Model A which is used in the present paper and in refs. [9,20] yields a mobility of the guest molecules that allows us to examine the diffusion mechanism in detail. Unfortunately the diffusion of methane adsorbed in the cation-free zeolite of type ZK4 has not been measured up to now.

Because of the relatively high value of the potential energy in model A (≈ -1.5 kJ/mol) and in model B (≈ -2.2 kJ/mol) the center of the large cavity is practically free of guest molecules except at very high loadings. In the vicinity of the wall of the large cavity the value of the potential energy is ≈ -10 kJ/mol in model A and ≈ -8 kJ/mol in model B. Notice that for model A deep minima of the potential energy are found in the centers of the windows (≈ -15 kJ/mol) while in the model B smaller minima (≈ -10 kJ/mol) appear at the inlet of the windows and the potential energy in the center of the window has a saddle point (≈ -6.5 kJ/mol) forming a threshold for diffusing particles (see fig. 4).

For a first order treatment of the diffusion mechanism we assume the zeolite lattice to be rigid. Thus we can take into consideration relatively large parti-

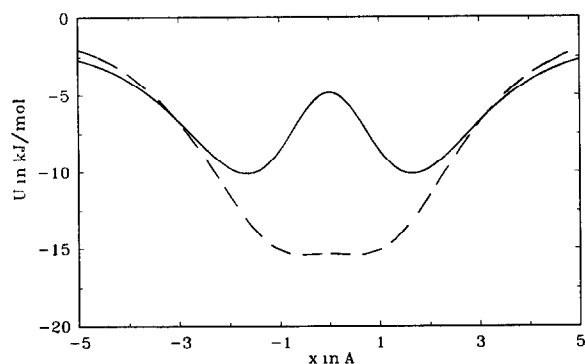


Fig. 4. The potential energy of a single methane molecule at different positions along the window axis: (---) model A, (—) model B.

cle numbers leading to a relatively high statistical accuracy which enables us to examine the consequences even of small variations of the parameters. Moreover, in our system relatively large fluctuations in the number of particles per large cavity can be observed (cf. ref. [9]) and the probability of artefacts connected with the finite size of the system is less than for smaller systems. Such large deviations from the mean occupation number may possibly be of importance for diffusion mechanisms strongly depending on the particle number in a given cavity.

The influence of the lattice vibrations on the absolute value of the diffusion coefficient cannot be neglected in general [6,7,8,14,22], however, for an inspection of general trends in the diffusivities it should be justified to neglect the vibrations. Moreover, the influence of lattice vibrations on the diffusivities obtained in these papers turns out to be much smaller than the influence of uncertainties in the choice of interaction parameters as considered in the present paper.

3. MD simulations

Depending on the loading the basic MD box used in our simulations contains between 64 and 343 large cavities. The mean occupation number I was varied between $I=1$ and $I=7$. The total number of guest molecules lies between 256 and 448. The usual periodic boundary conditions are applied. These are comparatively high numbers for simulations of

transport processes in zeolites and yield a high statistical accuracy (error $\leq 3\%$) for the desired diffusion coefficients. Usually in the literature only 1 to 8 large cavities have been considered. Each methane interacts with 576 lattice atoms.

To calculate the trajectories of the guest molecules we use the velocity version of the Verlet algorithm [2]. The time step is 5 fs. Starting with an arbitrary, but relatively homogeneous, configuration, the system evolution is simulated over an equilibration period of 20000 time steps to get a realistic fluctuation state. Then the evaluation is carried out during the next 150000 time steps.

In order to compare the results for different loadings the temperatures for the different runs must be well defined. Therefore we have used during the evaluation runs the weak thermalization procedure proposed by Berendsen et al. [23]. This weak thermalization algorithm can be adjusted to have no influence on the static and dynamic behaviour of the systems considered. We have found that already one tenth of the strength of thermalization proposed in ref. [23] is sufficient to reproduce the desired mean temperature up to ± 0.5 K while even the temperature fluctuations remain practically unaffected. Additional tests showed the agreement of the diffusion coefficients of runs with and without that thermalization within the statistical uncertainty.

To evaluate the diffusion coefficient we have used Einstein's equation

$$\langle (r-r_0)^2 \rangle = 6Dt, \quad (2)$$

which is valid for large values of time t . The applicability of this formula to molecular diffusion in zeolites has been shown in ref. [9].

In practice D is calculated as $\lim_{t \rightarrow \infty} D(t)$ with

$$D(t) = \frac{1}{6} \frac{d}{dt} \langle (r-r_0)^2 \rangle, \quad (3)$$

since the thus defined quantity $D(t)$ approaches its final value more rapidly than $\langle (r-r_0)^2 \rangle / 6t$.

4. Results and interpretation

For the diffusion the exchange of the guest molecules between the large cavities is decisive. That is why we have calculated residence times of molecules

in large cavities. To register such exchange events the passage of particles through a plane in the middle of the window perpendicular to the window axis is observed. In fig. 5 the probability density of the residence time of a methane molecule which has entered a large cavity is plotted for a loading of $I=1,3,7$ methane molecules per large cavity at a temperature of 300 K. The density is given in arbitrary units because very long times cannot be included. All curves exhibit characteristic maxima at ≈ 0.3 ps and ≈ 1.3 ps. Assuming an average thermal velocity of the methane molecule of about 0.7 nm/ps at 300 K the particle is not able to pass the next window in ≈ 0.3 ps. That means the first peak is due to a reversal of the molecule to the former large cavity and gives therefore no contribution to the diffusion coefficient. Analogously in fig. 6 the probability density of the residence time of a methane molecule in a large cavity is plotted for different temperatures ($T=200, 300, 500$ K) and a loading of $I=3$. Figs. 5 and 6 demonstrate that the rejection rate during the passage from one cavity into the adjacent one as represented by the peak at 0.3 ps increases with increasing loading and with decreasing temperature. This effect should be brought about therefore by collisions with the molecules in the large cavity which is entered by the molecule under study.

Figs. 7 and 8 show the projections of the trajectories of selected methane molecules on a plane through the centers of adjacent large cavities. The circles indicate the positions of the lattice atoms near this plane as a help for orientation. It can be seen that for higher

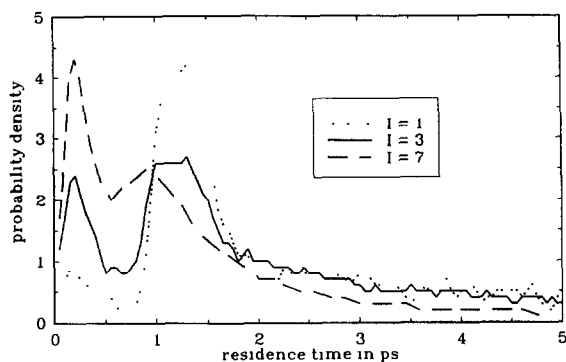


Fig. 5. Probability density (in arbitrary units) of the residence times of a methane molecule in a large cavity at temperature $T=300$ K for different loadings I .

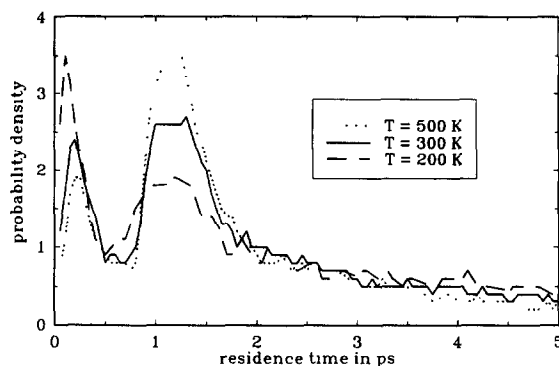


Fig. 6. Probability density (in arbitrary units) of the residence times of a methane molecule in a large cavity for different temperatures T at loading $I=3$.

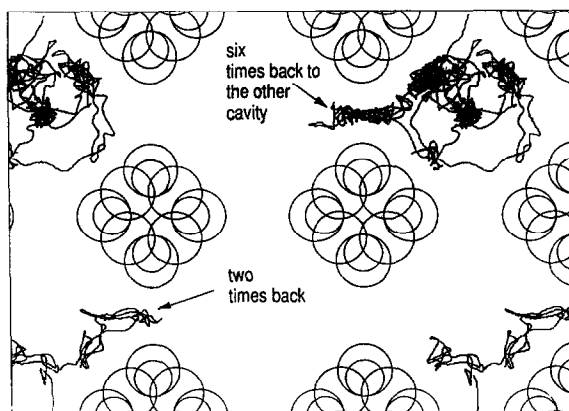


Fig. 7. Trajectory of a selected methane molecule at high loading ($I=7$, $T=300$ K). Some lattice atoms are indicated by circles.

loadings ($I=7$, fig. 7) the particle (only one of 28 is shown) will be more often pushed back into the former large cavity – possibly due to the higher density – than in the case of lower loadings ($I=1$, fig. 8). This corresponds to the increase of the first peak with higher loadings in fig. 5. The second peak in fig. 5 is obviously due to the passage of the particle which has just reached the large cavity considered into the next one through another window and is therefore of importance for the diffusion. While diffusion at higher loadings is especially restricted by the reversal of the particle into the former large cavity it seems to be difficult for a particle at lower loadings to get from one to another large cavity at all. One may say that the presence of other particles helps a given particle to

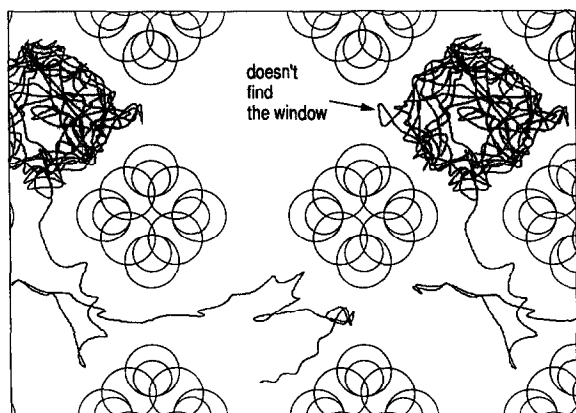


Fig. 8. Trajectory of a selected methane molecule at low loading ($I=1$, $T=300$ K). Some lattice atoms are indicated by circles.

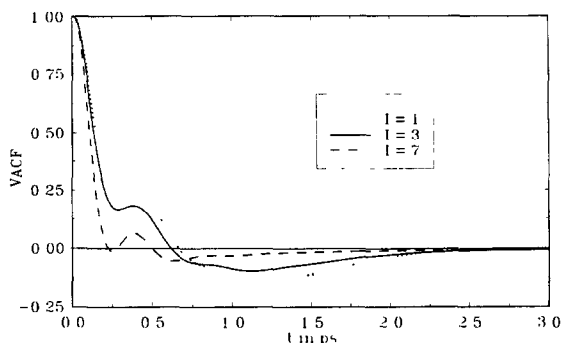


Fig. 9. Velocity autocorrelation function (VACF) for different loadings I at $T=300$ K.

find the inlet into the window. We assume this effect to be responsible for the pattern of loading dependence especially in the case of narrow windows, e.g. in the case of model B.

Figs. 9 and 10 show the velocity autocorrelation function (VACF) and its Fourier transform for different loadings. It should be noted that the velocity autocorrelation functions have local minima near $t=0.3$ ps which appear at the same time as the first peaks of fig. 5. Because each reversal of the particle velocity gives a negative contribution to the VACF, higher first peaks in fig. 5 should correspond with lower local minima in fig. 9. The Fourier transform calculated has an analogous behaviour (fig. 10).

Fig. 11 shows values for the diffusion coefficient in dependence on the loading for different temperatures calculated with parameter set A. It is found that

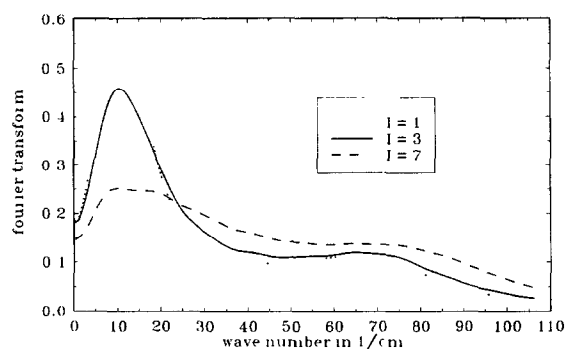


Fig. 10. Fourier transform of the VACF for different loadings I at $T=300$ K.

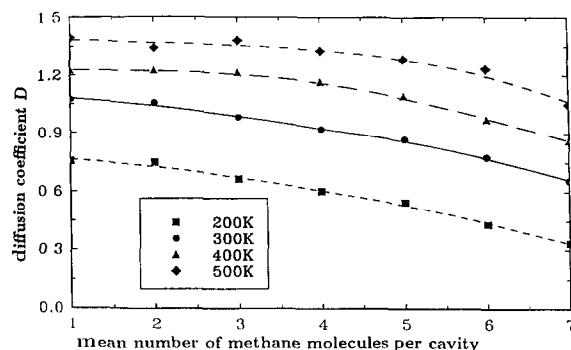


Fig. 11. Values for the diffusion coefficient in dependence on the loading with the temperature as a parameter (calculated with the parameter set A).

the diffusion coefficients decrease with increasing loading. This tendency is reversed with decreasing window diameter, e.g. for the parameter set of model B. This is illustrated in fig. 12 by comparing the diffusivities obtained at the temperature $T=300$ K for two different loadings with the parameter σ of the $\text{CH}_4\text{-O}$ interaction varied within the range used in the literature [1,5–9,12,19–20].

Comparing the curves for low ($I=1$) and high loadings ($I=6$) it can be seen that for large windows ($\sigma \lesssim 3.25$ Å) the diffusion coefficient will decrease with increasing loading while it will increase with increasing loading for smaller windows ($\sigma \gtrsim 3.25$ Å). This behaviour corresponds to the measured concentration dependence of the self-diffusion coefficient of methane in NaCaA zeolites [15,16]. Moreover, the absolute values of the diffusivities experimentally determined for NaCaA (4×10^{-10} and 8×10^{-10} m²/

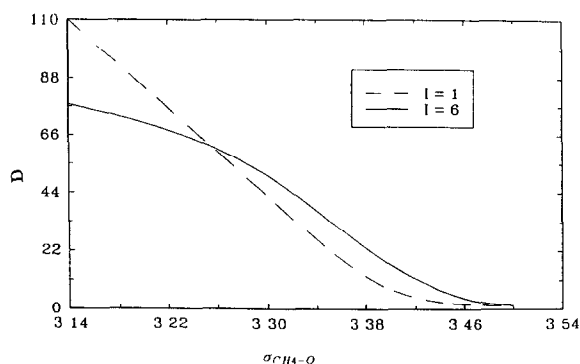


Fig. 12. Values for the diffusion coefficient D (in 10^{-10} m²/s) at 300 K in dependence on the value of $\sigma_{\text{CH}_4\text{-O}}$ (in Å) for $I=1$ and $I=6$ methane molecules per large cavity.

Table 1

Dependence of D (in 10^{-10} m²/s) on the parameter ϵ (in kJ/mol) of the methane lattice–oxygen interaction at 300 K ($\sigma_{\text{CH}_4\text{-O}} = 3.14$ Å)

ϵ	I	D
3.0	1	79.0
1.5	1	109.7
0.75	1	105.7
3.0	6	37.5
1.5	6	77.8
0.75	6	87.3

s for 1 and 3 molecules per large cavity at 293 K [16]) are in better agreement with the results of the present MD calculations for ZK4 using a larger parameter $\sigma_{\text{CH}_4\text{-O}}$. However, because of the presence of electric charges the polarization interaction will lead to a different mechanism of the diffusion in NaCaA so that conclusions from ZK4 with regard to this zeolite are by no means straightforward. Calculations for the NaCaA zeolite are the object of a forthcoming paper. Our calculations show that a variation of the parameter $\sigma_{\text{CH}_4\text{-O}}$, which is connected with a variation of the diameter of the windows between adjacent cavities (see fig. 1), very sensitively affects the value of the diffusion coefficient. By contrast, there is only a small influence of the potential parameter ϵ on the diffusion as shown in table 1.

Replacing the CH₄–CH₄ LJ (12,6) potential by a LJ (20,6) potential as used in refs. [5–8], leads to higher values of the diffusion coefficient (cf. table 2).

Fig. 13 gives a summary of interaction potentials

Table 2

Dependence of D (in 10^{-10} m²/s) on the form of the CH₄–CH₄ Lennard-Jones interaction potential at 300 K. Comparison for model A and the LJ(20,6) potential used by Demontis et al. [5–8] for a loading I of 1 and 6 methane molecules per large cavity

LJ(20,6)	I	Model A
113.9	1	109.7
82.9	6	77.8

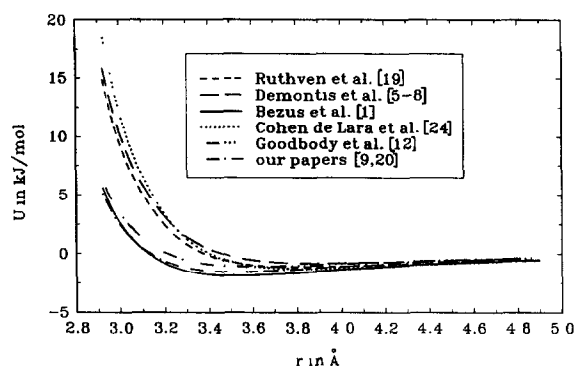


Fig. 13. Some LJ potentials for the CH₄–O interaction as used in the literature.

between CH₄ and O used in the literature [1,5,12,19,9,24]. In view of the substantial differences, it is a significant result of the present study that in the case of methane adsorbed in ZK4 it is the parameter $\sigma_{\text{CH}_4\text{-O}}$ rather than the parameter ϵ or the shape of the potential curve or even the influence of the lattice vibrations, which decisively affects the diffusion properties. The simulation results are found to be in satisfactory agreement with an Arrhenius law of the form

$$D(I, T) = D_0(I) \exp\left(-\frac{E_0(I)}{k_B T}\right). \quad (4)$$

In fig. 14 the results of fig. 11 are given as an Arrhenius plot. One finds straight lines in a very good approximation. Thus the validity of the Arrhenius law is confirmed in this case. This is not trivial because evaluations with other potential fields (corresponding to other zeolites) showed deviations from the Arrhenius law [25]. It should be noted that D_0 slightly increases with the loading so that at very high temperatures where the exponential factor is practically

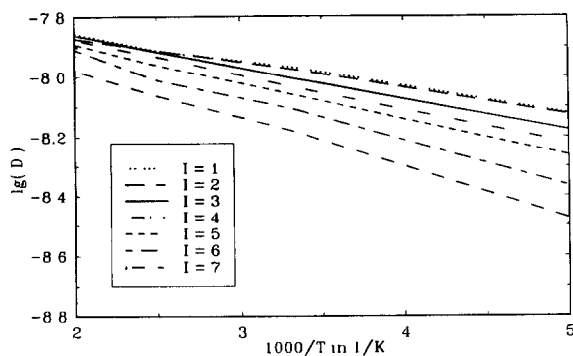


Fig. 14. Dependence of the logarithm of D (in m^2/s) as a function of the reciprocal absolute temperature (in $1/\text{K}$) (Arrhenius plot).

Table 3

Influence of the silicon atoms on the diffusion coefficient D (in $10^{-10} \text{m}^2/\text{s}$) at different temperatures T (in K) and for different values of the number I of methane molecules per large cavity

I	T	With Si	Without Si
1	200	76	80
6	200	43	44
1	300	107	111
3	300	98	102
6	300	78	75
1	500	140	137
6	500	123	119

equal to one one might find an increase of D with the loading even for model A.

In table 3 the values of D for simulations with and without interactions between methane and silicon are compared. It can be seen that the influence of the silicon atoms on the diffusion is very small. In correspondence with this finding, most authors do in fact neglect this interaction to save computer time.

5. Conclusions

The passage of the guest molecules through the window between adjacent large cavities is decisive for the diffusion processes. In the zeolite ZK4 in which the window diameter is comparable to the size of methane molecules and electric charges can be neglected, passages of the methane molecules from one large cavity to an adjacent one are apparently governed by

two effects. Firstly, a given methane molecule enters a window more frequently at high loading when other methane molecules form a kind of cage around the window inlet. Secondly, after passing through a window methane molecules are sometimes pushed back into the former large cavity. This effect which decreases the diffusivity is important particularly at high loadings. Variations of the window diameter show that the diffusion coefficient increases with increasing loading for small window diameters while the opposite is already true for somewhat larger diameters. This corresponds to an increasing importance of the first one of the two effects mentioned (that increases the diffusivity) for narrow windows. Additionally, it could be shown that the different sets of parameters for the lattice-guest interaction given in the literature lead to differences in the diffusion coefficients of nearly two orders of magnitude because this quantity is very sensitive with respect to the window diameter in the case of ZK4.

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