18 August 1995

ELSEVIER

Chemical Physics Letters 242 (1995) 361–366

CHEMICAL
PHYSICS
LETTERS

Influence of exchangeable cations on the diffusion of neutral diffusants in zeolites of type LTA. An MD study

S. Fritzsche [a], R. Haberlandt [a], J. Kärger [a], H. Pfeifer [a], K. Heinzinger [b], M. Wolfsberg [c]

[a] Universität Leipzig, Fakultät für Physik und Geowissenschaften, Augustusplatz 9-11, D-04109 Leipzig, Germany
[b] Max-Planck-Institut für Chemie, Saarstraße 23, D-55128 Mainz, Germany
[c] Department of Chemistry and Institute for Surface and Interface Science, University of California Irvine, Irvine CA 92717, USA

Received 6 June 1995

Abstract

Diffusion of methane in LTA type zeolites has been calculated from molecular dynamics simulations. Taking into account the polarization interaction of the exchangeable cations in the zeolite NaCaA with the methane molecules, the self-diffusion coefficients in NaCaA decrease by one order of magnitude in comparison with its cation-free analogue ZK4. The order of magnitude of the calculated values is in agreement with NMR data.

1. Introduction

Owing to their well-defined structure, zeolites play an important role in the understanding of the elementary processes of molecular transportation in porous media [1,2]. In addition, in view of their widespread applications as cation exchangers, catalysts and molecular sieves as well as their great potential as host frameworks for advanced materials, zeolites are also of substantial interest from a practical point of view [3]. Molecular dynamics (MD) simulations [4,5] are a valuable tool for supplementing experimental methods in the detailed understanding of diffusion processes of guest molecules in zeolites. The self-diffusion of guest molecules in different rigid and flexible zeolites has been investigated by several groups of scientists (see Ref. [3] and references therein). Some work has also been carried out on transport diffusivities [6,7].

A remarkable influence of the polarization interaction on the diffusion of unsaturated hydrocarbons in zeolites has been found experimentally by both nuclear magnetic relaxation [8,9] and pulsed field gradient (PFG) NMR diffusion studies with zeolites NaY and NaX. For saturated hydrocarbons, the presence of the sodium ions was found to be of negligible influence on the molecular mobilities [1] (pp. 451, 452). It has therefore been assumed for a long time that the polarization interaction is of minor importance in the diffusion of saturated alkanes in zeolites [2]. To examine this influence, MD simulations have been carried out including the polarization interaction. First MD results [10,11] that showed a remarkable influence of this interaction on diffusion

SSDI 0009-2614(95)00744-X

initiated further PFG NMR studies including zeolites containing bivalent cations. In this case, an influence of the polarization interaction on the diffusion has been found indeed for both methane and *n*-hexane [12].

This Letter presents a systematic MD study of the influence of the polarization interaction on the molecular motion of methane in zeolite NaCaA.

2. Model

2.1. Potential

Previous MD investigations of methane in a cation-free model zeolite of type LTA (see e.g. Refs. [10,11,13] and references therein) were carried out to contribute to a better understanding of the rate-determining mechanisms of molecular diffusion.

In particular, a microdynamic explanation of the remarkable increase in diffusivities with increasing concentrations as observed experimentally for paraffins and also for small alkanes such as methane in zeolite NaCaA [14] was expected. Such an increase could be simulated by choosing the largest Lennard-Jones distance σ from the different values used in the literature [15] for the interaction between the methane molecules and the oxygen atoms of the zeolite framework. However, the absolute values of the diffusivities in the simulations with the model zeolite – except for unrealistically large values of σ – were notably larger than the diffusivity measured in NaCaA. Including the cations in the present MD study the molecular diffusion is considered in a more real zeolite of type NaCaA. It shall be clarified, in particular, whether by including the polarization interaction both the absolute values and the concentration dependences as obtained by the PFG NMR studies are better reflected in the MD simulations.

The Ca^{2+} and Na^{+} cations in NaCaA are situated near to the center of the hexagonal faces in Fig. 1, which means at sites far away from the windows. Thus, the pure geometrical hindrance of the motion of the guest molecules by the cations is expected to be small. Fig. 2 shows the influence of the polarization interaction on the potential in NaCaA. In both potential maps the cations are present, but in the lower one the electric charges are put equal to zero so that the polarization interaction vanishes.

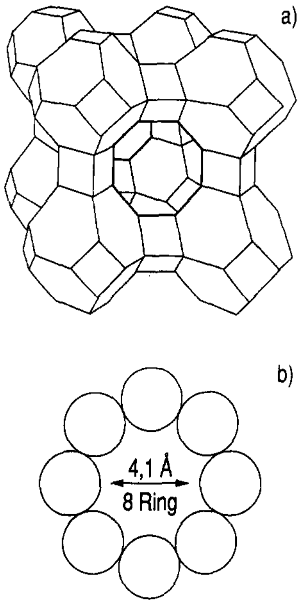

Fig. 1. (a) Geometry of the zeolites of type LTA. T atoms (Al, Si) are located at each vertex and connecting oxygen atoms are at the center of each line. The window in front of the picture as well as the visible part of the window in the backgound are indicated by heavy lines. (b) Cross section through the oxygen atoms of a window between adjacent cavities.

The considered zeolites NaCaA and ZK4 have a simple cubic structure [16]. The edge length of the unit cell is 24.6 Å and it contains eight so-called α cages. Since methane does not possess a permanent dipole moment, only short-range intermolecular forces must be taken into account in the case of the cation-free model zeolite ZK4 [15]. For NaCaA, polarization interaction must be considered additionally due to the cations [10,11]. The mutual interaction of the induced dipole moments of the methane molecules has been neglected in this Letter as a second-order effect.

Following the common use for systems with polarization interaction, the Lennard-Jones parts of the interaction potentials are given in the form

$$U_{ij} = -\frac{A_{ij}}{r_{ij}^{6}} + \frac{B_{ij}}{r_{ij}^{12}}. \qquad (1)$$

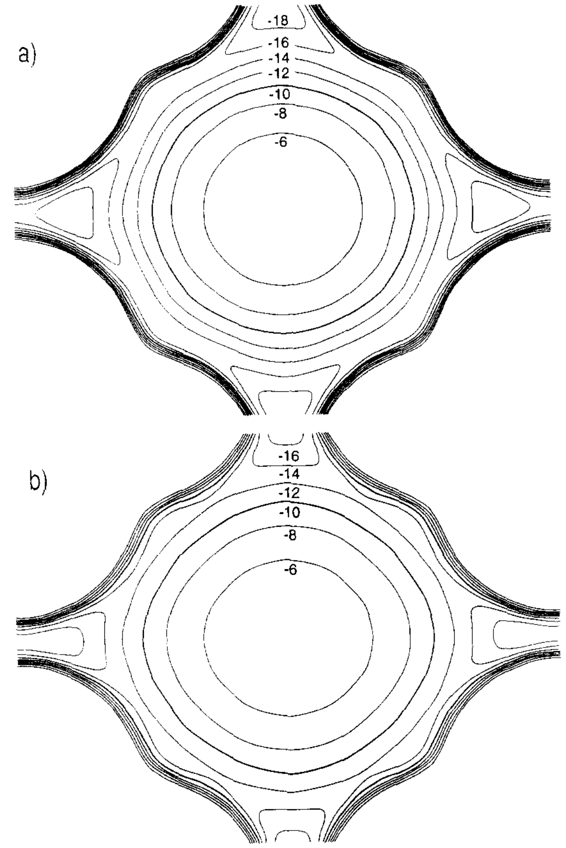

Fig. 2. Potential energy maps of a single methane molecule in the zeolite in a plane containing the center of a large cavity and four windows. (a) Zeolite NaCaA, (b) also NaCaA but the cations are treated as LJ particles without electric charge.

For the CH_4–CH_4 and CH_4–O interaction this notation may be transferred without any complication into the common form of a Lennard-Jones potential,

$$U_{ij} = 4\epsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right], \qquad (2)$$

with the understanding that the parameters σ_{ij} are a measure of the particle sizes. For the methane–cation interaction the parameters A_{ij} and B_{ij} are generally introduced by involving the polarization interaction. In Ref. [17], for example, after obtaining A_{ij} from the Kirkwood–Müller formula [18], B_{ij} is chosen so that for a methane molecule approaching the single cation the potential minimum will appear at a distance which is the arithmetic mean of the van der Waals radii of methane and the cation. Hence, σ and ϵ in Eq. (2) are meaningless for this interaction unless the polarization interaction is also taken into account.

The procedure of Ref. [17] is somewhat problematic since the polarization interaction cannot be split into pair contributions. However, since the cations are not situated in the vicinity of the windows their geometrical size is not very important for the diffusion. Therefore, we adopted from Ref. [17] not only the values of the polarizabilities and magnetic susceptibilities but also the procedure for calculating A_{ij} and B_{ij}. In Ref. [17] these quantities are calculated both using the Kirkwood–Müller and the Slater–Kirkwood formula. Since the results are slightly different, in Ref. [17] the arithmetic mean of the two results is used. We preferred to use here only the results following from the Kirkwood Müller formula. The values used in the present simulations are given in Table 1. The interaction of CH_4 with aluminum and silicon is neglected. For the CH_4–O interaction, two different parameter sets are taken into account which are widely used in the literature [15]. Set A leads to larger windows. Thus, simulations are performed with parameter sets A and B. The parameters for the CH_4–Ca and the CH_4–Na interactions are the same in both parameter sets. The important interaction CH_4–O has been calculated also with the data for polarizibilities etc. They were taken from Ref. [19] in the case of parameter set A and from Ref. [17] in the case of parameter set B.

The CH_4–CH_4 interaction is also the same in both parameter sets. The values are $A_{ij} = 1.5241 \times$

Table 1
Lennard-Jones parameter for the interaction

	CH_4–O, set A	CH_4–O, set B	CH_4–Na	CH_4–Ca
A_{ij} (10^3 Å^6 kJ/mol)	5.91	5.34	0.895	2.41
B_{ij} (10^6 Å^{12} kJ/mol)	6.19	8.75	9.49	3.81

10^4 Å^6 kJ/mol and $B_{ij} = 4.7134 \times 10^7$ Å^{12} kJ/mol. They were calculated from second virial coefficients [20].

The force resulting from the polarization interaction on a methane molecule at position $\boldsymbol{r}$ is

$$F_p(\boldsymbol{r}) = \alpha \boldsymbol{E}(\boldsymbol{r}) \cdot \nabla \boldsymbol{E}(\boldsymbol{r}). \tag{3}$$

α is the polarizability of the methane molecule. Since both $\boldsymbol{E}(\boldsymbol{r})$ and the tensor $\nabla \boldsymbol{E}(\boldsymbol{r})$ include summations over all cations, Eq. (3) contains cross terms and cannot be split into a sum of pair contributions. With $\boldsymbol{r}_i$ being the distance from the site $\boldsymbol{r}$ to the ith cation, the electric field at site $\boldsymbol{r}$ is given by

$$\boldsymbol{E}(\boldsymbol{r}) = \sum_i \boldsymbol{E}(\boldsymbol{r}_i), \quad \boldsymbol{E}(\boldsymbol{r}_i) = \frac{q_i}{r_i^3}\boldsymbol{r}_i. \tag{4}$$

According to Ewald's summation method [4,5], each summand $\boldsymbol{E}(\boldsymbol{r}_i)$ can be split into

$$\boldsymbol{E}(\boldsymbol{r}_i) = \boldsymbol{E}_s(\boldsymbol{r}_i) + \boldsymbol{E}_l(\boldsymbol{r}_i),$$

$$\boldsymbol{E}_s(\boldsymbol{r}_i) = \gamma(r)\frac{q_i}{r_i^3}\boldsymbol{r}_i,$$

$$\boldsymbol{E}_l(\boldsymbol{r}_i) = [1 - \gamma(r)]\frac{q_i}{r_i^3}\boldsymbol{r}_i. \tag{5}$$

The so-called screening factor $\gamma(r)$ is chosen to be equal to 1 for short distances and to decay to zero for large ones. $\boldsymbol{E}_s(\boldsymbol{r}_i)$ is a short-range interaction that corresponds to the true interaction in the vicinity of the cation i. This part of the interaction is treated like other short-range interactions in the system. For the long-range part $\boldsymbol{E}_l(\boldsymbol{r}_i)$ a Fourier expansion is usually carried out. Commonly, the screening factor is chosen to be the error function

$$\gamma(r) = \mathrm{erfc}(\eta r) = \frac{2}{\pi^{1/2}}\int_{\eta r}^{\infty} \exp(-\rho^2)\,\mathrm{d}\rho. \tag{6}$$

The parameter η must be chosen so that the short-range part $\boldsymbol{E}_s(\boldsymbol{r}_i)$ is negligible for distances r_i larger than or equal to half the MD box length. By using

$$\gamma_1(r) = \xi^2(\xi^2 - 2) + 1, \tag{7}$$

with $\xi = r/r_c$ we have introduced a different screening factor γ_1. In comparison with $\gamma(r)$, the thus defined factor $\gamma_1(r)$ remains close to 1 for larger distances, and decays more rapidly afterwards, as demonstrated by Fig. 3. It becomes zero at the cut-off distance r_c and this value is also used for $r_i > r_c$. r_c can be put equal to half the MD box length. It was confirmed by test calculations, that by using this screening factor $\gamma_1(r)$ in the case of NaCaA the long-range part can be neglected, so that

$$\boldsymbol{E}(\boldsymbol{r}_i) = \gamma_1(r)\frac{q_i}{r_i^3}\boldsymbol{r}_i \tag{8}$$

is a good approximation. Thus, the Fourier expansion of the long-range part which would be expensive computationally, turns out not to be necessary in this case.

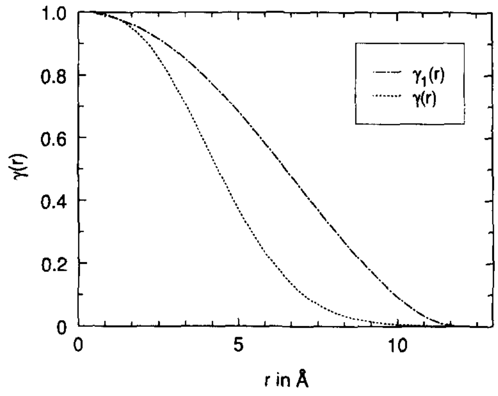

Fig. 3. Comparison of the two screening factors γ and γ_1.

2.2. Simulation

The velocity Verlet algorithm [4,5] is employed to integrate the Newtonian equations for the diffusing particles. Each simulation run has a length of 2500000 steps, the time increment per step being 10^{-14} s. The calculations were performed on the CRAY-Y-MP of the Höchstleistungsrechenzentrum Jülich and partially on the C90 of the San Diego Supercomputer center.

Table 2

Self-diffusivities D (in 10^{-11} m^2/s) for different types of zeolite LTA at 173 K as a function of the number of molecules per cavity (I)

I	NaCaA, A	NaCaA, B	ZK4, A
5	62.2	1.22	410
6	49.0	0.64	340
7	55.2	9.60	250
8	92.3	34.9	182

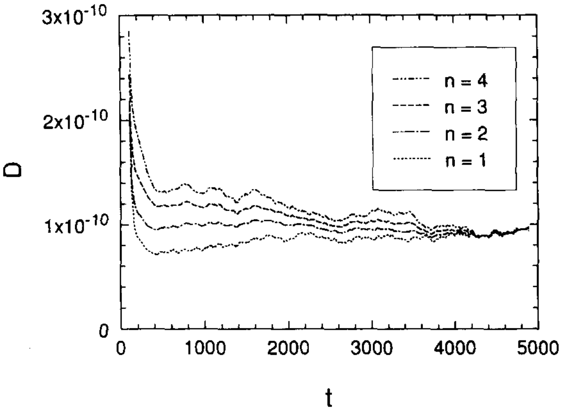

Fig. 4. Self-diffusivities D (in m^2/s) obtained from the different moments of the displacement as a function of time. The time is given in ps. The loading is 7 methane molecules per cavity and the temperature in 173 K. Parameter set B is used.

3. Results and discussion

Table 2 gives a summary of the diffusivities deduced from the simulation runs. Fig. 5 compares the data with the results of PFG NMR measurements [14] as well as with the results of simulations of methane in ZK4 at 173 K [15]. The results from parameter set A at loadings higher than five guest molecules per cavity show good agreement with the experimental data.

It should be noticed, however, that it has been shown in Refs. [13,21] that for ZK4 in the case of parameter set B and at high temperatures, simulations including the lattice vibrations lead to considerably higher D values than in the case of rigid lattice simulations. Thus, further investigations including both lattice vibrations and polarization interaction are necessary [22].

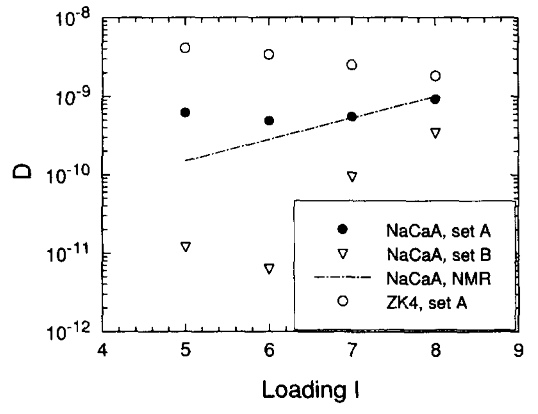

Fig. 5. Self-diffusivities D (in m^2/s) from different MD runs compared with experimental data.

It follows from Fig. 5 that the statistics of the D values are poor in the case of NaCaA with parameter set B. This is a consequence of the low diffusivities which require extremly long calculations. Thus, even runs of more than 10 h of CPU time on the C90 per data point turned out not to be sufficient for gaining better accuracy.

Acknowledgement

We thank Professor Suffritti, Professor Demontis (University of Sassari), Professor Brickmann (TH Darmstadt) and Professor Theodorou (UCB) for stimulating discussions and thank DP G. Hofmann for performing some calculations. We are indebted to the Deutsche Forschungsgemeinschaft (SFB 294) for financial help. RH and HP thank the Fonds der Chemischen Industrie, Frankfurt, for financial support. MW acknowledges with thanks a reinvitation from the Alexander von Humboldt Stiftung under a Humboldt Award. Finally, we are thankful for a grant of computer time by the Höchstleistungsrechenzentrum Jülich and the office of Academic Computing, University of California, Irvine.

References

[1] J. Kärger and D.M. Ruthven: Diffusion in zeolites and other microporous solids (Wiley, New York, 1992).
[2] General Discussion during the Faraday Symposium 26 on Molecular Transport in Confined Regions and Membranes, J. Chem. Soc. Faraday Trans. 87 (1991) 1797.
[3] J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich, Studies in surface science and catalysis, Vol. 84 Zeolites and related microscopic materials: state of the art 1994, Proc. Int. Zeol. Conf., Garmisch, 1994 (Elsevier, Amsterdam, 1994).
[4] M.P. Allen and D.J. Tildesley, Computer simulation of liquids (Clarendon Press, Oxford, 1989).
[5] R. Haberlandt, S. Fritzsche, G. Peinel and K. Heinzinger, Molekulardynamik (Vieweg, Wiesbaden, 1995).
[6] E.J. Maginn, A.T. Bell and D.N. Theodorou, J. Phys. Chem. 97 (1993) 4173.
[7] S. Fritzsche, R. Haberlandt and J. Kärger, Z. Physik. Chem. 189 (1995) 211.
[8] H. Pfeifer, Phys. Rept. 26 (1976) 293.

[9] H. Pfeifer and H. Winkler, in: Proceedings of the 4th Specialized Colloque Ampere (Leipzig, 1979) p. 31.

[10] S. Fritzsche, R. Haberlandt, J. Kärger, H. Pfeifer and M. Waldherr-Teschner, Studies in surface science and catalysis 84 (1994) 2139.

[11] S. Fritzsche, Phase Transitions 52 (1994) 169.

[12] W. Heink, J. Kärger, S. Ernst and J. Weitkamp, Zeolites 14 (1994) 320.

[13] P. Demontis and G.B. Suffritti, Chem. Phys. Letters 223 (1994) 355.

[14] W. Heink, J. Kärger, H. Pfeifer, P. Salverda, K.P. Datema and A. Nowak, J. Chem. Soc. Faraday Trans. 88 (1992) 515.

[15] S. Fritzsche, R. Haberlandt, J. Kärger, H. Pfeifer and K. Heinzinger, Chem. Phys. 174 (1993) 229.

[16] W.M. Meier and D.H. Olson, Atlas of zeolite structure types (Butterworth-Heinemann, London, 1992).

[17] D.M. Ruthven and R.I. Derrah, J. Chem. Soc. Faraday Trans. I 68 (1972) 2332.

[18] H. Margenau and N.R. Kestner, Theory of intermolecular forces (Pergamon Press, Oxford, 1971).

[19] A.G. Bezus, A.V. Kiselev, A.A. Lopatkin and P.Q. Du, J. Chem. Soc. Faraday Trans. II 74 (1978) 367.

[20] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird: Molecular theory of gases and liquids (Wiley, New York, 1954).

[21] G.B. Suffritti and P. Demontis, Phase Transitions 52 (1994) 191.

[22] S. Fritzsche, R. Haberlandt, M. Wolfsberg, P. Demontis, G.B. Suffritti and K. Heinzinger, in preparation.