

Structure and Self-Diffusion of Water Molecules in Chabazite: A Molecular Dynamics Study

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Using classical molecular dynamics (MD) simulations, we have studied some structural and diffusive properties of water molecules adsorbed in chabazite. In particular, we have investigated the variation of the self-diffusion coefficient of the water molecules as a function of their concentration and the nature of the hydration shells of the extraframework Ca^{++} ions with varying concentrations of water. Our study indicates that the well-defined and stable hydration shells of this ion play an important role in the diffusion process. The diffusion anisotropy is computed at $T = 600$ K. It is compared with theoretical results based on jump models and qualitatively compared with pulsed field gradient nuclear magnetic resonance (PFG NMR) experiments of a single chabazite crystal at 293 K and with tracer diffusion studies.

1. Introduction

Zeolites are nanoporous crystalline compounds with applications in several chemical and industrial processes. Because of the numerous interesting effects observed, for example, for diffusion processes of guest molecules inside of zeolites, they are also of high scientific interest for experiments and theory.^{1–3} Zeolites are used in numerous technical applications such as catalysis, molecular sieves, gasoline production, washing agents, the drying of gases, and even the cooling of beer. In many of these applications, the water adsorbed by the zeolites plays an important role. Since diffusion is the primary process by which guest molecules in zeolites move from one region to another, understanding diffusion in these confined geometries is of fundamental importance.

Most zeolites are strongly hydrophilic. The presence of water in zeolites influences the diffusion of other molecular species significantly and plays an important role in several of the above-mentioned applications. Chabazite (structure see Figure 1) is a natural zeolite. It was chosen for this study because experimental diffusion data are available⁴ for this system. Chabazite can be represented in the trigonal space group $R\bar{3}m$ and is expected to show diffusional anisotropy because of its unique channel structure.^{1,5–7} The material is essentially a hydrated aluminum silicate. It finds application in industry to remove cations from solutions, for example, ¹³⁷Cs and ⁹⁰Sr from radioactive effluents. The pores of chabazite can hold, under normal conditions (i.e., room temperature and normal pressure), several water molecules, and it is of considerable interest to study the structural arrangement of these water molecules and their diffusional behavior with varying water concentrations. Since the water molecules are strongly attracted by the Ca^{++} ions (also known

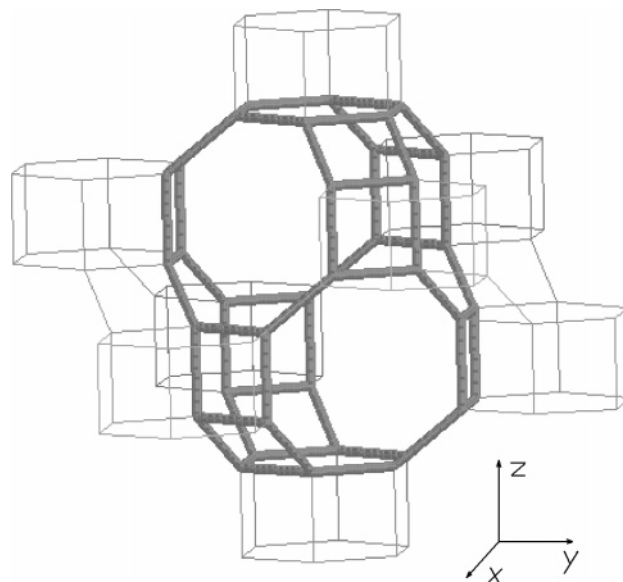


Figure 1. The cage structure of chabazite. Lines symbolize oxygen bridges between Si and Al atoms.

as extraframework cations) in the chabazite structure, the diffusion process can be rather slow, particularly at low concentrations and temperatures. Even though classical molecular dynamics simulations are increasingly used to study diffusion phenomena in confined systems (see, e.g., refs 1–3, 8, and 9), the present simulations may be close to the limit of what can presently be done with this approach.

In this paper, we present selected static and dynamic properties of water adsorbed in chabazite at different water concentrations in the network. Well-established interaction potentials between the constituent atoms of the lattice and water molecules are available for simulations of these systems. The effect of the formation of partial hydration shells around the

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TABLE 1: Partial Charges on the Atoms, in Units of e , and Typical Details of the Simulated Systems

$q(\text{H})$	$q(\text{O}_{\text{H}_2\text{O}})$	$q(\text{Si})$	$q(\text{Al})$	$q(\text{Ca})$	$q(\text{O}_{\text{L1}})$	$q(\text{O}_{\text{L2}})$
+0.33	-0.66	+2.05	+1.75	+2.0	-1.2	-1.025
$N_{\text{H}_2\text{O}}$	N_{Ca}	$\langle T \rangle$	length of runs			
80–312	48	≈ 300 K	≈ 20 ns			
80–312	48	≈ 600 K	≈ 10 ns			

Ca^{++} ions on the diffusion mechanism has been studied. We have also computed the self-diffusion coefficients along the two principal directions to estimate the degree of anisotropy of the diffusion coefficients for the chabazite geometry and compared them with experimental data. In the following, we discuss the model potentials and the computational details of our work. The results and their discussion are presented next, with particular attention paid to the dynamics of the diffusion process. The role of the formation of a hydration shell around Ca^{++} ions is discussed, and an explanation for the nonmonotonic concentration dependence of the self-diffusion coefficient is presented. We conclude our discussion by noting that the self-diffusion coefficient obtained in our work is somewhat higher than that obtained from PFG NMR studies.

2. Simulations

In order to study the long-time dynamics, we need a well-tested and computationally efficient interaction model. We chose a combination of empirical and “quantum chemical” potentials taken from the literature, as explained in detail below. With the exception of the intramolecular part of the water potential, we have modeled all of the interactions as pair potentials consisting of a short-range part of either Lennard-Jones (LJ) or Buckingham type and a long-range Coulomb part. In earlier papers, it was shown that zeolite lattice vibrations can have a moderate influence on the self-diffusion coefficient^{10,11} for some systems, while in other cases, this influence is negligible.¹² For the sake of computational efficiency and with respect to the limited statistical accuracy that we can achieve in the present case, we have neglected the lattice flexibility in this work, except for the extraframework Ca^{++} ions, which can move during the simulation.

The interactions between the water molecules have been modeled using the Bopp–Jancsó–Heinzinger (BJH) potential, which has been well-tested in several earlier studies of water and aqueous solutions¹⁴ and, in particular, of CaCl_2 solutions.¹⁵ Its combination with a potential for the calcium–water interactions, which was fitted to quantum chemical calculations,¹⁵ has thus been successfully tested for solutions. The hydration shell of the Ca^{++} ions in zeolites may differ from that in solutions, but among the existing potentials, this one seems to us to be the best choice. Only the electrostatic part of the Ca^{++} – Ca^{++} potential¹⁵ was used since the short-range terms are completely negligible in the force calculations for the dynamics in the distance range sampled here by the ions.

The potentials for the lattice–guest interaction are taken from ref 16, except for the partial charges, which are given in Table 1.¹⁷ The partial charges for lattice atoms in the literature vary between $-0.25e$ and $-1.2e$ for the lattice oxygen, 0 and $2.5e$ for Si, and 0 and $1.75e$ for aluminum. We decided to follow the arguments of Jaramillo/Auerbach, with partial charges given in Table 1. These charges in balance with those of the cations preserve the electroneutrality of the system. The oxygen position L1 corresponds to lattice oxygens that are bridging a Si and an Al atom, and L2 corresponds to lattice oxygens at positions bridging two Si atoms.

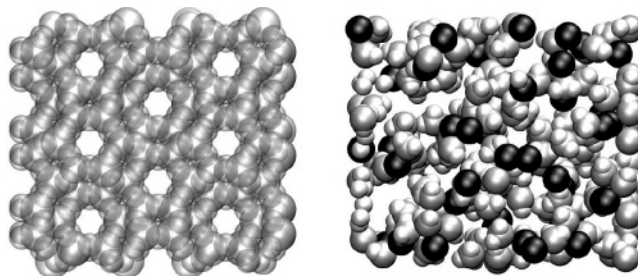


Figure 2. Simulation box (x – y plane) for chabazite with 13 water molecules per unit cell. Left: zeolite lattice only. Right: ions (dark) and the aqueous phase (gray).

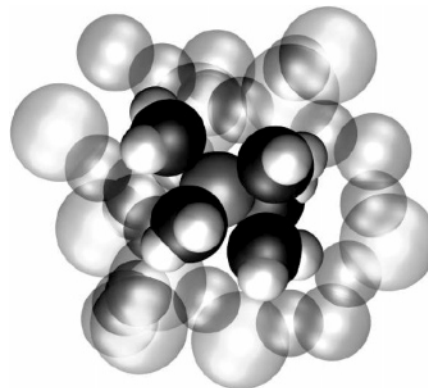


Figure 3. A partially hydrated Ca^{++} ion in the zeolite framework. The ion (center) and its hydration shell are dark gray, and the framework atoms are light gray.

Throughout this paper, the energies are given in kilojoules per mole. The short-range (i.e., non-Coulomb) parts of the interactions between the lattice atoms and the water molecules are listed below

$$\begin{aligned}
 V_{\text{O-O}}^1 &= (112010/r^{8.86}) - 1.0465 \exp[-4(r - 3.4)^2] - \\
 &\quad 1.0465 \exp[-1.5(r - 4.5)^2] \\
 V_{\text{O-H}} &= 26.1/r^{9.2} - 41.86/(1 + \exp[40(r - 1.05)]) - \\
 &\quad 16.744/(1.0 + \exp[5.493(r - 2.2)]) \\
 V_{\text{H-H}} &= 418.767/(1 + \exp[29.9(r - 1.968)]) \\
 V_{\text{Ca-O}} &= -1572/r^2 + 259700 \exp(-3.49r) \\
 V_{\text{Ca-H}} &= 626/r^2 + 120200 \exp(-6.79r) \\
 V_{\text{Al/Si-O}} &= -56.5/r^6 + 1028/r^{12} \\
 V_{\text{O-O}}^2 &= -3100/r^6 + 3500000/r^{12} + 15/r^4 \quad (1)
 \end{aligned}$$

In the above expression, $V_{\text{O-O}}^1$ stands for the intermolecular interaction between the oxygen atoms of water molecules, while $V_{\text{O-O}}^2$ is for the interaction between the oxygen atoms in the water molecules and the host lattice. In the present simulations, we have taken into account the long-range Coulomb interaction by using a method developed by Wolf and co-workers;¹⁸ in ref 19, it is also validated for water in zeolites.

Conventional methods like Ewald summation or the reaction field methods are computationally very expensive. Taking into account the statistical accuracy that we could achieve even in a series of long runs (about 20 days each run; see above), the accuracy of this model seems to be sufficient, and a very expensive, more accurate treatment of the long-range forces would not improve our results substantially.^{18–20}

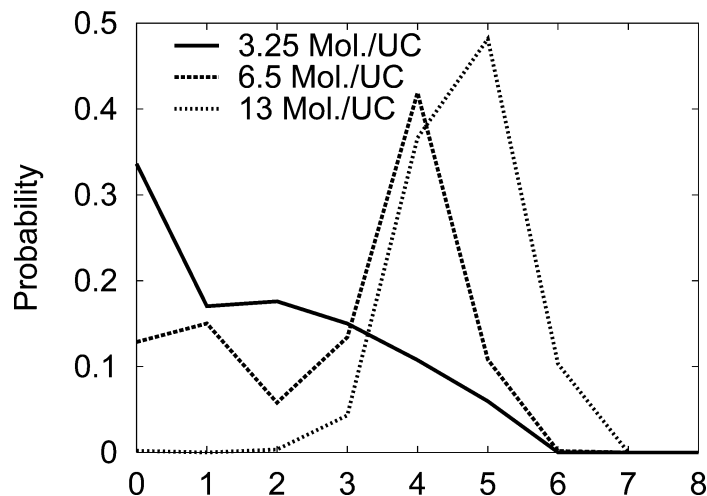


Figure 4. The probability of finding, at $T = 300$ K and three different concentrations, a Ca^{++} ion with a given number of water molecules (abscissa) in its first hydration shell, as defined in the text.

Furthermore, we have truncated these short-range forces at a distance of 11 Å with a shifted-force correction. By varying the cutoff for this correction, we have verified that the results are reasonably independent of the value chosen. To further improve the efficiency of our MD runs, a multiple-time-step algorithm, RESPA,¹³ has been used. The algorithm has been implemented with three different time steps; the intramolecular forces are calculated every 0.25 fs, the short-range part of the interatomic forces are computed every 0.5 fs, and finally, the long-range parts of the forces are generated every 2 fs.

The boxes for the simulation runs (for a typical example, see Table 1) have dimensions of about $26 \times 23 \times 30 \text{ \AA}^3$, containing 864 lattice atoms, corresponding to $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24}$, per cage for 24 cages and additional the water molecules. Figure 2 shows such a simulation box and, separately, the chabazite lattice and the aqueous phase.

Two cations per cavity are initially put at random positions, and they relax during the thermalization part of the simulations to stable positions at the eight-membered oxygen rings that connect the windows. However, their position is not a central one in the window. Instead, their site is at the oxygens close to the position of the Al atom of the lattice.

For the calculation of the self-diffusion coefficient, the MD trajectories have been generated for a period of 10–20 ns. Even with the improvements and approximations described above, a typical MD run takes about 20 days on a HP-RX2600 workstation or similar machines from IBM.

3. Results and Discussion

3.1. Ion Hydration. Figure 3 shows a partially hydrated Ca^{++} ion in the zeolite lattice after system equilibration. In this particular instance, the ion is close to a framework Si atom, kept at the oxygens surrounding this Si. This leaves space to accommodate only five hydrated water molecules. (The hydration number of this ion in low to medium concentrated aqueous solutions is 8–9.¹⁵) Besides coordinating the central ion, these molecules attempt to form hydrogen-bond-type interactions with framework atoms carrying negative partial charges or other water molecules (not drawn in Figure 3). From X-ray diffraction studies,²² it has been postulated that ions are usually attached to framework oxygen atoms next to aluminum atoms.

In Figure 4, we have plotted the probability of finding a Ca^{++} ion with a defined number of water molecules in its nearest-neighbor shell, defined here as a sphere with a radius of 2.4 Å

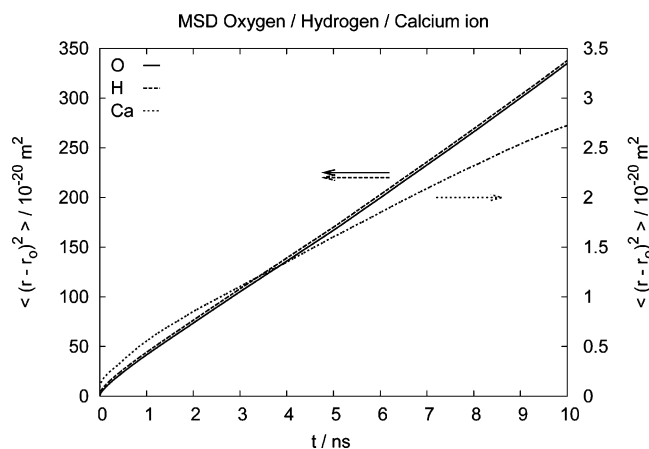


Figure 5. The mean-square displacements of water molecules and cations.

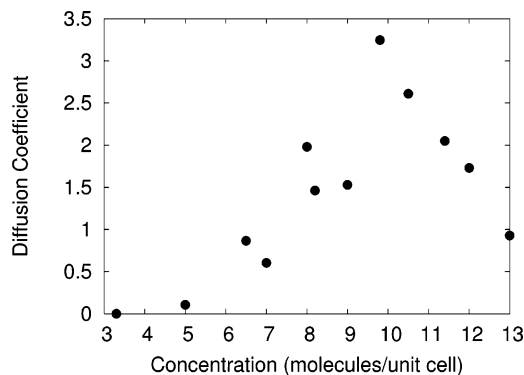


Figure 6. The variation of the average self-diffusion coefficient D , in units of $10^{-10} \text{ m}^2 \text{ s}^{-1}$, with concentration at $T = 600$ K, as discussed in the text.

around the ion. This value, corresponding to the position of the first peak maximum in the Ca^{++} –O radial pair distribution function (RDF) in bulk solution,¹⁵ is used here instead of the more usual position of the first minimum as a more stringent definition of the “nearest-neighbor shell” because of the steric constraints imposed by the lattice.

For the highest concentration (13 water molecules/unit cell in this study), the average coordination number (CN) with this definition is about 5, although there is a wide distribution of CNs. With decreasing water concentration,²¹ the average CN drops to ≈ 4 at 6.5 molecules/unit cell and even lower at ≈ 3

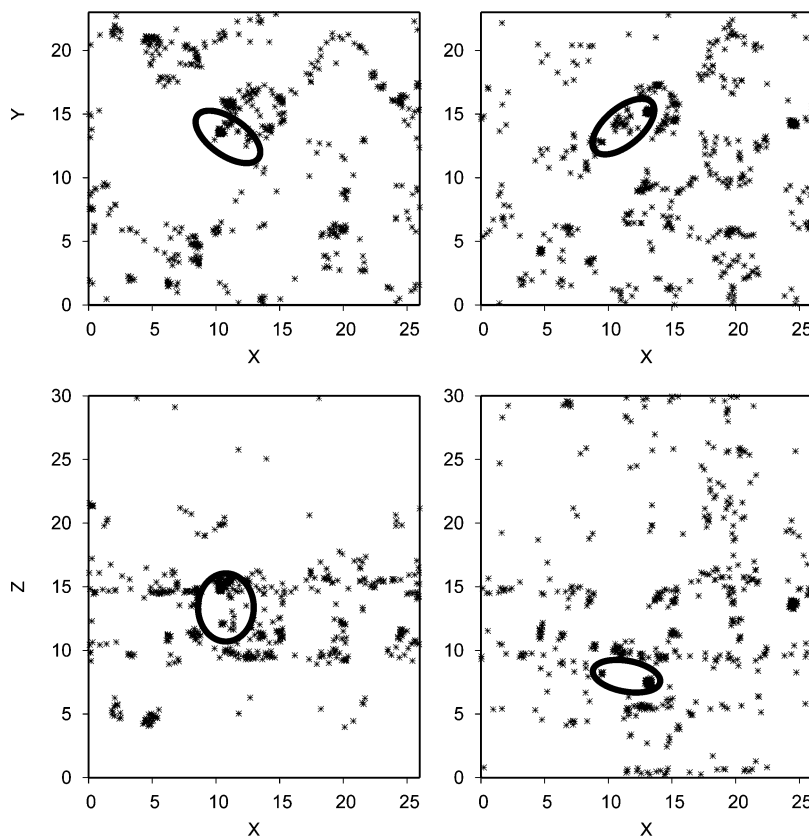


Figure 7. Two trajectories (left and right) over about 17 ps of the five water molecules initially bound to a given calcium ion. The ion remains inside of the ellipsoid during the entire 17 ps. The ion in the left-hand frame is the one also shown in Figure 3. Top frames: projection onto the x - y plane. Bottom frames: projection onto the x - z plane. The other water molecules and cations present in the simulation box are not indicated.

molecules/unit cell. This is as expected. It is interesting to note, however, that the shape of the CN distribution changes with water concentration; at the lowest concentration, approximately 33% of Ca^{++} ions are not hydrated at all. This number is larger than would be expected by random occupancy of water molecules around cations.

3.2. Self-Diffusion. The self-diffusion of guest molecules in chabazite is anisotropic because of the structure of this zeolite. The diagonal elements D_x , D_y , and D_z of the self-diffusion tensor of water have been determined from the mean-square displacements of the oxygen atoms and are, for all practical purposes, equivalent to the center of mass of the molecule. For example, according to the Einstein relation, for the x direction, we have

$$D_x = \lim_{t \rightarrow \infty} \frac{\langle (x_i(t_0 + t) - x_i(t_0))^2 \rangle_{i,t_0}}{2t} \quad (2)$$

where $x_i(t)$ is the x component of the position of particle i at time t , and the average, denoted by $\langle \rangle$, is to be taken over equivalent particles i and time origins t_0 . An average diffusion coefficient D can be defined by

$$D = [D_x + D_y + D_z]/3 \quad (2)$$

As due to the symmetry (see Figure 1) $D_x = D_y$, a completely equivalent and more accurate quantity $D_{xy} = [D_x + D_y]/2$ can be introduced.

Since self-diffusion of water in chabazite proceeds at a very low rate (much lower than, e.g., in NaX or NaA), the calculation of reliable numerical values for D_s at room-temperature turned out to be rather difficult. We have, therefore, focused in Figure 6 on the runs at 600 K to highlight the concentration dependence of the D of water. A plot of the mean-square displacements for

water and for the cations at 600 K and seven water molecules per unit cell is given in Figure 5. We note that the self-diffusion of the Ca^{++} ions is 2 orders of magnitude smaller than that of the water molecules.

At the lowest water concentration, the diffusion is slow. As the concentration increases, the diffusion coefficient increases to a maximum at about 75% of the maximum concentration (about 9 or 10 water molecules/unit cell) and then decreases in the expected fashion. At low concentration, water molecules can be easily accommodated, and the majority of them are bound to the cations, the mobility of which is low compared with that of water, as can be seen from Figure 5. With increasing concentrations, the favorable sites, for example, the ionic hydration shells, fill up, and water is accommodated in energetically less favorable locations and thus becomes more mobile. At the highest concentration, the effect of mutual hindrance becomes dominating, and the diffusion slows down again. Water diffusion in chabazite is thus found to follow the type-(iv) pattern of zeolitic diffusion.¹

An interesting aspect of water diffusion in chabazite is the exchange of water molecules in and out of the hydration shells. Such an exchange must occur because, otherwise, the rather rigid hydration shells would block the free space in the lattice, especially in the vicinity of the window connecting the cages; see, for example, Figure 3. Figure 7 shows the trajectory of two water molecules initially found in the hydration shells of two ions (say, the five ones seen in Figure 3) and of the ions themselves. It is seen that the water molecules leave the hydration shell rapidly (on the time scale of the simulation, in nanoseconds) and diffuse through the framework. The ions, on

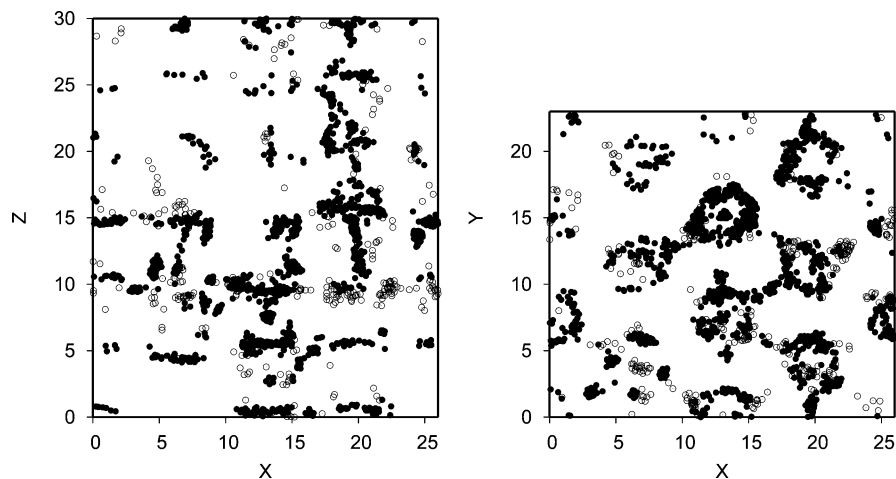


Figure 8. Trajectory, over about 17 ns, of the five water molecules initially bound to an ion, as in Figure 7. The sampling is more times more frequent than that in Figure 7. When water molecules are in the hydration shell of an ion, their position is indicated by a full circle; otherwise, it is indicated by an empty circle.

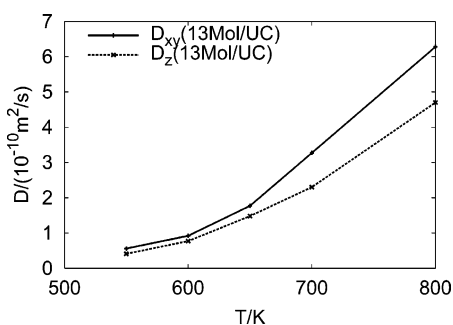


Figure 9. The self-diffusion coefficients of water along the two principal directions of the lattice as a function of temperature. The data correspond to the concentration of 13 molecules/unit cell.

the other hand, move little during this time. It seems that their diffusion would be adequately described as a jump process between neighboring sites.

Figure 8 provides some information about the importance of exchange processes between ionic hydration shells. It shows the same trajectory as those in the right panels of Figure 7; however, the positions of the diffusing water molecules (initially in the hydration shell of the ion) have been indicated by a full circle whenever these molecules are found in the hydration shells of some Ca^{++} ions.

These plots also provide some visual evidence that the self-diffusion might be faster in the x - y plane than in the direction perpendicular to it, owing to the symmetry of the crystal lattice (see Figure 1).

The temperature dependence of the self-diffusion coefficients was thus studied separately for these two directions. Figure 9 shows the formal self-diffusion coefficients D_{xy} and D_z along the two principal directions of the zeolite lattice. D_{xy} and D_z are computed like D_s in eq 2, and $D_s = 1/3 \cdot (2D_{xy} + D_z)$.

The anisotropy coefficient, defined as $\alpha = D_z/D_{xy}$, appears to be weakly dependent on temperature, increasing somewhat with temperature from slightly below 0.7 at our lowest temperature to $\alpha \approx 0.75$ at 800 K. Slightly larger values of α are obtained at lower concentrations.

We now compare our diffusion results with other theoretical and experimental data. In ref 4, the diffusion anisotropy of water in chabazite has been studied both experimentally by means of PFG NMR and also by a simple microkinetic jump model. Under the simplifying assumption that all processes of site exchange within one cavity (see Figure 1) proceed at a much

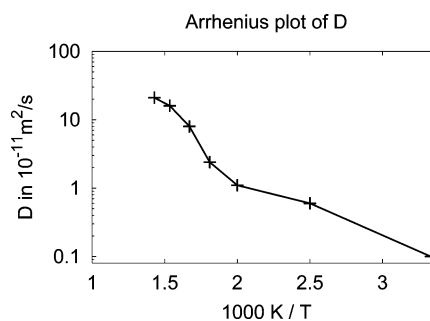


Figure 10. The self-diffusion coefficient of water averaged over all directions as a function of temperature.

larger rate than molecular jumps between adjacent cavities, only on the basis of geometrical considerations, the anisotropy factor α was found to be equal to 0.8. This result was in puzzling contrast with the experimental finding of $\alpha \approx 0.4$ which, in two completely independent sets of experiments, was found both with monocrystals and in zeolite powder samples. The present simulations provide a possible explanation of this difference since molecular exchange within one cage is found to, by far, not proceed instantaneously, leading to lower diffusivities in the z direction and hence into the direction of the measured diffusivities. Unfortunately, a direct quantitative comparison between the present studies and those reported in ref 4 is excluded by the fact that our present simulations are confined to much higher temperatures (600 K) than those (300 K) considered in ref 4.

To enable a comparison, one could try to extrapolate D via the Arrhenius law from higher temperatures to lower ones. As the statistical error of the D values obtained at 600 Kelvin is already to large to use them for extrapolation purposes, lower temperatures are out of the question. For temperatures considerably higher than 600 K, the cation mobility will increase, and this will change the diffusion mechanism completely. Even collective movements of water/cation clusters are possible at high temperatures. Some trial calculations have been carried out for lower temperatures. Figure 10 shows that no Arrhenius law can be observed in the considered range of temperatures. Therefore, we will use the present computer program and the data as a starting point for calculating the D values at lower temperatures by dynamically corrected transition-state theory in another paper.

Finally, we note that no significant deviation from isotropy was reported from tracer diffusion experiments.²³

4. Summary and Outlook

We have studied the self-diffusion of water molecules adsorbed in chabazite using molecular dynamics computer simulations. Our study indicates that the self-diffusion in water is strongly sensitive to the water concentration. The dependency upon water concentration is nonmonotonic. The formation of hydration shells around the extraframework Ca^{++} ions plays an important role in the diffusion process because the number of water molecules that can freely move increases with increasing saturation of the hydration shells around the cations. The diffusion anisotropy has been found to be smaller than that obtained from PFG NMR studies, being consistent with tracer diffusion studies where anisotropy was not observed.

The density distribution of water molecules within the cavity shows clearly that the cations serve as adsorption sites. The simple jump model derived in ref 4 did not consider the finite rate of molecular exchange between the cation sites within one cavity and should therefore be modified, resulting in a slightly reduced diffusivity in the z direction.

At lower temperatures, the self-diffusion coefficients should be evaluated by other methods, such as transition-state theory (TST). Because of the complexity of the system, transition path sampling (TPS) could particularly be appropriate. Already in the case examined in the present paper (600 K), the transition from one cavity to an adjacent one is a rare event. Therefore, this case could be used as a starting point for TPS, providing the possibility of comparison between MD simulations and TPS calculations.

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