Molecular Dynamics Studies of Sodium Diffusion in Hydrated Na$^+$-Zeolite-4A

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Received: April 9, 1998

Molecular dynamics simulations of hydrated Na$^+$-zeolite-4A incorporating a mobile zeolite framework have been performed at 298 K for a range of hydration. The sodium ions in Na(1) sites, located at the centers of the six-rings, are found to be virtually immobile at all hydrations. These ions may diffuse very slowly by knock-on events in which an ion is knocked out of position by a mobile ion and immediately replaced. The sodium ions in Na(2) and Na(3) sites, associated with the eight-rings and four-rings respectively, diffuse between these sites with a self-diffusion coefficient ranging from 7×10^{-12} m^2/s in the dehydrated crystal to about 100×10^{-12} m^2/s in the fully hydrated material. The self-diffusion coefficient of the mobile ions increases with hydration, in agreement with the results of conductivity experiments. Although the mobile ions each make several elementary hops during the 0.5 ns of the simulation, this time scale is still too short to be certain that the diffusion coefficients reflect intercavity diffusion rather than intracavity diffusion. Finally, it is shown that the sodium ions in the Na(2) and Na(3) sites are preferentially hydrated at low hydration.

I. Introduction

One challenge in modern materials science is to understand the static and dynamic behavior of fluids in confined geometries. There is much to be learned about the inter-relationship between macroscopic phenomena such as diffusion and the microscopic interactions between atoms and molecules. Zeolites, a class of aluminosilicates, have formed the focus of considerable research effort because of their technological importance and because they act as excellent model systems for the investigation of confined fluids. Zeolite crystal structures consist of SiO$_4$ and AlO$_4$ tetrahedra arranged in space to produce a network of interconnecting pores and cages. The internal cavities are large enough to allow small molecules to migrate resulting in interesting and important catalytic, ion-exchange and molecular-sieve properties.[1,2]

The present studies focus on Na$^+$-zeolite-4A, an important commercial zeolite. The true unit cell consists of 96 AlO$_4$ and 96 SiO$_4$ tetrahedra with each oxygen atom bonded to one aluminum atom and one silicon atom as illustrated in Figure 1.[1] Charge neutrality is provided by 96 sodium ions, and the full chemical formula of the true unit cell is Na$_{96}$Al$_{96}$Si$_{96}$O$_{384}$. Zeolite-4A contains two types of cavity; the large α-cages have internal cavities of 11.4 Å diameter, while the small β-cages have diameters of 6.6 Å. There are eight α-cages and eight β-cages per unit cell. The arrangement of oxygen atoms in zeolite-4A produces eight-membered, six-membered, or four-membered rings referred to as 8R, 6R, or 4R respectively, for brevity. Examples are illustrated by bold lines joining oxygen atoms in Figure 1. Each 6R comprises three oxygen atoms approximately 2.3 Å from the ring center, conventionally labeled O(3), and three oxygen atoms about 2.9 Å from the center, labeled O(2). All remaining oxygen atoms are labeled O(1).

The computer simulation has an important role to play in establishing the relationship between microscopic and macroscopic quantities. Studying zeolite systems under a controlled environment provides insight into the behavior of small
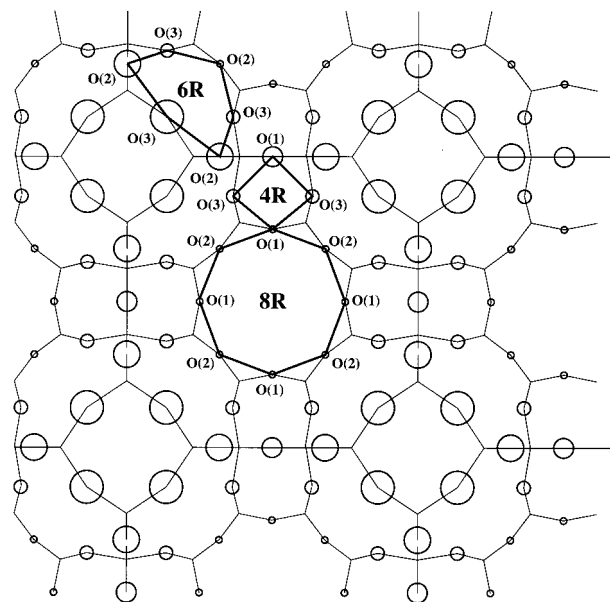

Figure 1. Schematic diagram of the zeolite-4A crystal. Only the oxygen atoms are shown and are represented by circles with the size of circle indicating depth. Examples of an oxygen eight-, six-, and four-ring are illustrated by bold lines and labeled 8R, 6R, and 4R, respectively. The oxygen atoms are labeled O(1), O(2), and O(3) according to convention.

molecules at the microscopic level, leading to a greater understanding of their overall behavior and hence aiding the design of new and improved products. Molecular dynamics (MD) studies of zeolite structures have become practical in recent years with the availability of increased computer power. Many workers have demonstrated the value of MD modeling by showing that it is possible to obtain good agreement with experimental values of macroscopic quantities derived from the simulation.[3−8]

This paper reports results from extensive MD simulation studies of hydrated Na$^+$-zeolite-4A with the focus on the diffusion of the sodium cations. Previous experimental and

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theoretical studies indicate that the sodium ions occupy three main sites.[1] These sites are referred to as Na(1), Na(2), and Na(3) and correspond to locations associated with the 6Rs, 8Rs, and 4Rs, respectively. There are 64 6Rs, 24 8Rs, and 96 4Rs in the true unit cell. Previous workers have concluded that each 6R and each 8R contain approximately one sodium ion, accounting for 88 of the 96 ions in the cell with the remainder found at random Na(3) sites.[1,9] These conclusions were confirmed by the present author who presented results from MD simulations at 298 K on dehydrated and fully hydrated Na⁺-zeolite-4A,[10] hereafter referred to as DAF1. The ions in Na(1) sites are in a low-energy configuration bonded to three O(3) oxygen atoms and hence are relatively immobile. By comparison, the ions in the Na(2) sites form a coplanar bond with zeolitic oxygen atoms and are able to move between four equivalent sites in the plane of the 8R, approximately 1.2−1.4 Å from the center of the ring. Ions in the Na(2) sites may also move out of the plane of the ring (DAF1). The sodium ions in Na(3) sites are displaced away from the plane of the 4R toward the center of the α-cage. The minimum energy position is located about 1.65 Å from the plane of the 4R, but this average distance appears to be greater at room temperature (DAF1).

The primary source of experimental information on the diffusive behavior of cations is through macroscopic techniques such as electrical conductivity and ion exchange measurements (see reviews in refs 1 and 11). For instance, the activation energy for sodium diffusion has been deduced from conductivity measurements,[12] and Stamires has measured the effect of hydration on conductivity.[13] Direct measurements of the intracrystalline self-diffusion coefficient for sodium ions in Na⁺-zeolite-4A have not been performed partially because the primary experimental focus has been on migrating adsorbed species, frequently simple hydrocarbons, and partially because of the technical difficulties. Experiments on proton-bearing adsorbates using pulsed field gradient nuclear magnetic resonance (PFG NMR) yield intracrystalline self-diffusion coefficients,[14] and quasi-elastic neutron scattering has been employed to examine the motion of adsorbates in zeolitic materials, including water (for example, ref 15). The cations, however, may influence the diffusion of the adsorbate, especially polar adsorbates, because of electrostatic interactions and steric effects. Direct measurements of the self-diffusion coefficient of the sodium cations, although possible in principle by fringe-field high-gradient NMR, are technically very challenging because experiments must probe diffusion over sufficiently short times for crystallite edge effects to be negligible. The inter-relationship between the dynamics of the water in hydrated zeolite and the cations constitutes an important focus. Two groups have performed MD simulation studies of hydrated Na⁺-zeolite-4A. First, Lee and co-workers employed a rigid zeolite lattice and performed MD simulations on the dehydrated[16] and fully hydrated zeolite at 298 K.[4] They examined the diffusive behavior and average potential energy of the sodium ions, but their simulations were limited in size, length, and range by the availability of computer resources at the time. Second, the present author performed extensive MD simulations at 298 K on dehydrated and fully hydrated Na⁺-zeolite-4A, incorporating a fully mobile zeolite lattice (DAF1). This work concentrated on the structural properties of Na⁺-zeolite-4A and the water and sodium ions contained in its pore network with results compared to X-ray data and previous computational work. Very good agreement was obtained, confirming that the chosen potentials provide reasonable representation of the structural features of the Na⁺-zeolite-4A system. Demontis et al. and Shin

et al. have investigated the structure and dynamics of *dehydrated* Na⁺-zeolite-4A using MD, and their work serves as a useful comparison.[17,18]

This paper reports the results of an extended program of MD simulations performed at room temperature for a range of hydration in which the sodium ion dynamics are investigated in detail. A future publication will focus on the dynamics of the water molecules. Section II outlines the model and simulation, section III describes the results, and section IV contains the discussion and general conclusions.

II. Molecular Dynamics

A single true cell of Na⁺-zeolite-4A (space group $FM\bar{3}c$), formula $Na_{96}Al_{96}Si_{96}O_{384}$, was used in all simulations. The cubic cell dimension is 24.555 Å.[19] Silicon and aluminum atoms are assumed to alternate so that each oxygen atom is bonded to one atom of each type and a fully flexible zeolite framework is employed. The interatomic potentials are the sum of two-body Coulombic, Lennard-Jones, Buckingham and three-body harmonic potentials. The water molecules interact via the SPC/E potential in which the water molecule is rigid with a hydrogen−oxygen bond length of 1.000 Å and a hydrogen−hydrogen bond length of 1.633 Å.[20] The water oxygens interact via a Lennard-Jones potential. The Ewald summation technique was used to determine the long-range Coulomb interactions, also as described in DAF1. MD simulations were performed in the *NVT* ensemble at 298 K using the program DLPOLY, version 2.7. Periodic boundary conditions were used throughout. Water molecules were placed at random within the crystal to the desired concentration and allowed to equilibrate at 298 K for at least 0.1 ns. In all simulations, the time step was 2 fs and simulations were run for a total time of about 0.5 ns with the atomic positions output every 5 ps. Simulations were performed with 0, 56, 84, 112, 168, and 224 water molecules in the simulation cell, the last corresponding to approximately full hydration.[1]

III. Results

First, it is necessary to assign ions to Na(1), Na(2), and Na(3) sites by defining a volume of space associated with each type of site. The centers of the eight 6Rs per α-cage are located at approximately (±3.8 Å, ±3.8 Å, ±3.8 Å) relative to the center of each α-cage. Sodium ions are defined to occupy Na(1) sites if within 2 Å of the center of a 6R. The centers of the six 8Rs associated with each α-cage are located at positions that are permutations of the vector (0, 0, ±6.1 Å) with respect to the center of the α-cage, and a sodium ion is deemed to occupy a Na(2) site if it is located within 3 Å of the center of a 8R. The larger radius is employed in this case because sodium ions in Na(2) sites are more mobile and can occupy four equivalent locations in the plane of the ring offset from its center and can move easily out of the plane of the ring (DAF1). The Na(3) sites are defined by moving 1.9 Å from the center of each 4R in a direction approximately normal to the plane of the 4R, toward the center of its associated α-cage. Sodium ions are considered to be located at Na(3) sites if within a radius of 1.5 Å from this position. These designations are necessarily somewhat arbitrary but ensure that no sodium ion can simultaneously occupy two types of site and minimize the number of ions that cannot be assigned to any site.

Figure 2 presents the (*x*, *y*) position of all sodium ions for the simulation cell. All 96 ions are plotted at 5 ps intervals for the dehydrated and fully hydrated crystal. The figures serve as density plots, and the sodium ions associated with the 6Rs, 8Rs,
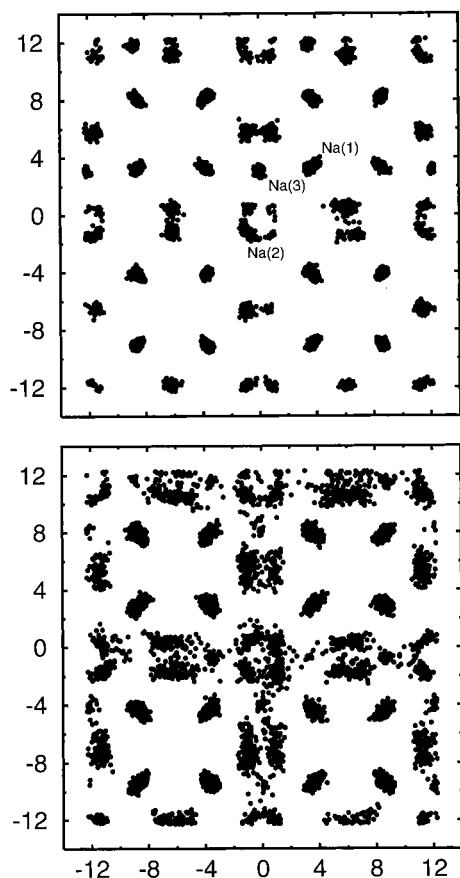
Figure 2. The (x,y) position of the sodium ions in Na$^+$-zeolite-4A at 298 K are plotted every 5 ps for the dehydrated (top) and fully hydrated (bottom) crystal. Distances are in angstroms.

Figure 3. Mean square displacement (MSD) of sodium ions in Na$^+$-zeolite-4A at 298 K in units of Å^2 are plotted as a function of time. Results for ions associated with Na(2)/Na(3) sites (●) and Na(1) sites (○) are shown separately. Only alternating data points are displayed for clarity.

and 4Rs are clearly visible with examples labeled Na(1), Na(2), and Na(3), respectively. In the hydrated zeolite, the water molecules hydrate the sodium ions and the density is accordingly more diffuse.

The potential energy of each sodium ion in the *dehydrated* zeolite was calculated by removing each ion in turn from the crystal and using DLPOLY to calculate the configurational energy of the system. The average potential energy of the ions associated with the Na(1), Na(2), and Na(3) sites was found to be -8.3 ± 0.4, -7.3 ± 0.4, and -6.5 ± 0.4 eV/atom respectively, where the uncertainty represents 1 standard deviation. These results confirm the stability of the Na(1) site. These potential energies are lower than those due to Lee et al.[4] because of the larger assumed charge on the sodium ions ($+1$ in the current simulations and $+0.55$ for Lee et al.). Both groups claim very good agreement with structural data on the position of sodium ions within the crystal for their chosen interatomic potentials (DAF1[4]). Structural data, however, is not especially sensitive to the choice of charge on the sodium ions, but the dynamic properties may be very dependent on the choice of charge. Shin et al. use $+0.625$ with their potentials, while Demontis et al. use $+1$ as in the current simulations. The activation energy of sodium ions in dehydrated zeolite-A, measured by Freeman and Stamires,[12] is just over 10 kcal/mol, equal to 0.4 eV/atom and likely to correspond to a hop from a Na(2) site to a Na(3) site.

Figure 3 displays the mean square displacement (MSD), $\langle r^2(t) \rangle$, as a function of time for the sodium ions at 298 K for different levels of hydration. Information on atomic positions and velocities are output every 5 ps, and each point is used as a new time origin for the calculation of the mean square
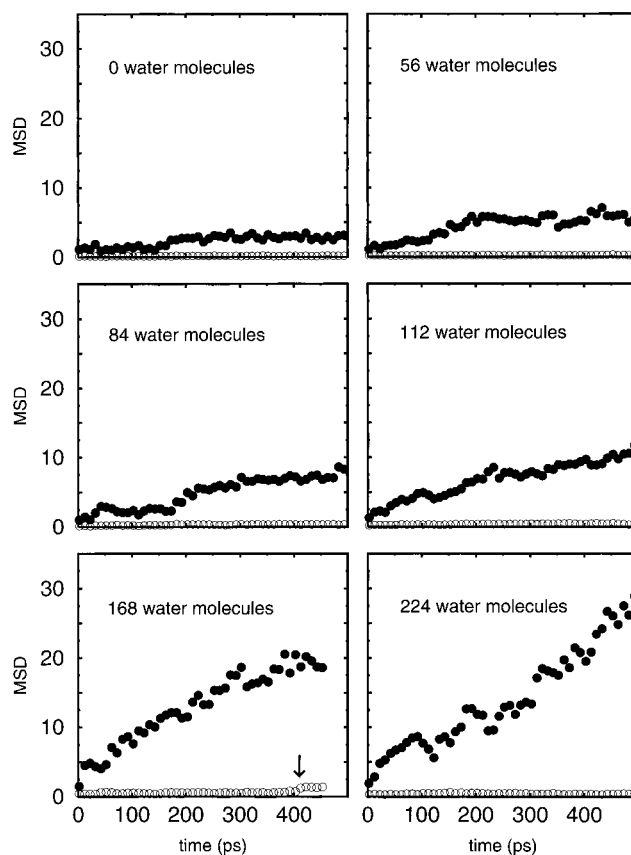
displacement (as described by L. Leherte in the discussion of ref 14),

$$\langle r^2(n\Delta t) \rangle = \frac{1}{N}\frac{1}{(N-n)}\sum_{i=1}^{N}\sum_{j=1}^{N}[r_i(t_j + n\Delta t) - r_i(t_j)]^2$$

where N is the number of time intervals and Δt their separation in time. In the current simulations $N = 100$ and $\Delta t = 5 \times 10^{-12}$ s. The data at shorter times therefore have better statistics than the data at longer times because the averaging has taken place over a larger number of data pairs. This averaging technique improves the statistical scatter of the calculated MSD but increases susceptibility to systematic error arising from the correlation between successive data points.

Each figure contains two curves, one for the sodium ions in Na(2) or Na(3) sites and one for the ions identified with Na(1) sites. The ions in Na(1) sites do not diffuse over the time scale of the simulations at any hydration, in agreement with Lee et al. and Shin et al.[4,18] In one event at 168 water molecules in the cell (indicated by an arrow in the figure), a mobile sodium ion knocked a sodium ion in a Na(1) site out of position and immediately replaced it. A few additional events were also observed in which an ion in a Na(1) site was knocked out of position by a second ion for a short period of time before returning to its original Na(1) site. It is proposed therefore that ions in Na(1) sites diffuse by a series of knock-on events whereby the ion is knocked out of its Na(1) site and diffuses between Na(2) and Na(3) sites before eventually knocking another ion from its Na(1) site and replacing it.
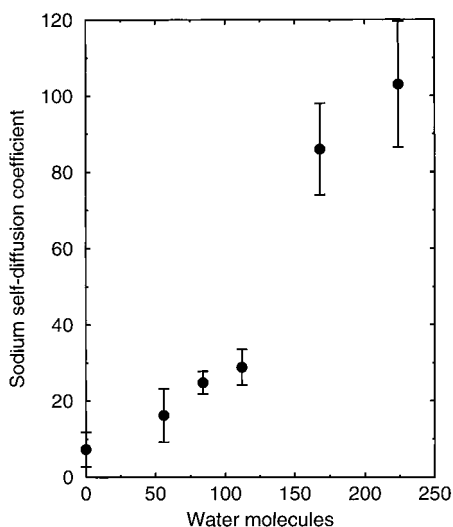
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Figure 4. Self-diffusion coefficient in units of 10^{-12} m^2/s of the sodium ions associated with Na(2) and Na(3) sites is plotted as a function of the number of water molecules in the simulation cell.

Almost all the diffusion of the sodium ions is due to moves between Na(2) and Na(3) sites. The 8Rs can accommodate more than one sodium ion, and so a vacant Na(2) site is not necessary for a successful hop from a Na(3) site to a Na(2) site. These conclusions are consistent with Shin et al. for dehydrated Na⁺-zeolite-4A.[18]

The self-diffusion coefficient for ions in the Na(2) or Na(3) sites, D_t, is evaluated in the normal way from the mean square displacement using the Einstein relation $D_t = \langle r^2(t) \rangle / (6t)$ for three-dimensional diffusion using a least-squares best-fit gradient through the data in Figure 3. D_t is plotted as a function of the number of water molecules in the simulation cell in Figure 4. The diffusion coefficient increases with hydration, as expected, with values ranging from about 7×10^{-12} m^2/s in the dehydrated crystal to about 100×10^{-12} m^2/s in the fully hydrated material. Lee et al.[4] obtained values in the range $(6000-10000) \times 10^{-12}$ m^2/s at full hydration for the sodium ions in Na(2) and Na(3) sites, some $1-2$ orders of magnitude larger than the present values. This difference arises from a combination of factors. Lee et al. evaluate their diffusion coefficient from the mean square displacement evaluated over a very short period of time, 4 ps, compared to 500 ps for the current simulations. Diffusion coefficients evaluated over such short times are notoriously unreliable. Indeed, if the diffusion coefficient was evaluated from the *current* results from the mean square displacement over the first 25 ps or less, it can be seen from Figure 3 for 168 and 224 water molecules per cell that the result for D_t would be at least a factor 5 larger. The desirability of determining self-diffusion coefficients from simulations of at least 0.1 ns is well documented. Second, as commented earlier, the use of different interatomic potentials will make a difference to mobilities. The higher average potential energy of the mobile ions in the fully hydrated crystal of Lee et al. will lead to greater diffusivity in their simulations.

Figure 4 shows an increase in D_t between 112 and 168 water molecules per unit cell. The simulations reveal that almost all moves by sodium ions can be associated with hops from Na(2) sites to Na(3) sites and vice versa. This is true at all values of hydration except at 168 water molecules per cell. In this case the simulation results show three sodium ions making a large number of "moves" but not being associated with any specific type of site. These three ions make a significant contribution to D_t. The diffusion data displayed in Figures 3 and 4 result from

only a few mobile ions and are therefore subject to significant statistical error.

The maximum MSD in Figure 3 indicates that the average distance moved by the mobile ions is about 5 Å at full hydration, less at lower hydration, compared to the α-cage diameter of about 12 Å. The diffusion coefficients presented in Figure 4 may therefore represent *intra*cavity diffusion rather than *inter*cavity diffusion. Much longer simulations would be required to determine conclusively whether simulations of 0.5 ns are sufficient for good estimates of long-range D_t. Certainly, the MSD for 56 water molecules does not appear to increase linearly with time. However, diffusion arises by hops between Na(2) and Na(3) sites, and the Na(2) sites are in the plane of the 8Rs that form the interface between α-cages. This is the elementary diffusion step. If the motion of the sodium ions is uncorrelated, there is an equal chance that a sodium ion in a Na(2) site would move to a Na(3) site in a new cage rather than its previous cage. Furthermore, the mobile cations make several elementary hops. For these reasons it is possible that the values of D_t are indeed representative of long-range diffusion of cations in zeolite-4A, but one should remain cautious on this point until very long simulations have been performed.

It is possible to estimate jump rates, τ^{-1}, from D_t by using the Einstein equation $\tau^{-1} = 6D_t/l^2$, assuming that motion is uncorrelated, all hops are between Na(2) and Na(3) sites only, and that hops of length l are between the centers of each type of site. These are crude approximations. The value of l^2 is about 19 Å^2, leading to jump rates of between 0.2×10^9 and 3.2×10^9 s^{-1} for zero and full hydration, respectively. These jump rates plus information on site positions and site energies (assumed that energy barriers are small) could be incorporated into a Monte Carlo jump diffusion model as demonstrated by Jousse et al.[22] for the diffusion of butene isomers in several zeolite types.

It is difficult to make a direct comparison of the self-diffusion coefficients obtained from the MD simulation with experimental results. Preliminary fringe-field high-gradient NMR measurements on hydrated Na⁺-zeolite-4A plugs at room temperature suggest that D_t is very small, probably less than predicted by the current simulation results.[21] On the other hand, these NMR measurements probe a much longer time scale than the simulation, and confinement of sodium ions to within crystallites may lead to measurements of D_t close to zero.

Stamires[13] investigated the effect of hydration on the conductivity of Na⁺-zeolite-4A and concluded that conductivity increases with hydration until about 60 water molecules per unit cell, at which point the conductivity increased at a lower rate. It was concluded that ions in the Na(2) and Na(3) sites were hydrated first and that 60 water molecules/cell constituted complete hydration of these ions. The addition of more water resulted in the hydration of the ions in the less mobile Na(1) sites. The MD results show a steady increase in D_t with hydration, but the increased mobility of sodium ions at higher levels of hydration is not due to the mobility of ions in Na(1) sites. However, the assertion that the sodium ions in Na(2) and Na(3) sites are preferentially hydrated is confirmed in Figure 5. Here, the fraction of water molecules contained within a sphere of radius 4.0 Å surrounding sodium ions in the Na(2) and Na(3) sites is plotted as a function of the number of water molecules in the simulation cell. If water molecules surrounded all sodium ions at random, the fraction would be about 33% because 32 of the 96 ions in the simulation cell typically occupy sites of type Na(2) or Na(3). At high hydration, the value of 33% is approached, whereas at lower hydration up to 54% of
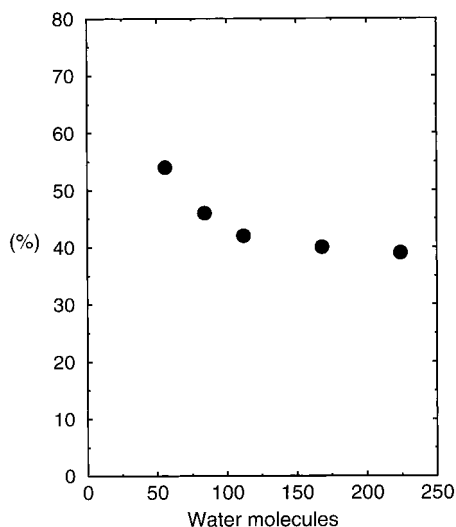
Figure 5. Fraction of water molecules contained within a sphere of radius 4.0 Å around the sodium ions in the Na(2) and Na(3) sites is plotted as a function of the number of water molecules in the simulation cell.
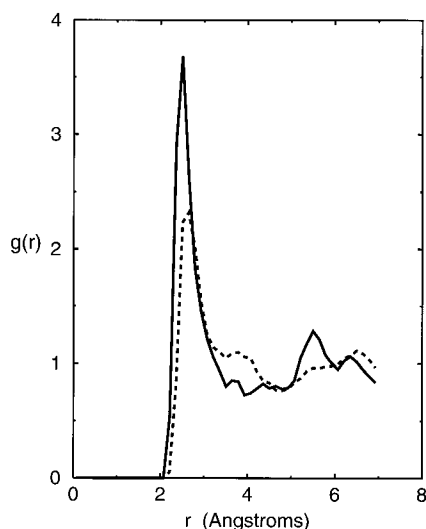

Figure 6. Sodium−water oxygen radial distribution function for Na⁺-zeolite-4A at 298 K with 56 (—) and 224 (- - -) water molecules in the simulation cell.

the water molecules are associated with sodium ions in the Na(2) and Na(3) sites. These results confirm the preferential hydration of the mobile sodium ions in the Na(2) and Na(3) sites at low levels of hydration.

Finally, the sodium−water oxygen radial distribution function is plotted in Figure 6. The density of water about 2.3 Å from the sodium ions is, on average, 3−4 times the average water density with 56 water molecules per cell and just over twice the average water density at full hydration.

IV. Conclusions

Molecular dynamics simulations of hydrated Na⁺-zeolite-4A incorporating a mobile zeolite framework have been performed at 298 K with 0, 56, 84, 112, 168, and 224 water molecules in the simulation cell. The sodium ions in Na(1) sites are found to be virtually immobile at all hydrations over the duration of the simulation, although a few events suggest that diffusion may occur by a series of knock-on events. Diffusion is due primarily to sodium ions in Na(2) and Na(3) sites moving between these sites with a self-diffusion coefficient increasing from 7×10^{-12}

m^2/s in the dehydrated crystal to about 100×10^{-12} m^2/s in the fully hydrated material. The increase in self-diffusion coefficient with hydration is in agreement with limited experimental data, but measurements of the intracrystalline self-diffusion of the cations are insufficient at this stage for quantitative comparison or to permit firm conclusions regarding the choice of interatomic potentials for the Na⁺-zeolite-4A system.

Furthermore, although these simulations are long by MD standards, the average distance moved by the mobile ions is typically less than about 5 Å, and so the results may reflect *intra*cavity diffusion rather than *inter*cavity diffusion. On the other hand, the elementary diffusion step occurs between Na(2) and Na(3) sites and the mobile cations make several elementary hops. It is possible therefore that the values of D_t are indeed representative of long-range diffusion of cations in zeolite-4A, but one should remain cautious on this point until very long simulations have been performed.

The MD simulations show that the sodium ions in the Na(2) and Na(3) sites are preferentially hydrated at low hydration, in agreement with Stamires[13] who investigated the effect of hydration on the conductivity of Na⁺-zeolite-4A. The simulation results indicate that about 54% of the water molecules are associated with sodium ions in the Na(2) and Na(3) sites at 56 water molecules in the simulation cell, decreasing to about 39% at full hydration. The sodium−water oxygen radial distribution function indicates that the density of water about 2.3 Å from the sodium ions is, on average, 3−4 times the average water density in the crystal when there are 56 water molecules per cell and the water density is just over twice the average at full hydration.

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