

Comparison of the Behavior of Water in Silicalite and Dealuminated Zeolite Y at Different Temperatures by Molecular Dynamic Simulations

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The behavior of water in silicalite and dealuminated zeolite Y (DAY), two highly hydrophobic zeolites, was investigated at different temperatures in the range 100–600 K by molecular dynamics simulations using the Compass force field. The full flexibility of water molecules and the zeolite framework was considered. This study confirmed behavior of water in silicalite pores reported previously by several authors, and extended previous work to include the different behavior of water in DAY pores. The results show that the behavior of water is more complex in silicalite than in DAY. Three different activation energies for water diffusion were obtained in silicalite in the range 250–600 K compared to two for DAY. The values of these activation energies are discussed in detail and are related to the strength of hydrogen bonds and the zeolite structure. Moreover, from the radial distribution functions (RDFs), it is shown that water mostly exists in the gas phase at room temperature in silicalite, whereas liquidlike water is observed in DAY. The self-diffusion coefficients of water and the RDFs were obtained as functions of temperature in order to explain the different behaviors of water in the two all-silica zeolites. The influence of loading on the self-diffusion coefficients also was investigated for both crystals. The results compare favorably with previous experimental and theoretical studies.

Introduction

Recent experimental observations on the adsorption of organics in a high silica ZSM-5 (silicalite) and a dealuminated zeolite Y (DAY) suggested that the interference of water was negligible in one case (silicalite), but significant in the other (DAY).^{2–4} A recent theoretical study based on statistical thermodynamics supported those conclusions.⁵

Silicalite and DAY are two very hydrophobic zeolites. Consequently, the interactions between water molecules contained within channels of these zeolites are much stronger than the interactions between water molecules and the zeolite frameworks. However, pure silicalite and DAY with no defects (silanol groups) and no aluminum are difficult to obtain and, unfortunately, the experimental results such as the diffusion coefficients or the adsorption capacities are greatly affected by these crystal abnormalities. Several different hydrophobicity scales^{5,6} have been defined that gave similar hydrophobicities for both zeolites.⁴ Therefore, in this work, we considered the zeolites as being all-silica and defect-free and we compared our results with previous experimental and theoretical studies.

Silicalite and DAY differ by their structures, dimensions, and symmetries. Silicalite belongs to the family of pentasil zeolites as the framework is built up from five-membered rings.⁷ The unit cell is composed of 96 SiO₂ units and contains elliptical straight channels with a diameter of 5.7–5.8 Å × 5.1–5.2 Å and circular sinusoidal, or zigzag, channels with a diameter of 5.4 Å. Silicalite has a reversible phase transition at 340 K. Below 340 K, silicalite belongs to the monoclinic symmetry group (P2₁/n11 space group), whereas above 340 K, silicalite belongs to the orthorhombic symmetry group (Pnma space group). The

framework density is 1.8 g/cm³ and the specific pore volume is 0.19 cm³/g. Synthetic DAY has the same structure as the mineral faujasite, except that DAY theoretically does not contain any aluminum atoms. DAY has an open structure with a pore volume of 0.38 cm³/g and a high symmetry (cubic FD-3) that makes distinguishing between cages and windows difficult. The framework is composed of sodalite units interconnected through six-membered oxygen bridges. These units form supercages that are connected to neighboring cages through four tetrahedrally directed twelve-membered rings with a free diameter equal to 7.5 Å.⁷ The unit cell is composed of 192 SiO₂ tetrahedral units. The structure and detailed structural information for silicalite and DAY, and numerous other zeolites, can be found at the International Zeolite Association Structure Commission's web-site: www.iza-structure.org/databases.

The Compass force field used to simulate diffusion of water in these two crystals is a commercial software package.¹ This force field takes into account the electrostatic interactions modeled by a Coulomb potential and the van der Waals, London, and hydrogen-bonding interactions modeled by a 6-9 Lennard-Jones potential. The parametrization procedure consisted of two phases: an ab initio parametrization and an empirical optimization.

The temperature range was 250–600 K where normal diffusion takes place so that the Einstein relationship, which relates the mean square displacement, denoted $\langle r^2(t) \rangle$, with time was used:

$$\langle r^2(t) \rangle = 2kDt \quad (1)$$

where $k = 1, 2$, or 3 , depending on the dimension of the system (1D, 2D, or 3D diffusion, respectively), and D is the self-diffusion coefficient.

At temperatures below 250 K and/or at high loading levels, the normal diffusion process does not occur, and the resulting

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self-diffusion coefficients cannot be compared with those obtained for normal diffusion. For example, we observed a single-file diffusion regime for diffusion of water molecules in silicalite at 130 K with 8 water molecules per unit cell. Single file diffusion has been observed previously for temperatures below 225 K with 8 water molecules per unit cell.¹⁰ As single file diffusion is due to hindrance, when molecules cannot pass each other in the channels,^{10,19–21} it is predictable that single file diffusion occurs at low temperatures and/or high loadings. The influence of high loadings on the diffusion regime is noted in the second part.

Water Behavior in Silicalite

The system was composed of two unit cells elongated in the *c* direction containing 8 water molecules each. In total, 2×96 SiO₂ units and 16 water molecules were considered, which is the maximum experimental amount of water that can be adsorbed by silicalite.^{2–4} Initially, at $t = 0$, the water molecules were placed at the intersections between the straight and the zigzag channels. Intersections are good starting regions because the potential energy there is higher than in the channels where molecules immediately proceed to. Originally the average number of hydrogen bonds per water molecule is four, but this number quickly decreases when molecules enter the channels. However, the initial position of water molecules does not affect the self-diffusion coefficients as long as the simulation time is sufficient. Three-dimensional periodic boundary conditions were employed to simulate effectively infinite systems. Indeed, when periodic boundary conditions are used, atoms in the unit cell interact not only with the other atoms in the unit cell, but also with their translated images. As periodic boundary conditions were used, a cutoff radius smaller than one-half of the smallest simulation cell side was considered. The values were 6 Å for silicalite and 12 Å for DAY. In a computer simulation, the unit cell under periodic boundary conditions is viewed as the container. Volume, pressure, and density can be calculated only when the structure is recognized as periodic. The zeolite framework and water molecules were flexible during the simulations. The value of using a flexible framework is still debated.^{8,22–25}

Before performing the production run itself, a minimization and an equilibration run were carried out to bring the system to the most probable configuration. The conjugate gradient method was used to perform the energy minimization. The microcanonical ensemble NVE (constant loading, constant volume, constant energy) was used.

The simulation time was 150 ps for the equilibration run and 300 ps for each production run. As sufficient simulation time is necessary to avoid incorrect estimation of the self-diffusion coefficients,²⁹ we verified that the volume and energy converged during the equilibration run. Moreover, preliminary production runs performed at 50 ps gave results very close to the ones obtained at 300 ps. The time step was 0.5 fs.

Hydrogen bonds are crucial to explain water behavior in these two confined media. The maximum H...O bond was 2.5 Å in order to ensure that all hydrogen bonds were taken into account. This value was chosen on the basis of the first minimum in the hydrogen–oxygen RDFs (2.5 Å) and by considering that the hydrogen atoms are too mobile for a clear-cut criterion.

Self-Diffusion Coefficients as a Function of Temperature.

The mean squared displacement (MSD) was obtained as a function of time in the range 250–600 K. The results are given in Figure 1 and in Table 1. A linear dependence of the MSD with respect to time was observed, so the Einstein relationship

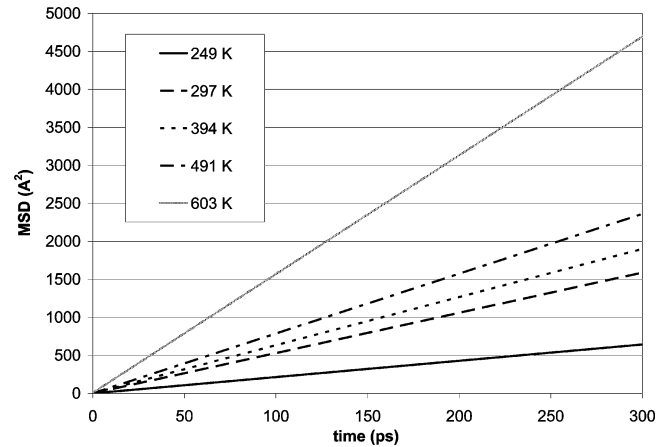


Figure 1. Total mean squared displacement of water molecules in silicalite as a function of time from 249 to 603 K

TABLE 1: The Diffusion Coefficients of Water ($\times 10^9 \text{ m}^2 \text{ s}^{-1}$) in Silicalite as a Function of Temperature and the Two Parameters β and δ as a Function of Temperature

<i>T</i> (K)	<i>D</i>	<i>D_x</i>	<i>D_y</i>	<i>D_z</i>	β	δ
249	3.57	1.34	2.03	0.28	1.29	6.04
270	5.83	1.82	4.00	0.37	1.44	7.94
297	8.83	2.33	6.17	0.67	1.14	6.34
354	10.00	2.50	6.34	0.70	1.14	6.29
394	10.55	2.96	6.76	0.78	1.19	6.24
437	13.11	3.76	7.53	0.84	1.34	6.70
491	16.53	7.16	8.57	1.84	0.95	4.27
603	26.13	10.51	13.34	2.28	1.16	5.23

corresponding to normal diffusion was used. As the temperature was increased, the self-diffusion coefficients increased in all directions. Moreover, the highest self-diffusion coefficient was obtained for the *y* direction, which is along the straight channels. Diffusion in the *z* direction, a combination of the straight and sinusoidal channels, was the slowest. These results stem from the fact that the structure of silicalite is anisotropic.

There are two parameters of interest used to evaluate the diffusion mechanism of water in microporous materials.^{10–13} The first parameter measures the discrepancy from a simple random walk model⁷ and is denoted as β , where

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

In this equation, *a*, *b*, and *c* are the dimensions of the silicalite unit cell in the *x*, *y*, and *z* directions, respectively. When $\beta = 1$, the random walk model can be applied. If $\beta < 1$, then water molecules prefer going from one channel type to the other. If $\beta > 1$, water molecules diffuse preferentially along the same channel after crossing an intersection. This last case is the one obtained for this system, except at 491 K where β is close to 1, as seen in Table 1.

The second parameter is the diffusion anisotropy parameter and is denoted δ where

$$\delta = \frac{1/2(D_x + D_y)}{D_z} \quad (3)$$

For a random walk model, δ should be close to 4.4 in silicalite.⁷ In our simulations, δ is larger than 4.4—even though, at high temperatures, δ seems to decrease. It means that water molecules do not behave as spherical particles in smooth channels with the topology of silicalite.

TABLE 2: Comparison of the Simulated Self-diffusion Coefficient with Previous Simulations and with Experimental Data at 298 and 393 K

temperature (K)	D (10^9 m ² /s)			
	this work	MD ¹⁰	MD ¹⁴	PFG-NMR ¹⁵
298	8.8	8.6	3.3	1.7
393	10.5	10	6.7	1.5

Comparing the results we obtained with previous works given in Table 2, one observes that the values of the self-diffusion coefficients are close to the previous molecular dynamic simulations especially to the ones obtained by Demontis et al.¹⁰ On the other hand, the values of the diffusion coefficients reported from experimental observations are lower, although within the same order of magnitude.

There are several reasons that explain these differences. Real silicalite may contain defects such as aluminum T-atoms or silanol groups if an Si—O—Si bridge is broken. Thus, the self-diffusion coefficients and the adsorption capacities will be slightly different than predicted for the pure-silica pore system. In particular, if aluminum atoms are present, there are countercations to keep the system electrically neutral and the self-diffusion coefficients would be expected to be lower, because water molecules tend to cluster around the cations. On the other hand, the sorption capacities are higher when countercations (or aluminum) are present in the system.²⁶ Additionally, the Pulsed Field Gradient-NMR gives weak signals, which can lead to errors after integration. The presence of water in the outer surface of the crystal also influences the results,⁴ which is why experiments were conducted at 393 K.¹⁵

Activation Energy for Diffusion. After determining the self-diffusion coefficients of water molecules in silicalite, the activation energy E_a for diffusion was determined, with E_a defined from

$$D = D_0 e^{-E_a/RT} \quad (4)$$

The Arrhenius plot is given in Figure 2. Within the temperature range 250–600 K, a single value of E_a was not obtained, but three temperature ranges were characterized by three different activation energies.

From 249 to 297 K, an activation energy of about 11.6 kJ/mol was obtained. This value is lower than that obtained for bulk liquid water (ca. 20 kJ/mol¹⁶) even though it is in the same order of magnitude. One possible explanation for this lower value can be found by considering the hydrogen-bonding network and the influence of the lattice. It was suggested by Demontis et al. that at low temperatures the lattice vibrations facilitate the diffusion of water.¹⁰ Moreover, as will be shown later, the hydrogen bonds are easily broken in silicalite, even at low temperature (250–300 K). Since hydrogen bonds have a stabilizing effect, the reduction of hydrogen bonds between water molecules in silicalite makes the diffusion process easier, as reflected by the higher self-diffusion coefficient seen in Figure 2. These combined phenomena can explain the lower value for the activation energy obtained for silicalite compared to bulk liquid water.

It is also interesting to note that for temperatures between 300 and 400 K, the activation energy is about 1.8 kJ/mol. A low value (ca. 1 kJ/mol) also was obtained over the same temperature range by Demontis et al.¹⁰ It was shown that when the lattice is kept fixed, this transition phenomenon for the activation energy does not exist.¹⁰ Moreover, within the temperature range 300–400 K, an external energy source, the lattice vibrations, help the diffusion of water molecules in the silicalite

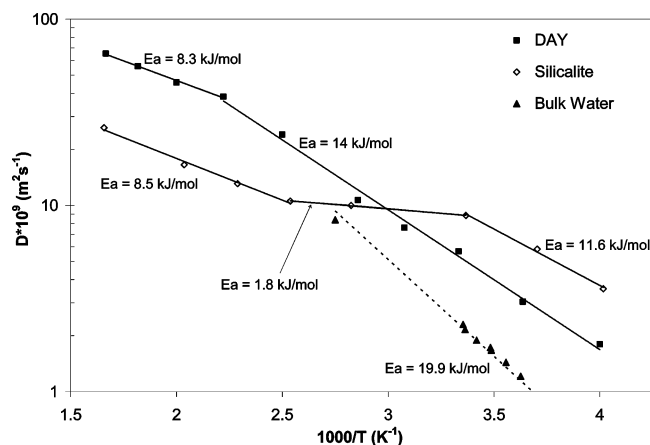


Figure 2. Arrhenius plot of the activation energies for diffusion of water in silicalite and in zeolite DAY in the range 250–600 K on a logarithmic scale. The Arrhenius plot for bulk liquid water is also given.¹⁶

pores. If the energy provided by the lattice is close to that necessary for water molecules to reach the optimal diffusivity, then the activation energy for diffusion is low within this range of temperatures. This temperature range also corresponds with that range where the potential energy of water molecules in silicalite was predicted to be increasing with increasing temperature by Demontis et al.¹⁰ That is, in the range of 300–400 K, as the temperature increases the number of hydrogen bonds between water molecules decreases, and the potential energy increases from a lower plateau to a higher plateau.

Considering these values for activation energy, it follows that between 250 and 300 K, water behaves like a liquid, even though the absolute values of the diffusion coefficients are higher than in liquid water, and the activation energy is slightly less. For temperatures higher than 300 K, water behaves like a gas. From previous results, the existence of water in the gas phase in silicalite was suggested at room temperature.^{2–4}

For temperatures higher than 400 K, the activation energy is about 8.5 kJ/mol and water molecules are in the gas phase. It is important to note that at temperatures greater than 400 K, the lattice vibrations do not help the diffusion of water molecules. It was shown by Demontis et al. that at high temperatures the diffusion of water molecules is lower when the lattice is flexible.¹⁰ This point is important in understanding the decrease of the activation energy for diffusion at high temperature.

It is interesting to compare the diffusion coefficients obtained for water in silicalite and bulk supercooled liquid water¹⁶ in the range 255–364 K. It appears that the confinement of water by hydrophobic silicalite enhances the diffusion process for pores with a diameter equal to about 5–6 Å. This enhancement of diffusion is most noticeable between 250 and 333 K where self-diffusion coefficients of water in silicalite and bulk liquid water are different by about a factor of 5. It was shown by Hartnig et al. that the polarity of the pores influences the diffusion rate of water confined in cylindrical pores.¹⁷ Water transport was found to be fast for nonpolar pores and slow for polar ones. Our results support these findings by showing that weak interactions between polar water molecules and the hydrophobic nonpolar channels of silicalite enhance diffusion compared to more polar channels. In another recent simulation study, water was predicted to move through hydrophobic nanopores in clusters, and self-diffusion transport rates were predicted to be 2–3 times faster compared to bulk water transport rates.¹⁸

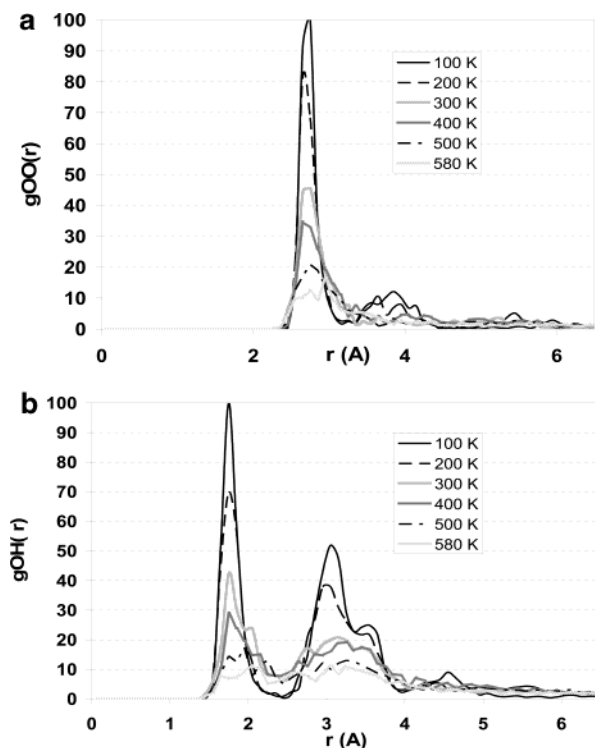


Figure 3. Intermolecular radial distribution functions of water in silicalite. (a) g_{OO} from 100 to 580 K. (b) g_{OH} from 100 to 580 K.

Hydrogen Bonds. Two different radial distribution functions (RDFs) were taken into account: $g_{OO}(r_{OO})$ and $g_{OH}(r_{OH})$. g_{OO} is defined as the probability of finding two oxygen atoms of two different water molecules separated by the distance r_{OO} . The plots for g_{OO} and g_{OH} for silicalite are shown in Figures 3a and 3b. The RDF data were obtained for simulations performed between 100 and 580 K. The first peaks were obtained at $r_{OH1} = 1.8$ Å and $r_{OO1} = 2.8$ Å for g_{OH} and g_{OO} , respectively. The 1.8 Å peak for the g_{OH} function is the distance characteristic of stable hydrogen bonds.¹⁰ The next peaks at ca. 2.8–3.5 Å represent the population of next-nearest neighbors in adjoining pores, and are characteristic of the geometry of the water molecules inside the pores. For example, the second peak of the g_{OO} function is characteristic of the tetrahedral arrangement of the water molecules. One can observe in Figure 3a that the second peak disappears very quickly as the temperature increases. However, this peak is more important for bulk liquid water.

At very low temperatures, the RDFs show isolated peaks, which is characteristic of the solid state or stable clusters of water. As the temperature increases, the peak heights decrease, but the maxima of g_{OO} and g_{OH} remain at the same positions, meaning that hydrogen bonds still form but become less stable. As the temperature increases, water clusters tend to melt, showing liquidlike then vaporlike behavior.

The number of hydrogen bonds per water molecule as a function of temperature was calculated from the peak at 1.8 Å in the RDFs. The ratio of the area under the first g_{OH} peak at various temperatures relative to the same area at very low temperatures was determined. The values in Figure 4 were found by multiplying the ratio by four, since at very low temperatures four hydrogen bonds per molecule are expected. From our simulations, it is shown that the number of stable hydrogen bonds decreases quickly, even at low temperatures. At 250 K, the number of stable hydrogen bonds per water molecule is less than two. Above 400 K, the number of stable hydrogen bonds

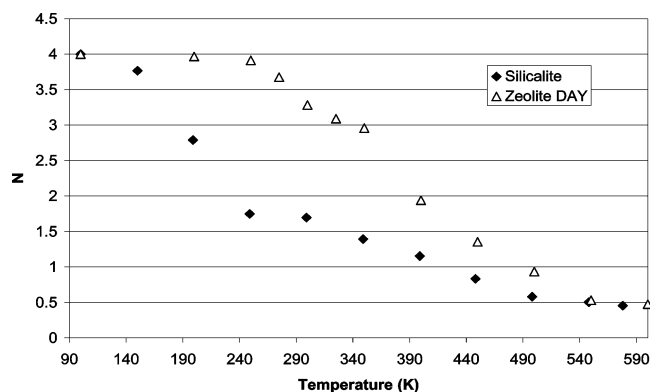


Figure 4. Average number of stable hydrogen bonds per water molecule as a function of temperature between 100 and 600 K in silicalite and zeolite DAY.

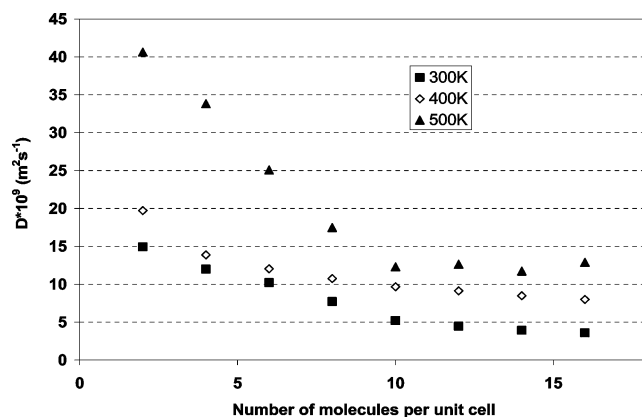


Figure 5. Influence of loading on the self-diffusion coefficients of water in silicalite at 300, 400, and 500 K.

is typically less than one, which means that, on average, water does not form any stable hydrogen bonds above 400 K. These results suggest that water is in the gas-phase in silicalite, even at room temperature.

Loading Influence on the Self-diffusion Coefficients. The loading influence on the self-diffusion coefficient was studied at three different temperatures: 300, 400, and 500 K. The results are reported in Figure 5. For a given temperature, the self-diffusion coefficients are plotted as a function of the number of molecules per unit cell. From these results, the following conclusions can be drawn:

(i) Similar trends were obtained for these three different temperatures: for a loading ranging from 2 to about 10 molecules per unit cell, the self-diffusion coefficients decreased as loading increased. Then, for a loading ranging from about 10 molecules to 18 molecules per unit cell, the self-diffusion coefficients became almost constant or decreased only slightly. The mean square displacement plots as a function of time were not linear at loadings greater than 18 molecules per unit cell. That is, normal diffusion was not observed for loadings greater than 18 molecules per unit cell. This observation was made at relatively high loadings and low temperatures for both silicalite and DAY, but at slightly different temperatures and loadings for each.

(ii) Hydrogen bonds have a stabilizing effect; i.e., they decrease the total entropy and the total potential energy. That is why one can suspect that at low loading, when the number of hydrogen bonds is small, the stabilizing effect is small or even negligible if the system contains, for example, one water molecule per intersection. In this situation, it is reasonable that for low loadings, the self-diffusion coefficients are relatively

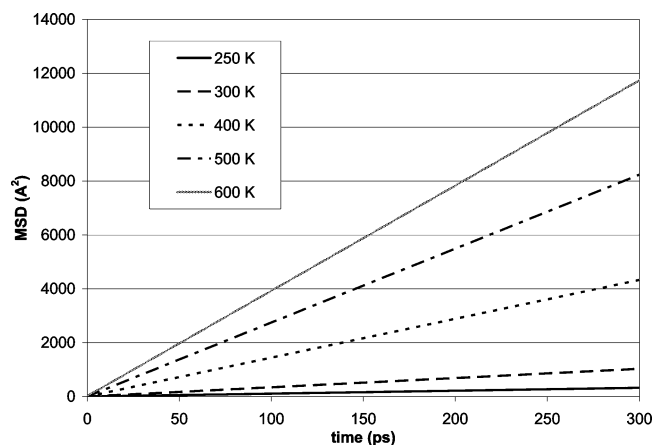


Figure 6. Total mean squared displacement of water molecules in DAY as a function of time from 250 to 600 K.

high especially at high temperatures. As the number of hydrogen bonds increases with loading, the stabilizing effect becomes increasingly important and the self-diffusion coefficient decreases before reaching a limiting value. This limiting value is not surprising, because the number of hydrogen bonds per water molecule has a limit. Since the self-diffusion coefficient depends strongly on the number of hydrogen bonds, it is reasonable that if the number of hydrogen bonds has a limiting value, so will the self-diffusion coefficients.

(iii) From previous experimental work it is interesting to note that the maximum amount of water that was adsorbed in silicalite was around 8 molecules per unit cell at room temperature.^{2–4}

Finally, where this study overlaps with the results reported by Demontis et al.,¹⁰ the two studies have made similar predictions.

Water Behavior in DAY

We considered the same parameters and the same thermodynamic ensemble as those used for silicalite. The number of water molecules per unit cell was kept constant at 8, and we considered 2 unit cells elongated in the *c* direction. The lattice and the water molecules were flexible.

Again, we considered a perfect zeolite with no defect and no aluminum atoms. As the dealumination procedure does not yield a 0% aluminum content zeolite, the real zeolites are not aluminum-free; a Si/Al ratio equal to 100 is characteristic of a high-silica zeolite. Aluminum atoms modify the adsorption capacities²⁷ and the Brønsted acid strength.²⁸ Hence the real diffusion of water molecules is different and believed to be lower in real zeolites. Nevertheless, we chose an all-silica zeolite DAY in order to compare the two zeolites with the same chemical compositions and similar hydrophobicity.⁴

Self-Diffusion Coefficients as a Function of Temperature. The MSDs as a function of time at different temperatures in the range 250–600 K are given in Figure 6. A normal diffusion regime is observed, and the Einstein relationship was used to calculate the self-diffusion coefficients shown in Table 3. From these results, the diffusion is isotropic, which was expected due to the symmetry of the crystal (3D cubic FD-3).

One also observes from Figure 2 that for $T < 350$ K, diffusion of water molecules in silicalite is higher than in DAY. But, for $T > 350$ K, self-diffusion coefficients become much higher in zeolite Y than in silicalite. These results are likely due to the fact that at low temperatures, from 250 to 350 K, lattice vibrations are more efficient and have more influence in silicalite

TABLE 3: The Diffusion Coefficients of Water ($\times 10^9 \text{ m}^2 \text{ s}^{-1}$) in Zeolite Y as a Function of Temperature

<i>T</i> (K)	<i>D</i>	<i>D_x</i>	<i>D_y</i>	<i>D_z</i>
250	1.8	0.60	0.67	0.53
275	3.04	0.85	1.01	1.18
300	5.72	1.90	1.85	1.95
325	7.6	2.37	2.53	2.70
350	10.69	3.55	3.96	3.35
400	24.05	7.18	8.20	7.22
450	39.11	10.09	11.97	10.30
500	45.75	15.56	16.82	13.33
550	55.95	15.77	19.14	17.24
600	65.31	17.94	20.97	20.02

than in DAY. This would be the case because water molecules are closer to the walls of the pores in silicalite than in DAY, so they can exchange energy with the walls more easily. Moreover, silicalite is more disruptive for hydrogen bonds leading to a lower stability effect and a higher ability for water molecules to diffuse. At higher temperatures, the smaller silicalite pores become more confining.

Activation Energy for Diffusion. The Arrhenius plot is given in Figure 2. Two activation energies were obtained for two temperature ranges. For temperatures between 250 and 425 K the activation energy is 14 kJ/mol. This value is less than that of 20 kJ/mol obtained for bulk liquid water at room temperature.¹⁶ The value we determined is lower, because of the confinement which influences the thermodynamics of the system and the hydrogen bond geometries. We show in this section that the hydrogen bond strength and the average number of hydrogen bonds per water molecule decrease as temperature increases. Moreover, the number of hydrogen bonds per water molecule is lower in the DAY pore system than in bulk liquid water in this temperature range. Thus, the stabilizing effect provided by hydrogen bonds between water molecules also is lower in DAY compared to bulk water, leading to a lower activation energy for diffusion.

Comparing the activation energy for diffusion within the range 250–300 K for the two crystal structures shows that the values of 14 and 11.6 kJ/mol for zeolite DAY and silicalite, respectively, are similar. We demonstrate in the next section that hydrogen bonds are more easily disrupted in silicalite than in DAY. The average number of hydrogen bonds per water molecule, for temperatures in the range 250–300 K, is lower in silicalite than in DAY. Accordingly, the stabilizing effect at low temperature is lower for silicalite compared to DAY. This result also can be related to the pore volume. Indeed, the pore volume for DAY is about double that of silicalite. Consequently, a stable hydrogen bond network is more likely to form in DAY than in silicalite, and lattice vibrations are less important in the larger pore system. On the basis of pore volume considerations, it is reasonable that the activation energy for diffusion of water molecules in DAY is closer to that of bulk liquid water.

For temperatures between 425 and 600 K where water molecules are in a gaslike phase, the activation energy for water in DAY is 8.3 kJ/mol, and is lower than the activation energy of 14 kJ/mol obtained at lower temperatures. Water molecules are more energetic and the translational and rotational barriers for diffusion are overcome more easily at higher temperatures than at lower temperatures.

Several observations can be made by comparing these values to those obtained for pure silicalite. First, in the low-temperature range, water behaves more like bulk water in DAY than in silicalite. We observed two activation energies for DAY over the 250–600 K temperature range. It is noteworthy that the activation energy obtained for silicalite between 300 and 400

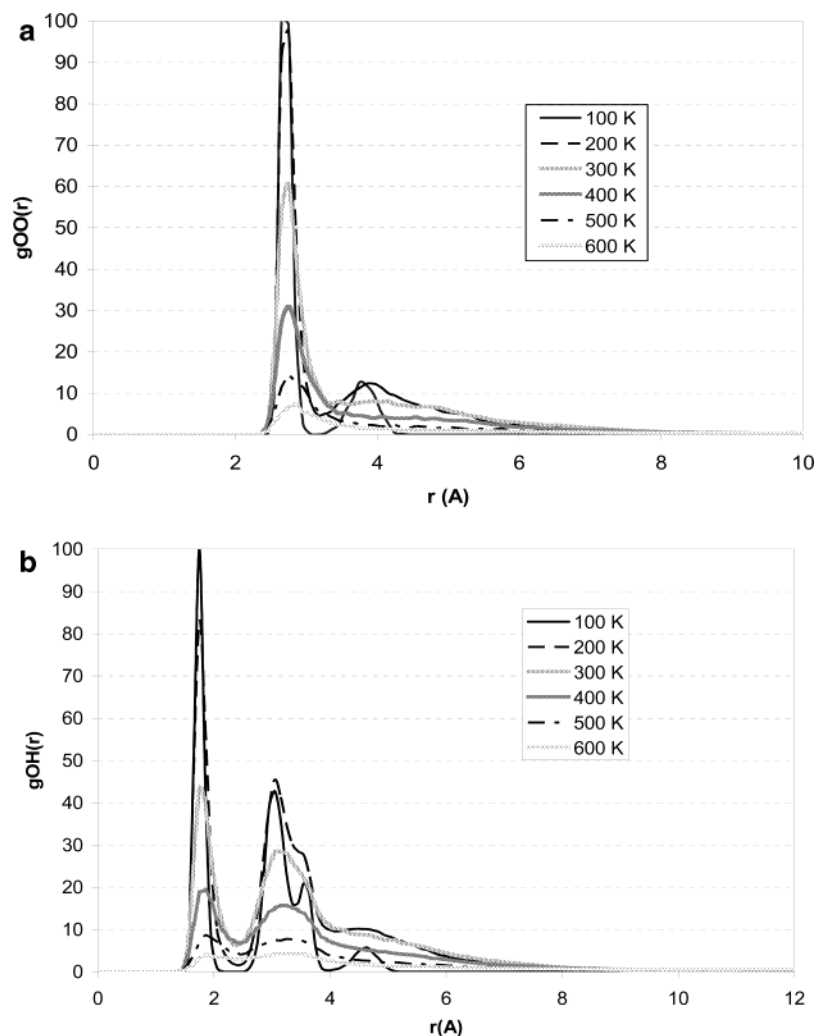


Figure 7. Intermolecular radial distribution functions of water in DAY. (a) g_{OO} from 100 to 600 K. (b) g_{OH} from 100 to 600 K.

K, equal to 1.8 kJ/mol, is not present for DAY. This transition regime between liquid- and gaslike phases for silicalite was an indication of the complex behavior of water in silicalite. Increasing the pore dimensions from ca. 5.5 Å to ca. 7.5 Å has an influence on the presence of this transition regime characterized by a very low activation energy. Second, at high temperatures where the molecules are in the gas phase and occupy the entire volume of the pores, the activation energies for water molecules in silicalite and DAY are close (8.5 and 8.3 kJ/mol, respectively), even though the absolute transport rates are slightly higher in DAY due to the larger diameter of the pores. At high temperatures, water molecules are very energetic, and the confining medium has a decreasing influence. We expect to find a similar activation energy for water molecules in similar hydrophobic zeolites at high temperatures.

Comparing the self-diffusion coefficients of water in silicalite and in bulk liquid water/supercooled water¹⁶ in the range 255–364 K, gives a similar conclusion: the hydrophobic confinement makes the diffusion process easier. Moreover, the enhancement is greater for silicalite in the lower temperature range. The enhancement is greater for silicalite than DAY. From Figure 2, Table 1, and Table 3, one can observe that the self-diffusion coefficients are five times larger in silicalite than in supercooled/bulk liquid water, whereas the self-diffusion coefficients are only twice larger in DAY compared to supercooled/bulk liquid water in the lower temperature range. Moreover, the activation energies for diffusion are lower in silicalite (11.6

kJ/mol) than in DAY (14 kJ/mol). This enhancement may be related to the lattice vibrations, which are more effective for silicalite than for DAY, because the water molecules are closer to the walls of the pore in silicalite. At higher temperatures, no enhancement is observed, because water molecules tend to diffuse along the axis of the silicalite pores, which makes the influence of the lattice vibrations less important.⁸

Hydrogen Bonds. RDFs similar to those of silicalite presented in the last section are given in Figure 7 for DAY. The first peaks are obtained at $r_{OH_1} = 1.8$ Å, which is characteristic of stable hydrogen bonds, and $r_{OO_1} = 2.8$ Å for g_{OH} and g_{OO} , respectively. The peak heights, and the area under the corresponding peaks, decrease as the temperature increases. Thus, the number of stable hydrogen bonds decreases as temperature increases in DAY.

The g_{OH} function reflects the extent of hydrogen bonding between water molecules, and the area under the first peaks at 1.8 Å were integrated to determine those values, as noted previously. The average number of stable hydrogen bonds per water molecule as a function of temperature for silicalite and DAY is given in Figure 4.

Between 100 and 500 K the number of hydrogen bonds is higher in DAY by 1–2 hydrogen bonds than in silicalite. The maximum number of four hydrogen bonds is extended up to about 250 K in DAY, while there are fewer than 2 in silicalite at that temperature. The number of hydrogen bonds at room temperature in DAY is about the same as the number of

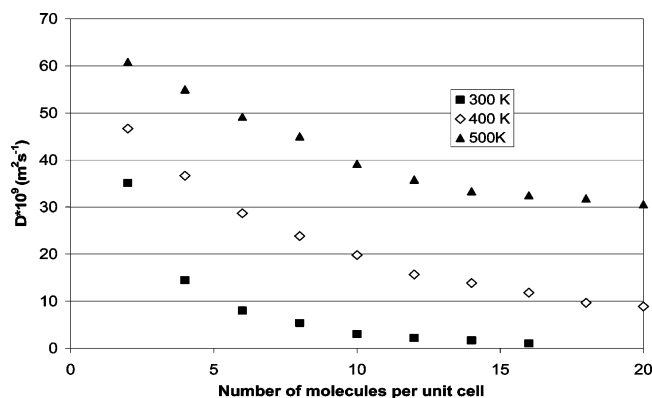


Figure 8. Influence of loading on the self-diffusion coefficients of water in DAY at 300, 400, and 500 K.

hydrogen bonds in bulk liquid water (around 3–3.5). These results suggest that water behavior in DAY is not complex, and that liquid water exists in DAY at room temperature, in contrast to silicalite where liquid water does not exist at room temperature. These results confirm the experimental observations made by Giaya et al.^{2–4} At higher temperatures, between 500 and 600 K, the number of hydrogen bonds is the same in DAY and silicalite and the diffusion is predicted to behave as a gas.

Loading Influence on the Self-diffusion Coefficients. The influence of loading on the self-diffusion coefficient is given in Figure 8. As was observed previously with silicalite, self-diffusion coefficients decrease in magnitude as loading increases. The curves show two types of behavior. For a loading between 2 and 10–12 water molecules per unit cell, the self-diffusion coefficients decrease significantly. For higher loadings, self-diffusion coefficients decrease only slightly as loading increases.

It is not surprising that the transition in diffusion behavior as a function of loading occurs for 10–12 water molecules per unit cell. This value is higher than for silicalite (8 water molecules/unit cell) as expected, since silicalite has a smaller pore volume and a lower water adsorption capacity than DAY. Two points are missing at high loading for $T = 300$ K, because normal diffusion was not predicted at these conditions. We observed two curved lines for the MSD as a function of time at these conditions:

$$\langle r^2(t) \rangle = At^\alpha \quad (5)$$

where $\alpha = 0.4$. Anomalous diffusion is mainly due to the hindrance inherent to the high loading (around 40 water molecules in the two unit cells).

Conclusions

The behavior of water confined in silicalite and DAY pores was evaluated using molecular dynamics calculations, and was noted to be different in the two pore systems. The differences can be explained mainly by considering the number of hydrogen bonds between water molecules and the influence of the pore dimensions on the diffusion coefficients.

The Compass force field is promising as it can reproduce experimental observations by monitoring the diffusive movement of water molecules in the microporous systems at various temperatures and loadings. Diffusion was shown to be aniso-

tropic in silicalite, but isotropic in DAY, as expected because of their different pore networks. Radial distribution functions were used to predict the distances between neighboring water molecules throughout the unit cells. And, the average number of hydrogen bonds per water molecule in silicalite and in DAY were computed at various temperatures by integrating the peak in the gOH function at ca. 1.8 Å. These results revealed that silicalite is much more disruptive to the formation of hydrogen bonds than DAY, since the number of hydrogen bonds decreases more quickly with increasing temperature in silicalite, even at relatively low temperatures.

At room temperature, water is liquidlike in DAY, but vaporlike in silicalite. These results are in agreement with previous experimental observations.^{2–4}

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