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Ab initio potential energy surface and molecular dynamics simulations for the determination of the diffusion coefficient of water in silicalite-1

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Abstract

The silicalite-1/water potential function has been developed using quantum chemical calculations at the Hartree–Fock level using the 6-31G* basis sets. The silicalite-1 crystal structure is represented by three fragments, in which the chemical compositions are O₁₀Si₁₀H₂₀, O₃₀Si₂₂H₄₄ and O₃₅Si₂₉H₅₈. Ab initio calculations have been performed for 1032 fragment–water configurations where water coordinates are generated inside the fragments. The intermolecular silicalite-1/water potentials developed from those data points have been used in the molecular dynamics simulations. The obtained diffusion coefficients at 298 K of $3.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and at 393 K of $6.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ are in agreement with those of the PFG-NMR measurements. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The interaction of water with zeolites is a subject of great scientific and technological interest, as water plays strong and essential roles for both absorption and catalytic properties of zeolites [1–3]. As coadsorbents, the presence of water has a large impact on the arrangement of the cations in the zeolite. Among non-cationic zeolites, interest is focused on silicalite-1, which due to its selectivity has been widely used in the separation of mixtures

between light hydrocarbons and water or dipole solvents [4–7]. Several attempts have been made to study the absorption and diffusion of hydrocarbons in silicalite-1 by means of both theoretical, [8–10] and experimental [11–14] investigations. However, very little information is available on the water/silicalite-1 interaction because one believes that water is not able to enter and diffuse in a hydrophobic zeolite such as silicalite-1.

Recently, we have investigated this issue intensively using quantum chemical calculations and found that water can enter the silicalite-1 channel [15]. An activation energy of approximately 1.9 kcal mol⁻¹ is required to diffuse through the linked domain to or from the intersection channel. In

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addition, preliminary results by Kärger et al. [16] using PFG-NMR measurements indicate that diffusion of water in silicalite-1 takes place even at room temperature.

As it is known that simulation results depend strongly on the quality of the potential function used, one of the best choices is to develop such a function by parameterizing directly from the data yielded from quantum mechanical calculations. However, in practice it is not possible, especially for large molecular systems, to generate such data even with a small basis set, because of the unreasonable computation time that would be required. Several attempts have been made with substantial success by Catlow et al. [17,18] and Sauer et al. [19–21]. The potential parameters were derived from the results of *ab initio* calculations. The molecular models, which represent typical structural elements of zeolites, consist of SiO_4 and protonated AlO_4 tetrahedra connected to chain rings and cages.

In this study, an alternative choice in deriving potential function parameters is proposed. Numerous silicalite-1/water energy points have been generated using quantum chemical calculations at the Hartree–Fock (HF) level. Molecular dynamics simulations have been performed using the newly developed *ab initio* potential and diffusion coefficients for water molecules in the silicalite-1 have been investigated.

2. Calculation details

2.1. Development of the intermolecular pair potential

To develop intermolecular potential functions representing the interaction between two molecules in all configurations, numerous coordinations of the second molecule around the first one have to be generated. The interaction energies of all configurations have to be calculated and the obtained data points must then be fitted to an analytical form.

Due to the size of the silicalite-1 lattice, in which a crystallographic cell [22] consists of 96 Si and 192 O atoms (Figs. 1a and e), it is not possible to take

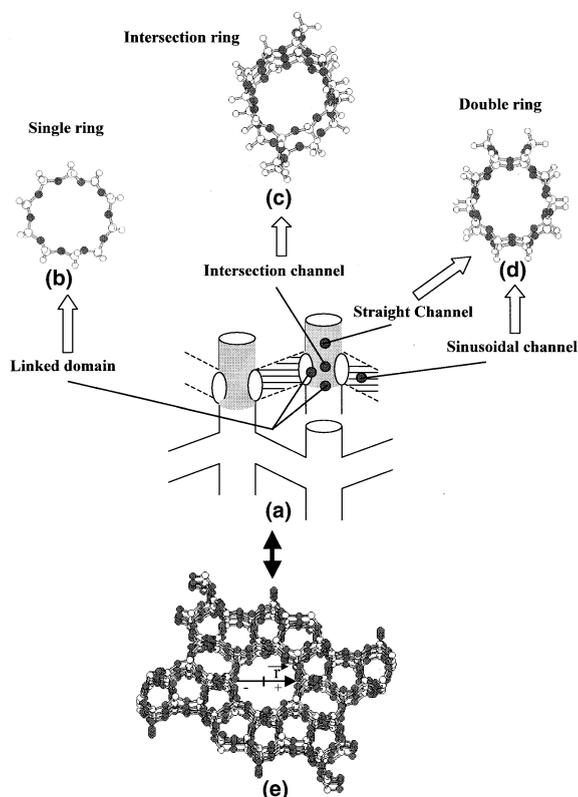


Fig. 1. Schematic representations of the (a) silicalite-1 crystal structure, (b) linked domain, (c) straight and sinusoidal channels, (d) intersection channel and (e) chemical structure of the silicalite-1 lattice.

into account the whole lattice in the quantum chemical calculations. Therefore, the silicalite-1 crystal structure was represented by three fragments (Figs. 1b–d), taken from different parts of the lattice, which contain different chemical compositions and structures. They were, for simplicity, named single, intersection and double rings. Their chemical compositions, after filling up the remaining valence orbitals of the silicon atoms with hydrogen atoms, are $\text{O}_{10}\text{Si}_{10}\text{H}_{20}$, $\text{O}_{30}\text{Si}_{22}\text{H}_{44}$ and $\text{O}_{35}\text{Si}_{29}\text{H}_{58}$, respectively. More details of the classification have been given elsewhere [15]. Numerous configurations of the water molecule have been generated inside the three fragments considered. *Ab initio* [23] calculations at the HF level with the extended 6-31G* basis sets have been performed for all water/silicalite-1 configurations.

Experimental geometries of water [24] and silicalite-1 [22] have been used and kept constant throughout. All calculations are performed using the G98 program [25].

More than 1000 ab initio data points were fitted to an analytical function of the form

$$\Delta E(w, s) = \sum_i^3 \sum_j^{288} \left\{ \frac{A_{ij}^{ab}}{r_{ij}^6} + \frac{B_{ij}^{ab}}{r_{ij}^{12}} + \frac{C_{ij}^{ab}}{r_{ij}^3} + \frac{q_i q_j}{r_{ij}} \right\}, \quad (1)$$

where 3 and 288 denote the numbers of atoms in a water molecule (w) and the silicalite-1 (s) unit cell, respectively. The constants A_{ij} , B_{ij} and C_{ij} are fitting constants and r_{ij} is the distance between atom i of water and atom j of silicalite-1. Also, q_i and q_j are the atomic net charges of atoms i and j in atomic units, as obtained from the population analysis of the isolated molecules in the quantum chemical calculations. Superscripts a and b on the fitting parameters have been used to classify atoms of equal atomic number but different environmental conditions, for example, oxygen and silicon atoms of silicalite-1 in the different channels. The third polynomial term (C_{ij}/r_{ij}^3) was added in order to obtain better numerical fitting. The silicalite-1/water fitting parameters were summarized in Table 1.

Concerning an assignment of a negative or positive value to the fitting parameters, it is generally not possible in all cases to control A/r^6 to be negative and B/r^{12} to be positive, in order to rep-

resent attractive and repulsive interactions of the pair, respectively. A fit in which the A/r^6 terms were separately forced to the van der Waals interaction and the B/r^{12} terms to the real repulsion have led to worse agreement with the quantum mechanical results. In these cases, physical meaning of the atomic-based pair potentials, 864 pairs running over $i=1-3$ and $j=1-288$ for Eq. (1), is not achieved. However, physical meaning, as well as quality, of the molecular-based water/silicalite-1 function is its ability in representing ab initio data. An advantage of this approach is that it is a one-to-one correspondence between the predicted (by the potential function) and the observed (by the ab initio calculation) interaction energies. Analogously, as well as for better numerical fitting, the third polynomial term (C_{ij}/r_{ij}^3) was added and not considered separately. Some examples are those in Refs. [26–28].

2.2. Molecular dynamics simulations

The silicalite-1 crystal structure used in this study is characterized by two types of channels whose symmetry group is $Pnma$. The crystallographic cell [22] contains 288 atoms ($\text{Si}_{96}\text{O}_{192}$), with lattice parameters $a = 20.07 \text{ \AA}$, $b = 19.92 \text{ \AA}$ and $c = 13.42 \text{ \AA}$. Simulations have been carried out at 298 and 393 K with the time step of 0.5 fs for the system consisting of two silicalite-1 unit cells. The box contains two water molecules per intersection of the silicalite-1 that means totally 16 in the MD

Table 1

Final optimization parameters for atom i of water interacting with atom j in each channel of the silicalite-1 lattice

i	j	q_i	q_j	A ($\text{\AA}^6 \text{ kcal mol}^{-1}$)	B ($\text{\AA}^{12} \text{ kcal mol}^{-1}$)	C ($\text{\AA}^3 \text{ kcal mol}^{-1}$)
O	Si _{sd}	-0.87	1.57	-9043.97	1161167.97	1418.92
O	Si _{st}	-0.87	1.67	-4159.83	989963.68	617.02
O	O _{sd}	-0.87	-0.78	1371.19	-21045.58	-351.61
O	O _{st}	-0.87	-0.84	-110.79	51208.44	-110.82
H	Si _{sd}	0.43	1.57	3724.97	-4314.90	-792.37
H	Si _{st}	0.43	1.67	2077.13	-8925.29	-415.82
H	O _{sd}	0.43	-0.78	-406.18	689.37	222.32
H	O _{st}	0.43	-0.87	34.87	32.84	102.59

Subscripts sd and st denote sinusoidal (zig-zag) and straight channels, respectively. Energies in kcal mol^{-1} , distances (r_{ij}) in \AA and atomic net charges (q) in atomic units.

box. Periodic boundary conditions have been applied. The potential proposed by Bopp et al. [29] was employed to describe water–water interactions while the newly developed potential shown in Eq. (1), with the optimal parameters summarized in Table 1, was used to represent the silicalite-1/water interactions. According to [30,31] the use of Ewald summations can be avoided in systems with total charge zero if shifted force potentials are applied instead. The evaluation part each run corresponds to trajectory length of 10 ns after 0.5 ps thermalization.

3. Results and discussion

3.1. Quality of the silicalite-1/water potential

With the analytical potential shown in Eq. (1), the lattice–water interactions in the straight channel have been calculated and plotted in Fig. 2. Here, the oxygen atom of the water molecule moves from one surface to the opposite surface along the vector \mathbf{r} (see Fig. 1e), its dipole moment points parallel to vector \mathbf{r} and its molecular plane is parallel to the window of the lattice. The ab

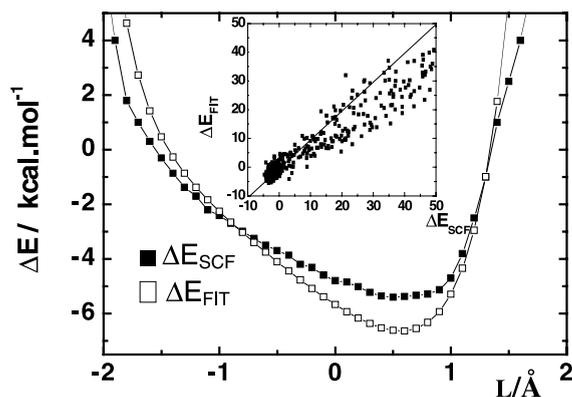


Fig. 2. Silicalite-1/water interaction energies (ΔE) obtained from the ab initio calculations (ΔE_{SCF}) with the extended 6-31G* basis sets and from the potential function (ΔE_{FIT}) according to Eq. (1), where the oxygen atom of the water molecule lies along the vector \mathbf{r} (see Fig. 1e), its dipole moment is parallel to \mathbf{r} and its molecular plane is parallel to the window of the lattice. All ab initio and fitted data points are also compared in the inset.

initio interaction energies at the same lattice–water configurations have been calculated and given also for comparison. Good agreement between the two curves in Fig. 2 clearly illustrates the reliability and quality of the fit. This conclusion was, again, confirmed by the plot shown in the inset of this figure, where all 1050 ab initio and fitted energies have been compared.

Some comments could be made concerning the quality of the ab initio interaction energies given in this study. Discrepancies and reliabilities of the data points due to the size of the fragments, the calculated methods and the basis sets used as well as an error due to the unbalance of the basis set, basis set superposition error, have been intensively examined and discussed in a previous paper [15].

3.2. Characteristics of the silicalite-1/water potential

To visualize characteristics of the silicalite-1/water potential function, the interaction energies for different orientations of the water molecule in the straight channel have been computed according to Eq. (1). The changes of the energies as a function of the distances along \mathbf{r} were plotted in Fig. 3.

Curves 1 and 4 in Fig. 3 show the minima at $L < 0$, and the interaction energies for $L > 0$ increase more slowly than those for $L < 0$. This occurrence can be clearly understood as water

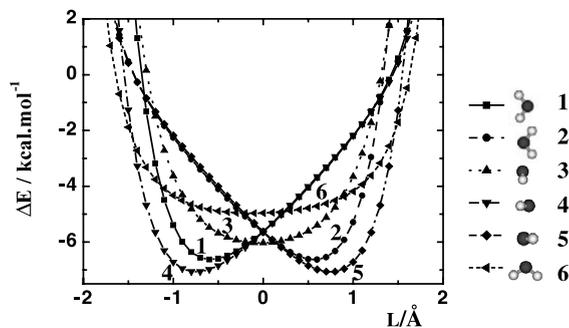


Fig. 3. Silicalite-1/water interaction energies (ΔE , kcal mol⁻¹) obtained from the potential function according to Eq. (1) for different orientations of a water molecule, where its oxygen atom lies along \mathbf{r} (see Fig. 1e) in the straight channel.

molecules in these configurations (at the right of this figure) approach the surface at $L > 0$ by pointing hydrogen atoms toward the oxygen atoms of the lattice, i.e., attractive Coulomb interactions between the hydrogen atoms of water and the oxygen atoms of the surface compensate the water–surface repulsion. This leads to a slow increase of the interaction energy and hence an asymmetry of the lattice–water potential. The difference between the shapes of the two curves indicates how sensitive the obtained function is. That means it is able to classify the two orientations of the water molecule which differ only by rotating the molecule by 90° around its dipole vector. The situation is very similar for curves 2 and 5, in which the minima take place at $L > 0$ and the interaction energies for $L < 0$ increase faster than those for $L > 0$. For curves 3 and 6, the shapes are much more symmetric than the other curves. The reason is that the water molecule in these configurations approaches the lattice, both for $L > 0$ and $L < 0$, by pointing its dipole vector parallel to the surface. Curve 6 is broader than curve 3 because in curve 3 water moves toward the surface in configurations for which distances from the surface to the two hydrogen atoms are identical. For curve 6, at the same position of water as in curve 3, one hydrogen atom is closer to the surface than the other (see legend of Fig. 3). This fact confirms the ab initio interaction energies reported in [15].

As can be seen from Eq. (1) and Table 1, different fitting data sets have been used to represent the interaction between the lattice and a water molecule lying in the sinusoidal (zig-zag) or in the straight channel. To visualize this effect, the interaction energies have been calculated separately for a water molecule in the two channels. In this example, the water molecule was in the same configurations as those of Fig. 2. The results are displayed in Fig. 4. The sensitivity of the silicalite-1/water potential to different environments has been clearly monitored, in addition to that due to water orientation as shown in Fig. 3. The difference between the interactions in the straight and the zig-zag channels is consistent with the energy data analyzed intensively in our previous work [12].

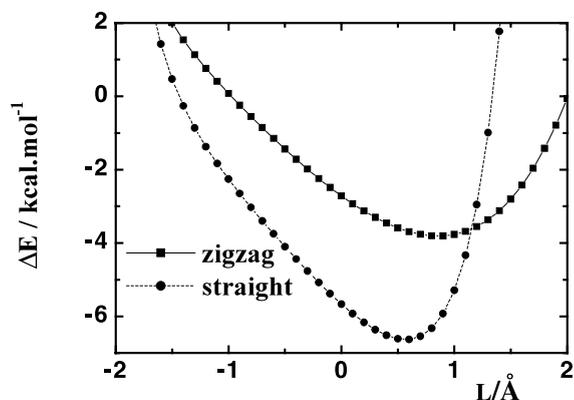


Fig. 4. Silicalite-1/water interaction energies obtained from the potential function according to Eq. (1), where water molecule lies in the same configurations as those of Fig. 2 in the sinusoidal and the straight channels.

3.3. Diffusion coefficients

To justify the quality of the model in representing a real system, MD simulations have been performed at 298 and 393 K for a loading of two water molecules per intersection of the silicalite-1. The diffusion coefficients have been calculated according to the method described in [32] from different moments of the particle displacements. The results obtained at 298 and 393 K are 3.3×10^{-9} and $6.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, respectively. These values are in satisfactory agreement with those from PFG-NMR measurements [16] at the same loading and temperature.

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