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Monte Carlo Simulations of Water Adsorption Isotherms in Silicalite and Dealuminated Zeolite Y

Matthieu Fleys[†] and Robert W. Thompson*

*Department of Chemical Engineering, Worcester Polytechnic Institute,
100 Institute Road 01609, Worcester, Massachusetts 01609-2280*

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Abstract: The affinity that adsorbents have for water can influence their effectiveness in organics removal from drinking water due to competitive adsorption. The extent of the affinity of microporous zeolites for water is determined, in part, by AlO_4^- tetrahedral sites (T-sites) in the crystal lattice and lattice defects in the form of silanol nests. In this study, water adsorption isotherms in silicalite and in dealuminated zeolite Y (DAY) were simulated using the Compass force-field. The results show that the simulations can predict the shape of water adsorption isotherms and predict adsorption levels comparable to literature results. Moreover, simulations revealed that the results are influenced significantly by the presence of AlO_4^- T-sites. The results confirm the capacity of the Compass force-field to predict water sorption properties in silicalite and in DAY.

Introduction

Numerous investigators have studied water adsorption in confined media, such as activated carbons and molecular sieve zeolites. Among these works, some are related to the competitive adsorption of water with other organic components,[1−4] while others deal with the single-component adsorption of water in zeolites.[4−13] Moreover, water can be used as a probe of zeolite properties such as the evaluation of the dealumination rate,[14−16] acid strength,[17] product quality, and micropore volume.[18] For these reasons, water is a particular component whose specific properties in confined media need to be elucidated.

Numerous simulations of the behavior of water in zeolites pore systems have been carried out over the past decade. In silicalite, the diffusion and the behavior of water was studied using MD simulations by Demontis et al.[19] Similarly, Bussai et al.[20−22] used both MD simulations and quantum calculations with ab initio potentials. Water behavior in zeolite NaA also was studied by Faux et al.[23,24] who were interested in diffusion of water and preferred adsorption sites in the α-

and β-cages. A study of water in SiO_2 pores with different diameters was reported by Hartnig et al.[25] in order to elucidate the hydration process and the nature of the hydrogen-bond network.

Recently, we investigated the behavior of water in silicalite and dealuminated zeolite Y (DAY) by Molecular Dynamics (MD) simulations.[26] The self-diffusion coefficients and the number of hydrogen bonds per confined water molecule were computed at temperatures in the range $100−600$ K, and at different loadings, using the Compass force-field. This force-field proved to be appropriate to explain experimental findings such as the observation that water is vaporlike in silicalite but liquidlike in DAY at room temperature and atmospheric pressure.[12,27] As a result of the previous successes, the Compass force-field was used in the present study where adsorption isotherms of water were computed at different temperatures and compared with experimental results.

Computational Details

The simulations were done with a Silicon Graphics workstation using the Compass force-field and the Sorption module developed by Accelrys in the Cerius2 environment. Electrostatic interactions modeled by a Coulomb potential and the van der Waals, London, and hydrogen-bonding interac-

* Corresponding author phone: (508)831-5525; e-mail: rwt@
   wpi.edu.
† Current address: Département de Chimie-Physique des Réactions, UMR 7630 CNRS, INPL-ENSIC, 1, rue Grandville -
   BP 451-54001 NANCY Cedex - France.

tions modeled by a 6−9 Lennard-Jones potential were taken into account.

The starting crystal structures were perfect, i.e., no defects such as bond breakages or silanol groups were considered. Initially, both zeolite frameworks were all-silica which is a hypothetical limit especially for DAY, as that assumes that the dealumination procedure was 100% effective. The consequences of this hypothesis will be discussed later. Simulations were carried out at different temperatures in two different pressure ranges; a low range (0−2.7 kPa) and a high range (0−500 kPa) for both crystal structures. After considering the all-silica end-member crystal types, additional simulations were done with Al-ZSM-5 where Si/Al = 47 and Na/Al = 1 so that more realistic zeolite structures could be studied.

After creating the zeolite structures and the adsorbent molecules, the next step consisted of calculating a Connolly surface in order to estimate the accessible micropore volume. The Connolly surface is overlaid on the zeolite structure, so that it is possible to visualize the accessible volume in the different channels. Because of the small size of water molecules, the accessible volumes were in the zigzag and straight pores in silicalite and in the sodalite cages and supercages in DAY. No blocking or dummy atoms were used in the simulations. The computed micropore volumes were in agreement with experimental and theoretical values and were found to be 0.18 cm^3/g for silicalite and 0.36 cm^3/g for DAY. It is important to note that these volumes do not correspond to the effective occupied volumes by water in the crystals but are an indication of the possible accessible volumes estimated on the basis of energy and steric hindrance considerations.

The value for the bad contact rejection factor used was 0.5, which was the default value. This means that if any water atoms and framework atoms were closer to each other than half of their van der Waals radii, the configuration was rejected and no energetic calculations were done. As the calculations were time-consuming, the purpose of this criterion was to save time.

The simulations were done in the grand-canonical ensemble where the number of adsorbed molecules was not fixed, but their chemical potentials were. Ten million steps were required before both energy and the loaded amount converged to their final values. Each simulation point obtained at a given temperature and pressure followed these steps.

The same parameters as the ones used in our last simulation work[26] were used. The interaction cutoff distance, which is the distance beyond which interactions between atoms are not taken into account, was about half the size of the smallest simulation cell, that is 6 Å for silicalite and 12 Å for DAY. Electrostatic interactions were considered by using the Ewald method which accelerated the long-range Coulomb calculation.

Similations with Al-Free Silicalite and Zeolite Y

Low Pressures. The adsorption isotherms for water in silicalite were simulated at five temperatures from 300 to

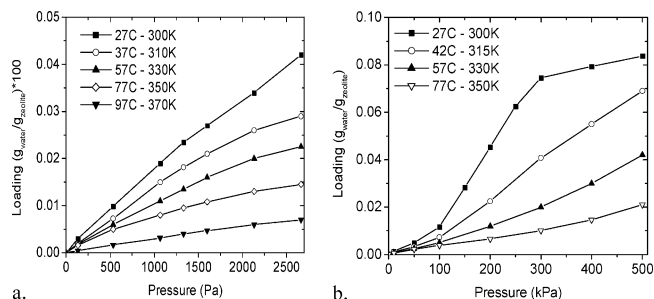**Figure 1.** a. Water adsorption isotherms in defect-free silicalite from 300 to 370 K at low pressures and b. from 300 to 350 K at high pressures.
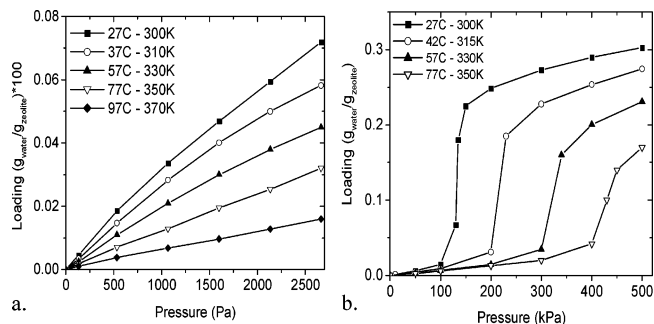

Figure 2. a. Water adsorption isotherms in defect-free DAY from 300 to 370 K at low pressures and b. from 300 to 350 K at high pressures.

370 K, shown in Figure 1a. The isotherms look very similar in shape to previous reported experimental works; however, the predicted amount adsorbed was substantially less than observed experimentally, discussed further below.[12,16] It is interesting to note that at 300 K, the isotherm shape is different from the others, as an increase of the adsorbed amount of water appears at about 2300 Pa (17 Torr). This phenomenon was observed by Olson et al.,[16] Giaya et al.,[12] and Sano et al.,[14] and its origin is not clearly understood. Olson et al.[16] suggested that a framework defect, such as silanol groups, could explain the phenomenon. But, since the phenomenon was observed in our simulations for the crystallographically perfect silicalite structure, the explanation may be different.

The major difference between hypothetical and real silicalite is the adsorption capacity. Indeed, the adsorbed amount of water is 50−100 times lower in the simulated isotherms compared to the experimental values.[12,14,16] Hence, this might suggest that the Compass force-field fails to estimate the adsorption capacity of water in silicate, despite its ability to predict isotherms shapes. However, another hypothesis needs to be considered before concluding this, i.e., that real silicalite is not perfect; it is a high-silica zeolite but not a pure-silica zeolite. Thus, it may contain aluminum T-atoms and associated cations which could modify the adsorption capacity of water.[14,16] This hypothesis will be developed and discussed in the last section.

Similarly, low-pressure water adsorption isotherms in DAY were simulated from 300 to 370 K and are shown in Figure 2a. The adsorbed amount increases linearly with pressure, and the adsorbed amount in this pressure range is twice as much as that predicted for silicalite. This result can

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be related to the pore volume which is also twice larger in DAY than in silicalite. As the dealumination procedure does not yield all-silica zeolite Y, real zeolite DAY also contains defects such as aluminum T-atoms. Hence, the simulated adsorbed amounts of water are expected to be underpredicted compared to experimentally measured values.

High Pressures. The simulations performed in the lower pressure range clearly show that silicalite and DAY are very hydrophobic. Only a small fraction of the accessible micropore volume is occupied by water molecules.[6] Thus, simulations at high pressures, from 0 to 500 kPa (5 bar), were carried out in order to characterize the increase of the adsorbed amount of water. The results are given in Figures 1b and 2b for silicalite and DAY, respectively.

In silicalite, the amount of adsorbed water increases slowly with pressure increases. The isotherms can be divided into three parts; first, the loading increases very slowly until a transition pressure is reached. Then, the adsorbed amount increases faster with pressure before reaching a plateau. The lower the temperature, the lower the transition pressure, and the faster the plateau is reached. Only the simulation at 300 K reached the plateau before 500 kPa. From these results, it can be said that the adsorbed amount of water increases so slowly with pressure that the maximum adsorbed amount will be reached at very high pressures. This result is in agreement with previous experimental work[28] where several "strongly hydrophobic zeolite-water" systems were submitted to increasing hydrostatic pressure from 0 to 120 MPa. It was shown that water molecules penetrated the pores when the capillary pressure was reached, that is, at about 90 MPa for the most hydrophobic zeolite, silicalite.

In DAY, the adsorption isotherms are different from those obtained in silicalite. First, the loading increases slightly with pressure but then, after reaching a critical pressure, the amount adsorbed increases sharply before reaching a plateau. Moreover, for simulations performed at higher temperatures, the step is smaller and less pronounced. The origin of this step can be explained by considering the micropore structure of DAY and the micropore filling mechanism. Zeolite DAY is composed of supercages (diameter 1.2 nm) interconnected by β-cages (diameter 0.8 nm). It was found that 4 water molecules can be accommodated per β-cage compared to 26−28 water molecules in the supercage.[10] Water adsorption proceeds by filling the β-cages first and subsequently by filling the supercages.[18] Hence, the step in adsorbed amount could be due to filling of the supercages. Moreover, it was reported that about 250 water molecules per unit cell can be accommodated at complete pore filling at 300 K.[10] In our simulations, at 500 kPa and 300 K, the loading is equivalent to 194 water molecules per unit cell. Hence, at 300 K and 500 kPa, a large proportion of the accessible micropore volume is occupied by water molecules. This means that no step is expected to occur after 500 kPa and that the step which is observed is significant and supports the pore filling mechanism proposed by Boddenberg et al.[18]

The filling process of the DAY cages is not straightforward. While the supercages are more accessible than the β-cages, the potential energy in the center of the supercages is higher than in the vicinity of the walls.[29] Hence, at low
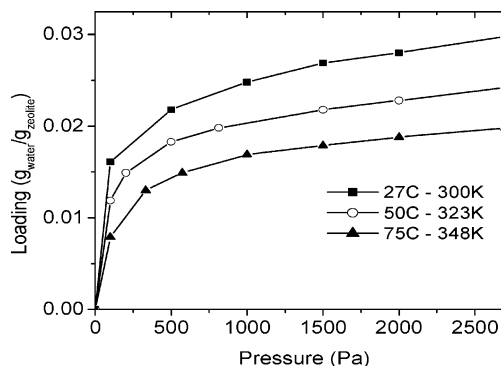

Figure 3. Water adsorption isotherms in Al-ZSM-5, with Si/Al = 47 and Na/Al = 1 from 300 to 348 K at low pressures.

loadings, water molecules locate close to the walls indicating that the supercages are not the preferential adsorption sites. This is shown by Faux's results[23,24] who also noted that water molecules located at preferred sites in the α-cages of zeolite NaA, while water located within the center of the α-cages only at higher loadings. It is important to note that the discussion presented by Faux about the self-diffusion coefficients took account only the mobile water molecules contained in the NaA α-cage volumes. Moreover, Faux considered high loadings (from 56 to 224 water molecules in the simulation cell), and at these loadings β-cages were already occupied by water molecules and represented about 15% of the total amount of adsorbed water. In this work, we considered rather low loadings, whereas Faux's paper dealt with diffusion at higher loadings.

Simulations with Al-ZSM-5 Where Si/Al = 47 and Na/Al = 1

After considering all-silica zeolites, simulations using Al-ZSM-5 were conducted in order to assess the influence of aluminum T-atoms with associated Na^+ cations in the crystal structure on the loading.[30] Simulations were carried out at different AlO_4^- loadings, between 0.5 and 2.5 Al atoms per unit cell. All the adsorption isotherms exhibited a type I shape in the IUPAC classification. Only the simulations with 2 aluminum atoms per unit cell (Si/Al = 47) are given in Figure 3 at three temperatures, 300, 323, and 348 K, in the low-pressure range from 0 to 2700 Pa, since the results were all similar in nature.

In these simulations, all the calculation parameters were conserved. It is noteworthy that the amounts of adsorbed water are in agreement with experimental values.[12,14,16] Nevertheless, the isotherm shapes are somewhat different from those shown in Figure 1a. In Figure 3, the loading increases very quickly at very low pressures before increasing slowly. This result is inherent to the presence of aluminum T-atoms with the associated Na^+ cations. The strong low-pressure sorption is attributed to the hydration of the Na^+ cation.[31] That is why, in Figures 1a and 2a corresponding to all-silica zeolites, the adsorption increases very slightly with pressure in the very low-pressure range, i.e., since no AlO_4^- T-sites and cations were present.

It is important to note that the purpose of the simulation reported in Figure 3 is to illustrate that the presence of defects
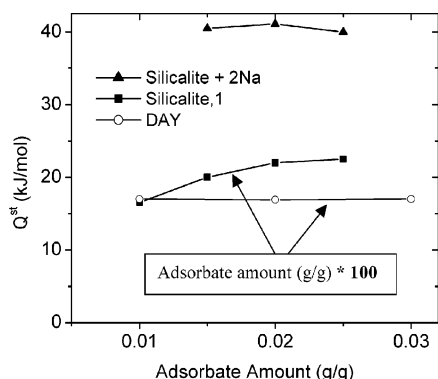
Figure 4. Isosteric heat of adsorption of water in defect-free silicalite and DAY (lower curves) and in Al-ZSM-5, with Si/Al = 47 and Na/Al = 1 (upper curve).

influences the predicted adsorption isotherms. But, it does not provide the exact nature of the defect. Different defects have different influences on the adsorption isotherms. For example, the particular cation is important. It was reported by Olson et al.[16] that the smaller proton, H^+, interacts more strongly than the large Cs^+ cation. Moïse et al.[8] reported that zeolite Y adsorbs more water with Mg^{2+} than with Na^+ as the compensating cation. The presence of internal or external silanol groups also has an influence on water adsorption capacities.[14] Silanol groups are adsorption sites for water molecules whose strength is less than a cation such as H^+.[14] All these different defects modify the adsorption isotherms in terms of shape and loading.

Isosteric Heat of Adsorption

The isosteric heats of adsorption, Q^{st}, were calculated from the isotherm data in Figures 1a, 2a, and 3 using

$$Q^{st} = -R\left[\frac{\partial(\ln P)}{\partial(1/T)}\right]_{loading} \tag{1}$$

The values are reported in Figure 4 for Al-free silicalite, Al-free DAY, and Al-ZSM-5 with Si/Al = 47. For DAY, the isosteric heat is constant with loading and equal to 17 kJ/mol. This value is low compared to the experimentally measured heat of vaporization for water at 25 °C, 43.99 kJ/mol,[32] and the value computed in this study for bulk liquid water, 46.1 kJ/mol. Experiments conducted with NaY, BaY, or CsY zeolites showed that the isosteric heat of adsorption was around 80 kJ/mol, and that Q^{st} decreased with loading.[8,18] Keeping in mind that our simulations were done with hypothetical all-silica zeolites, the comparison is not surprising. Indeed, cations have a significant influence on the isosteric heat. At low loadings, cations act as pumps, water molecules adsorb at cation sites, and the isosteric heat is high. Then, at intermediate loadings, a monolayer, and then multilayers, of water molecules cover the walls of zeolite DAY, leading to a decrease of the isosteric heat as the stronger sites were already occupied. In our simulation where no cations were present, there was no pumping effect to enhance adsorption, and the adsorbed amount was extremely low, as was the isosteric heat.

For silicalite-1, the isosteric heat increased very gently with loading, but the value was still low, equal to about 20 kJ/

mol, which is close to the value obtained for DAY. The reason the isosteric heat of adsorption was slightly higher in silicalite-1 than in all-silica zeolite DAY was probably due to the higher adsorbate−wall interaction energies in silicalite-1 compared to DAY. In silicalite, the pore diameters are smaller, and so the confinement effect is more important compared to zeolite DAY. The fact that the isosteric heat obtained for silicalite-1 and all-silica DAY are close reveals that the adsorption process is similar in both all-silica crystals where hydrophobicity is very high and loadings are very low.

The explanation for the low heat of adsorption is related to the low adsorbed amount of water. The behavior of water in silicalite and DAY pore systems, including radial distribution functions, was detailed in our previous paper.[26] The main results are the following: at ambient temperature, the number of hydrogen bonds per water molecule is ca. 1.6 in silicalite and about 3.3 in DAY. In the present paper, the simulated adsorbed amounts of water in Al-free silicalite and DAY are about 100 times lower than the measured values. Hence, in both cases the number of hydrogen bonds is extremely low and clusters do not form in the zeolite pores. Thus adsorbate−adsorbate interactions are not significant, which leads to a low value of the isosteric heat for both zeolites. Comparing the isosteric heats between silicalite-1 and Al-free DAY shows that the isosteric heat in silicalite-1 is slightly higher than in DAY. This is due to the fact that the adsorbate−wall interactions are higher in silicalite compared to DAY, because water molecules are more confined in the smaller pore silicalite compared to DAY.

For Al-ZSM-5 with Si/Al = 47 and Na/Al = 1, the isosteric heat is much higher than for silicalite-1 and equal to about 41 kJ/mol. This value is in agreement with experimental data,[12,16] which confirms the ability of the simulations to predict water sorption properties.

In silicalite and DAY the adsorbed amount is quite low. At these low loadings, water does not cluster, and water molecules are dispersed in the zeolite pore system. Only the water−wall interactions are important, since the water−water interactions are negligible at these low loadings. These interactions are slightly stronger in silicalite due to the stronger confinement, i.e., smaller pore size, compared to DAY. That is why the isosteric heat increases slightly with loading in Al-free silicalite. Water−water interactions become more important at higher loadings, as seen in the case if Al-ZSM-5 with Si/Al = 47.

Conclusions

Adsorption isotherms were simulated in all-silica ZSM-5 and DAY. The results show that the simulations predict the isotherm shapes at low and high pressures and that the results are in agreement with experimental measurements. However, it was observed that at low pressures the amount of adsorbed water was underpredicted in the all-silica zeolites. The reason for this is not related to algorithm issues or parametrization flaws but was due to the intrinsic properties of real zeolites which can contain impurities and defects. These observations can be used to compare the adsorption isotherms for ideal zeolites containing no defects, zeolites with T-atoms or defects included, and experimental isotherms to give at least

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qualitative insights on the possible structures of the real zeolites. Moreover, if the influence of the different defects on the adsorption isotherms can be identified, it should be possible to determine the defect types qualitatively. In this case, the experimental adsorption isotherm would be one characteristic feature of the zeolite, as noted previously.[14]

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