On the collective properties of water molecules in one-dimensional zeolitic channels

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The collective properties of water molecules hosted in the one-dimensional non-crossing channels of three zeolites are analyzed and discussed. In particular, we present new *ab initio* molecular dynamics simulations on the behaviour of water in the synthetic zeolite Na-ABW. New IR and thermogravimetric data are also presented and the comparison of these data with those obtained in the study of strictly related zeolites (bikitaite and Li-ABW) shows that moderate differences in the chemical composition and/or in the topology of the zeolite framework lead to quite different dynamical properties of the guest molecules. According to the balance between host-guest and guest-guest interactions, the behaviour of water in these channels ranges from that of a one-dimensional solid wire of hydrogen bonded H₂Os to that of a chain of independent water molecules hydrogen bonded to the framework oxygens.

Introduction

The confinement of molecules in ordered matrices is a technologically relevant approach for the tailoring of chemical and physical properties of new kinds of materials. Zeolites,¹ with their nanosized arrays of cages and channels are ideal matrices where such confinement may be successfully achieved. However, much effort is necessary in order to understand, at a microscopic level, the main characteristics of the confined-species-matrix interactions responsible for the stability and the behaviour of such nano-composite materials. Due to the very nature of the systems, *i.e.* molecules, ions and/or oligomers encapsulated in cages and channels, whose sections are comparable to (at least) one size of the guest compounds, a detailed knowledge of the energetics, statistical mechanics and in general of the host-guest interactions may be of paramount interest for synthesis and materials science research. In this regard, an atomistic level graining of the host matrices is also needed. Such a target may be hit by using sophisticated computer simulation techniques,^{2,3} combined with laboratory experiments, in order, on the one hand to increase, both in time and space, the resolution of standard experiments and on the other hand, to validate the simulation results by a thorough comparison with experiments. When the guest molecules, as in the present study, are water molecules, then the subject may be of greater interest. Indeed, H₂O in confined geometries may be pertinent also to the realm of biological systems (see e.g. ref. 4–6), and therefore the scope of studying confined water could have interesting fallout in such fields. Moreover, such studies may also be relevant for the phase diagram of water, indeed, supercooled water behaviour has been found in confined systems,^{7,8} such as water trapped in

amorphous porous materials and phyllosilicates. As stressed above, water molecules may interact both with their water neighbours and with the zeolitic framework, always via hydrogen bonds of comparable energy. Therefore competition should arise between host-guest and guest-guest interactions.

We present new results of combined experimental and computational studies on the synthetic zeolite Na-ABW.^{9,10} Pre-vious studies on bikitaite¹¹⁻¹³ and Li-ABW¹⁴ have shown to what extent the differences in host-guest interactions affect the properties of sorbed molecules such as water. Both zeolites at room temperature are characterized by the presence of onedimensional chains of water molecules hydrogen bonded to each other. In the case of bikitaite the water molecules behave like a solid one-dimensional ice structure, while in Li-ABW the water chain behaves more like a one-dimensional liquid, characterized by rotation of the water molecules. Such a rotational motion was not observed in bikitaite, where a strong dipolar interaction between the framework and the chain keeps the water molecules in their crystallographic position, the only allowed motion being the vibrational and the librational modes. In Li-ABW a weaker dipolar interaction with the framework and competition between the water-water and water-framework interactions allow the water molecules to rotate.14

Here we examine more thoroughly the problem by presenting new results of first-principles molecular dynamics simulations of the static and dynamical properties of Na-ABW, characterized by close similarities in topology, dimensions and chemical composition of the framework with Li-ABW. Moreover, new IR spectra and thermogravimetric data on bikitaite, Li-ABW and Na-ABW are reported.

Structures

In this section we describe the Na-ABW framework topology and, for comparison, we also report the structures of bikitaite

DOI: 10.1039/B102231H Phys. Chem. Chem. Phys., 2001, 3, 4158-4163

and Li-ABW. Bikitaite (Li[AlSi₂O₆] · H₂O), Li-ABW $(\text{Li}[\text{AlSiO}_4] \cdot \text{H}_2\text{O})$ and Na-ABW $(\text{Na}[\text{AlSiO}_4] \cdot n\text{H}_2\text{O}, n < 1)$, are aluminium-rich zeolites with some common features. Their framework is formed by layers of TO_4 tetrahedra (T = Al, Si), arranged to form a hexagonal pattern. The layers are connected in such a way as to form non-crossing channels. running parallel to the lavers themselves. While Li-ABW and Na-ABW have the same topology, that of bikitaite is slightly different. The way each tetrahedron is linked to its neighbours in the hexagonal sheets and the way the sheets are linked together characterize the two different topologies. While in ABW frameworks the hexagonal layers are directly linked to each other, in bikitaite they are connected by chains of SiO₄ tetrahedra (pyroxene chains). However, for all three zeolites the channel's section is defined by eight tetrahedra (8-membered ring). Such channels contain both the extraframework cations (Li or Na) and the water molecules. The first two zeolites have been the subject of several diffractometric singlecrystal studies that have allowed a good refinement of the atomic positions.^{11,13,15,16} Moreover, computer simulation studies have been performed on bikitaite and Li-ABW at room temperature.^{12–14} The main characteristic of the two lithium zeolites is the presence in their non-crossing 8membered ring channels of one-dimensional arrays (one per channel) of water molecules, hydrogen bonded to each other. On the other hand, the structure of Na-ABW, obtained by exchange from Li-ABW, has not yet been refined. Only the Na-ABW cell parameters and stoichiometry have been published.¹⁰ However recent diffractional studies, though performed on a poorly crystallized powder, suggest a high degree of disorder of the extraframework Na cations and water molecules. Such high disorder in the channels and the water/ extraframework cation ratio (less than one H₂O molecule per cation) strongly indicate that the presence of chains of hydrogen bonded water molecules should be excluded.

Experiments and calculations

The water contents of the three zeolite samples were determined by thermogravimetric analysis on about 10 mg of sample using a Perkin Elmer TGA7 operating in air at 10 °C min⁻¹ from 20 to 1000 °C. The weight loss percentages so determined are: 8% in bikitaite, 14% in Li-ABW and 9.4% in Na-ABW. The water content of Na-ABW here determined (H₂O = 9.4 wt.%) corresponds to 0.83 water molecules per formula unit (pfu), in agreement with that reported by Norby *et al.*¹⁰ of 0.8 molecules pfu. The corresponding water content found for bikitaite and Li-ABW is 1.0 molecule pfu.

The micro-IR spectra were obtained by means of a Perkin Elmer Spectrum 2000 FTIR microscope. The data were recorded in transmission mode, working on pure Li-ABW and Na-ABW powder samples, and on a bikitaite single-crystal. The thin crystal slab necessary for the micro-IR analysis of bikitaite was obtained by applying an oriented pressure to a larger crystal.

The systems were simulated using the Car Parrinello molecular dynamics technique,¹⁷ that allows one to draw an accurate picture of the dynamical behaviour of a chemically complex system at finite temperatures. In the simulation of Na-ABW, the same technique and approximations adopted for bikitaite and Li-ABW were used.^{17,18} The wavefunctions were expanded in plane waves up to a cut-off of 60 Ry (only the Γ point in the BZ was considered); the time step adopted for the integration of the equations of motion was 0.121 fs and the fictitious mass for the electronic wavefunction coefficients was 500 a.u.. We used the gradient-corrected density functional¹⁹ approximations of Becke²⁰ and Perdew²¹ for the exchange and correlation energy respectively, while the ion– electron interactions were treated with norm conserving^{22,23} pseudopotentials²⁴ (d-nonlocality was adopted for Al, Si and O atoms, and local norm-conserving pseudopotentials for H and Na). Periodic boundary conditions were adopted for the studied systems.

The structures of the three zeolites along the 8-membered ring channels are reported in Fig. 1–3. For completeness, we report the cell parameters and stoichiometry used for the three zeolites. In all the simulations we have doubled the crystallographic unit cells along the direction of the channels (*b* for bikitaite and *c* for ABWs). No symmetry constraint was imposed on the atoms in the simulations.

In the bikitaite (space group P1) simulation,^{12,13} we adopted a triclinic unit cell¹¹ (a = 8.6146 Å; b = 9.914 Å; c = 7.6032 Å; $\alpha = 89.899^{\circ}$; $\beta = 114.394^{\circ}$; $\gamma = 89.934^{\circ}$), and the



Fig. 1 Representation of bikitaite along the 8-membered ring channels (*b* axis). Black spheres represent water oxygens, white spheres represent protons, gray spheres lithium. Dark gray tetrahedra represent SiO_4 units, light gray tetrahedra represent AlO_4 units.



Fig. 2 Representation of Li-ABW along the 8-membered ring channels (c axis). Black spheres represent water oxygens, white spheres represent protons, gray spheres lithium. Dark gray tetrahedra represent SiO_4 units, light gray tetrahedra represent AlO_4 units.



Fig. 3 Representation of Na-ABW along the 8-membered ring channels (c axis). Black spheres represent water oxygens, white spheres represent protons, gray spheres sodium. Dark gray tetrahedra represent SiO₄ units, light gray tetrahedra repre sent AlO₄ units. Dashed lines represent water-framework hydrogen bonds.

simulated chemical formula is $Li_4[Al_4Si_8O_{24}] \cdot 4H_2O$. The Li-ABW (space group $Pma2_1$) cell is orthorhombic (a = 10.313Å; b = 8.194 Å; c = 9.986 Å), and the chemical formula is $Li_8[Al_8Si_8O_{32}] \cdot 8H_2O$. The cell parameters of Na-ABW were taken from ref. 10; they are: a = 10.317 Å; b = 8.393 Å; c = 10.224 Å. As discussed above, less than one water molecule per Na is present in Na-ABW. Since the simulation of a system characterized by atomic proportions water/Na = 0.83would have required a much larger supercell, we have simulated a structure characterized by a slightly lower water/ extraframework cation ratio (water/Na = 0.75), with formula $Na_8[Al_8Si_8O_{32}] \cdot 6H_2O$. The water molecules were evenly located in the two independent channels of the simulation cell. The periodically repeated section of each channel therefore contains four Na and three water molecules, while in bikitaite¹³ and Li-ABW,¹⁴ where the water/extraframework cation ratio is one, there are four water molecules and four cations per channel. The starting coordinates for the Na-ABW simulation were obtained reporting the average fractional atomic coordinates calculated in the Li-ABW simulation to the Na-ABW cell. The simulation was performed at room temperature, as in the case of bikitaite and Li-ABW, and the dynamics of the system was followed for 4.1 ps.

Results and Discussion

Structure

The calculated average separation between H_2O molecules (defined as the oxygen–oxygen distance) is 2.831 Å in bikitaite and 2.916 Å in Li-ABW. The corresponding experimental values are 2.931 and 2.916 Å respectively.^{11,13,16} The small discrepancy between calculated and experimental values of the water–water separation in bikitaite (3%) is within the accuracy of the adopted approximations. However, such average distances indicate that H_2O molecules are close enough to be hydrogen bonded to each other, and to form one-dimensional arrays of molecules. Moreover, diffractometric studies indicate that one of the water's protons is closer to the framework in Li-ABW¹⁶ than in bikitaite.^{11,13} As far as Na-ABW's water is concerned, we can build our structural analysis only on the results of our *ab initio* simulations. From the calculated trajectory we obtain an average inter-water separation of 3.516 Å. This distance is too long for inter-water hydrogen bonding. On this basis we consider water molecules in Na-ABW as arrays of "isolated" water molecules hosted in a zeolitic channel. We point out here that our data are relative to a stoichiometric coefficient for water n = 0.75, only a little smaller than the $n \sim 0.8$ found experimentally.

The fact that the water/extraframework cation ratio is less than 1 in Na-ABW could be explained by inspecting Fig. 4, where the cation-framework's oxygen radial distribution functions for the three simulated structures are shown. While Li is close to the framework oxygens, Na in Na-ABW is found at larger distances from the framework, therefore "occluding" the channels more effectively than the smaller Li cations. As a consequence, Na cations leave less room for the water molecules and a lower stoichiometric coefficient of water in Na-ABW should occur.

Fig. 5 reports the calculated radial distribution functions $g_{OH}(r)$, between the oxygens and hydrogens of water for bikitaite, Li-ABW and Na-ABW. The $g_{OH}(r)$ s for the distribution among hydrogens and framework oxygens are also shown. In the region between 1.5 and 2.5 Å, no maximum is present in the inter-water g(r) in Na-ABW. This is the typical region for hydrogen bonds. It is clear, on the other hand, that interwater bonds are present in bikitaite and Li-ABW, with a more pronounced peak in the former case. In the same region, a quite different situation occurs for hydrogen-framework $g_{OH}(r)$ s. The peak disappears in bikitaite, its intensity is <1 for Li-ABW and >1 for Na-ABW. Such a trend indicates how moderate structural differences affect the probability of finding water molecules hydrogen bonded only to each other (bikitaite) or only to the framework (Na-ABW). An intermediate situation occurs in the case of Li-ABW, where water molecules have a finite probability of being linked both to other H₂Os and to the framework. This is supported by single crystal diffraction studies, indicating that the lowest Owater-Oframework distance is 3.003 Å in Li-ABW, and 3.111 and 3.138 Å for the two crystallographically different water molecules in bikitaite.

This analysis is confirmed by IR spectroscopy. The experimental IR spectra of the studied zeolites are reported in Fig. 6. We compare these results with the calculated power spectra obtained from the Fourier transform of the velocity autocorrelation functions from the corresponding simulations, and shown in Fig. 7. Let us focus now on the water bending region, around 1600 cm⁻¹. Due to the presence of a single absorption band this spectral region is easier to analyze than the multiple-band highly convoluted water stretching zone. The lowest bending frequency is found in the LiABW sample,



Fig. 4 Radial distribution functions Li–O_{framework} in Li-ABW (dashed lines) and Na–O_{framework} in Na-ABW (continuous lines). Thin lines refer to the respective coordination numbers.



Fig. 5 Radial distribution functions O–H in the three simulated zeolites. Top panel: $H-O_{\text{framework}} g(r)$ s. Lower panel: $H-O_{\text{water}} g(r)$ s.

while bikitaite and Na-ABW show higher bending frequencies. This trend is also reproduced by the simulated spectra, and can be explained by taking into account that, on average, a water molecule in Li-ABW is involved in hydrogen bonds both with other water molecules and with framework oxygens. In bikitaite and NaABW only one proton per molecule is involved in hydrogen bonds: in the former case with other molecules in the chain, while in the latter with the framework oxygens. As a consequence, it should be easy to accept that the force constant associated with the H–O–H bending mode in Li-ABW would be smaller than those of the other two systems, leading to the lowest wavenumber for the H_2O bending.

Water dynamics

Let us focus now on the motion of the water molecules in the three zeolites. In the elapsed time of our simulations (≈ 4 ps) we have detected rotations of water molecules only in Li-ABW, where at most only one molecule at a time rotates.¹⁴ Snapshots of the channels' content (water molecules and Li or Na cations) are reported in Fig. 8. In bikitaite, water molecules librate around their crystallographic positions and no rotation at room temperature has been observed. As pointed out before, in Li-ABW a water molecule has a finite probability of being engaged in two or three hydrogen bonds: one as a proton donor to the next water in the chain, one as a proton acceptor with the previous water in the chain and a third bond as a proton donor to the framework oxygens. On the other hand, in Na-ABW, the fact that the water molecules are well separated suggests that the number of hydrogen bonds per molecule is reduced and H₂O interacts only with the framework oxygens. In Li-ABW there is competition with the protons of H₂O searching for an oxygen either in the framework or in the nearest water molecule.

The behaviour of the orientational correlation functions²⁵ should reveal differences in the water dynamics in the three zeolites. We present two such functions: one describes the collective orientational correlations (or COR) and is calculated as the correlation function of the total dipole M of all the water molecules in the system;²⁶ the other, the single molecule



Fig. 6 Micro-IR spectra of bikitaite (1), Li-ABW (2) and Na-ABW (3).

orientational correlation function (or SMOR), describes the average correlation of a water molecule and is calculated by the average of the correlations of the dipole moment of each molecule.²⁶ The main mathematical difference between the two functions is that the COR also contains cross-correlation terms between different molecules, terms that are missing in the SMORs. As the dipole moment vector for a water molecule can be roughly approximated by the vector describing the bisector of the HOH angle, we have calculated the CORs and SMORs via the correlation functions obtained by the bisectors. The short-time behaviour of the CORs and SMORs calculated from the dynamics of the three systems is reported in Fig. 9. The same quantities, from a simulation of pure liquid water at room conditions,²⁷ are reported for comparison. The COR and SMOR of water in bikitaite have a nearly identical trend to those in Na-ABW, the only differences being that both the COR and SMOR decay faster in bikitaite than in Na-ABW. The qualitative behaviour of the two functions in Li-ABW is quite different, COR and SMOR have a different decay rate and both look like the same functions calculated for a liquid sample of pure water. The decay of both functions is slower in Li-ABW than in the other two zeolites, but is faster than those of pure liquid water. As mentioned before, water molecules in Li-ABW may rotate and there are approx-



Fig. 7 Fourier transforms of the velocity autocorrelation functions of the three simulated zeolites. Thin dashed lines refer to bikitaite. Thick dot-dashed lines refer to Na ABW. Thin continuous lines refer to Li-ABW.

imatly three hydrogen bonds that have to be continuously broken and formed as a rotation occurs. This bond breaking and formation has an energetic cost, and, consequently, the rotation of one H_2O is subject to friction by both the framework and the nearest water molecules. This is very similar to what happens in liquid water, where, moreover, the average number of hydrogen bonds involved in the rotation of an individual molecule is now higher, namely of the order of four, and so in liquid water the SMOR should decay slower than in Li-ABW. Cross terms should make the COR decay even slower. This is because a rotation of an individual H_2O mol-



Fig. 8 Representations of the water chains in the three zeolites: (a), bikitaite; (b), Li ABW and (c) Na-ABW. Black spheres represent water oxygens, white spheres represent protons, gray spheres lithium (Dark gray spheres represent sodium in Na-ABW).



Fig. 9 COR and SMOR functions (see text) for water molecules in the three simulated zeolites, and, for comparison, for liquid water at room temperature. Continuous lines represent the SMORs, dotted lines represent CORs.

ecule implies the change of sign of its dipole components, and this process also has an energetic cost, depending on the orientation of all the molecules in the neighbourhood of the target rotating one. Now, from the point of view of rotations, the behaviour of water molecules in Li-ABW is very similar to that found in liquid water, where, moreover, the molecules also have a diffusive motion not found in Li-ABW. Apart from this nontrivial difference, water in Li-ABW can be considered to be in a rotational liquid state, namely in a state where atoms during a rotation are continuously displaced from their crystallographic position. Such motion is not energetically free (it is not a gas) and is governed by a balance between thermal and interaction energies.

Let us now focus again on water in bikitaite. Here, on average, water molecules have a geometrical organization very similar to that in Li-ABW, but the framework's dipole moment in bikitaite is much higher than that in Li-ABW and we argue that one of the "frictions" that a water molecule has to overcome during a rotation is due to the reversing of its dipole vector. As such a dipole switch has an energetic cost, the higher dipole in bikitaite prevents the water molecules from rotating, at least up to room temperature. Only librational motion is present in bikitaite, and as this motion is fast, the decay of the correlation functions is fast as compared with water in Li-ABW. Also in Na-ABW we have found that water molecules do not change their orientations during the simulation, and therefore only the fast librational motion is evidenced by the SMOR. The fact that the COR and SMOR in Na-ABW have very similar behaviour, is easily understood by considering that in this structure the water molecules are not linked to each other, so that the dynamics of different molecules is uncorrelated and the cross terms in the COR function do not give any significant contribution. However, the fact that in bikitaite the COR and SMOR have very similar behaviour is very intriguing indeed. Water molecules in bikitaite are linked to each other, so it is hard to think that the cross terms in the COR give no contribution as in Na-ABW. A plausible answer may be that in bikitaite the close similarity



Fig. 10 DTG curves for bikitaite (top panel), Li-ABW (central panel) and Na-ABW (bottom panel). Heating rate 10 °C min⁻¹ from 20 to 1000 °C.

of the SMOR and COR implies that each single molecule's dynamics is deeply correlated to the motion of the others *via* the hydrogen bond chain. Hence the one-dimensional ice structure behaves as a unique body, where the cross-correlation terms in the COR bear no further information than the diagonal terms already accounted for in the SMOR function.

Thermogravimetric analysis

The results of thermogravimetric analysis on the three zeolites are shown in Fig. 10. We have measured the percent weight loss as a function of increasing temperature, and the derivatives with respect to temperature of the measured quantities are shown in the figure. Comparison of the three curves indicates that Na-ABW loses its water at a lower temperature than Li-ABW, which loses its water at a lower temperature than bikitaite. Moreover, while the ABW zeolites show a single peak, in bikitaite there are two peaks. This last finding is related to the fact that there are two crystallographically different water molecules in bikitaite and only one in Li-ABW. The thermogravimetric studies allow us to have also a deeper insight into the behaviour of water molecules in these zeolites. While in Na-ABW H₂O forms, on average, only one hydrogen bond with the framework, in Li-ABW each water molecule is involved in (at least) two such bonds, and the amount of energy required to evacuate water is therefore higher in Li-ABW. Also, the interaction of a water molecule with the Li cation is stronger than with the sodium cation. The thermogravimetric curve of bikitaite is qualitatively different from those of the other two structures. However, it is clear that, at temperatures at which water is still present in the bikitaite's channels, water is completely evacuated in the ABW structures. This means that the total amount of energy required for the dehydration to be completed is highest in bikitaite.

Conclusion

We have presented a combined theoretical and experimental study of the Na-ABW zeolite. The new data are compared with previous studies on related zeolites, Li-ABW and bikitaite. The main aim of this work was to present an analysis of the properties of water in three hydrated zeolites, characterized by one-dimensional non-crossing channels of comparable sizes. We have found that water in these similar environments shows quite different behaviour, governed by the balance of water-water and water-framework interactions. The results suggest that the leading interaction determines the physical properties and the dynamical behaviour of the guest system. In more detail, whenever inter-guest interactions are favoured, the guest system may behave as a quasi-unique body (a sort of polymer). On the other hand, if host-guest interactions play the dominant role, the guest system may be considered as a set of weakly interacting individual molecules adsorbed in a host matrix. Moderate modifications of the zeolitic matrix affect the collective properties of the H₂O molecules. In particular, as shown and discussed in this paper, a rich phase diagram can be shown by water in such non-crossing zeolitic channels, ranging from one-dimensional ice behaviour to chains of nearly independent water molecules, passing through a one-dimensional water system in a rotational liquid state. A clear-cut assessment of the above statements may be achieved by studying the temperature and pressure dependence of the systems, and this is currently being pursued in our laboratories, together with more accurate diffraction studies on Na-ABW at ESRF.

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