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Modelling the effect of water on cation exchange in zeolite A

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Classical energy minimisation techniques have been employed to model the effect of hydration on the adsorption behaviour of extra-framework cations Na^+, Cs^+, Ca^{2+}, Ba^{2+}, Cd^{2+} and Sr^{2+} in zeolite A. The experimental structure of zeolite CaNa-A (Si/Al = 1) is reproduced accurately, while the energetically preferred position for water molecules is calculated to be inside the α-cage, in agreement with experiment. The preferential locations for the sodium and calcium ions in the hydrated zeolite A are governed by the water molecules and are calculated in the siliceous structure to be the β-cages (S6R position) for Na^+ and β-cages (S6R′ positions) for Ca^{2+}. These locations are in agreement with experimental findings of zeolite A structures, but have not previously been calculated for the calcium position.

Introduction

Heavy metals and radionuclides in soils have received increasing attention in recent years, partly because of the growing scientific and public awareness of environmental issues, and partly because of the development of analytical techniques to measure their concentrations accurately and rapidly, thereby facilitating environmental monitoring.[1] Ion exchange is regarded as one of the key processes that regulate the mobility of these hazardous species within the environment, but it can also be the process used for the decontamination of polluted soil, (ground)water or effluent.[2–4] An ion exchanger, often a zeolite chosen for its selectivity to the type of contamination, can be used to remove and concentrate the pollutant.[4–6] In addition, the soil ion exchange capacity is to a considerable extent due to its zeolitic content[7,8] and we have therefore decided to model the ion exchange and adsorption behaviour of a range of cations in two zeolite Linde-A structures.

The synthetic zeolite Linde-A (from here on referred to as zeolite A) was chosen as it has been well characterised and its ion exchange and adsorption behaviour has been the subject of many investigations.[9–14] Industrially they are used as water softeners in detergents (removing calcium and magnesium)[15,16] and as catalysts,[17,18] while on a smaller scale they are employed in the medical profession for the entrapment of CO_2 and anaesthetic gases.[19]

Water will always be present in experimental zeolite structures. Even when the zeolite is dehydrated, residual water molecules are still retained in the crystal, *e.g.* approximately four water molecules per full unit cell for zeolite Ca_5Na_2-A.[10] Thus, when we investigate the location of different extra-framework cations within the zeolite lattices, and if we are to compare our calculated results with experimental findings, we need to include the effects of water in our simulation studies. Water molecules greatly influence the position of exchangeable cations and as a result the chemical properties of the zeolite. When extra-framework cations are strongly hydrated, they are reluctant to exchange to sites where they are required to shed some, or all, of their coordinated water molecules. In addition, the motion of the water molecules themselves regulates the efficiency of the ion-exchange and sorbing processes as this governs the mobility of the cations.[20] The rôle of water in zeolites is two-fold; firstly to complete the coordination of the cations present in the zeolite pores and cavities and secondly to minimise the electrostatic repulsion between framework oxygens.[21] Furthermore, the concentration of water adsorbed in the zeolite structure is governed by the aluminium content, as the zeolite becomes more hydrophilic with decreasing Si/Al ratio.[22]

The location of water molecules and their interactions with the zeolite framework and extra-framework cations have been the subject of many experimental studies,[23–26] yet a clear picture of local structure and mobility of water and exchangeable cations is still required. Computer simulation techniques can be a valuable tool for the study of water molecules and their interactions with the zeolite framework and exchangeable cations, but apart from the recent work by Ruiz-Salvador, Lewis and co-workers,[27] few computational studies have included the interactions of water molecules when investigating extra-framework cations in zeolites. However, in previous work of dehydrated zeolite A structures,[28] we found some discrepancies between our calculations and experimental data. For instance, crystallographic data identify the adsorption site for calcium to be inside the sodalite cage,[10] but we calculated the lowest energy position for calcium adsorption to be inside the larger α-cage. This discrepancy could be explained by the small amounts of residual water present inside the experimental dehydrated zeolite crystal (~4 water molecules per full unit cell for zeolite Ca_5Na_2-A).[10] Hence, in this work we use atomistic simulation techniques to investigate the locations of water molecules in the relaxed framework of zeolite A and their effect on the location and stability of a range of extra-framework cations, in order to gain an understanding of the mechanisms regulating the mobility of water and exchangeable cations at the internal zeolite surfaces.

Theoretical methods

The energy minimisation code PARAPOCS[29] was used to calculate the effects of hydration on the structural parameters of the aluminated and fully charge compensated zeolite

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structures so as to include the long-range effects of the interactions between close-neighbour aluminium atoms and extra-framework cations as these greatly influence the atomic distributions.[30] We next employed the computer code CASCADE[31] to calculate the defect energies of the exchangeable cations at various possible starting locations in the zeolite lattice to identify stable cation adsorption sites. CASCADE employs an embedded cluster method to simulate point defects in otherwise perfect lattice structures. The approach is to first calculate the minimum lattice energy of the perfect crystal and then the minimum energy of the defective lattice energy, in this case the zeolite lattice with extra-framework cations, giving the energy difference as a defect energy, taking into account the self-energy of the water molecule. This defect energy corresponds to the internal energy of the defect, which is assumed to be directly comparable to the enthalpy of the defect obtained from experimental measurements.[32] The crystal in the calculations is divided into two regions. Region I consists of a sphere of the crystal around the defect, in which the ions (between 250–300 species) are relaxed explicitly to calculate an energy minimum. The energy in the outer region (region II) is assumed to be a simple quadratic function of the distance from the defect, which is justified when the displacements of the defect are small. This approximation[33] is used to calculate the equilibrium position of the defect by assuming that the external field is the electric field due to the charge of the defect at the origin. Previous work has shown that, provided one uses a sufficiently large region I, the CASCADE program, in combination with reliable interatomic potentials, can produce accurate values of the energies of ion adsorption, substitution and migration.[34–37]

We used a combination of established potential parameters for the simulation of the zeolite framework itself and the interactions with extra-framework cations and the full potential model used in this work is given in Table 1.[28,38–47] The potential parameters for the interactions between zeolite framework and cations were used in previous work to model the effect of lattice relaxation on cation locations,[28] while the cation–water interactions were derived for this work, following a modified version of the approach by Schroder *et al.*, where the short-range parameters between the cations and lattice oxygen ions (charge -2) are scaled down for use in the interactions between cations and water oxygen ions (charge -0.8) to allow for the difference in charges and hence Coulombic forces between the cations and the two different types of oxygen ions.[48] The short-range interactions between water and cations were then further refined following comparison with available experimental measurements, such as interatomic separations for solvated ions.

Results and discussion

The crystallographic structure of zeolite A may be described as an octahedral array of sodalite units. These sodalite units, or β-cages, consist of 6 four-membered rings (4R) separated by 8 adjoining six-membered rings (S6R).[49,50] By arranging the β-cages at the corners of a cube, linking them in double four-membered rings (D4R), the zeolite framework is obtained. This cubic structure creates large α-cages separated by single eight-membered rings (S8R) on the face of the cube (Fig. 1).[51] Extending the zeolite framework in the *x*, *y* and *z* directions creates a three-dimensional network of channels, giving rise to the molecular sieve character.[52,53] Three crystallographically different oxygen sites are observed in the zeolite A structure: O(1), O(2) and O(3). In the β-cage, the oxygens that build up the four-rings consist of O(3), while the six-rings are built up from both O(2) and O(3). The O(1) oxygens form the bridges between the adjacent sodalite units. The framework is stoichiometric with a Si/Al ratio of 1 : 1, which gives rise to a net negatively charged unit cell $(Si_{24}Al_{24}O_{96})^{24-}$ that needs to be compensated by exchangeable cations, which are located in specific adsorption sites inside the zeolite framework.[50,52] Our initial zeolite A configuration was simulated starting from crystallographic data of a commercial dehydrated zeolite 5A.[10] The crystallographic structure was determined by neutron powder diffraction techniques in the cubic space group $Fm\bar{3}c$ ($a = 24.65$ Å) with two unique cation adsorption sites. Both the calcium and sodium species are located near the six-ring windows, although the sodium atoms are located inside the α-cage, while the calcium sites are inside the sodalite units (β-cages). We investigated the effect of hydration in two zeolite A type structures: the siliceous form, where the aluminium(s) and charge compensating cations, either sodium or calcium, were at infinite dilution, which lead to a unit cell volume reduction of the dehydrated structure of 12.6%; and a framework structure with Si/Al = 1, fully charge compensated with Ca/Na = 1 (referred to as CaNa-A). The advantage of this stoichiometry is that all the symmetry sites are filled, and hence cation ordering over different sites need not be considered. We first introduced water molecules into the purely siliceous and CaNa-A zeolite structures to study the effect of water on the zeolite structures, after which we investigated the interactions of the water with extra-framework cations in more detail in the siliceous zeolite by choosing a number of starting positions for the cations and the surrounding water molecules to ensure that, as far as possible, the lowest energy position has been identified. We concentrate on the purely siliceous structure in this, our first paper on the effect of water on cation exchange in zeolite structures for a variety of cations, in order that we may compare directly with our earlier work, where we studied the effect of lattice relaxation but did not take into account the effect of water in the framework. Moreover, the inclusion of aluminium explicitly would add an unnecessary degree of complication to the calculation at this stage, as the thrust of the work reported in this paper is to investigate the interaction between water and extra-framework cations.

Adsorption of water in siliceous zeolite A

A single water molecule was introduced into the siliceous zeolite A framework at three different locations, namely in the eight-ring window (S8R) or in the six-ring window, either just inside the α-cage (S6R) or inside the β-cage (S6R′) (Fig. 2(a)–(c)). The most stable adsorption site for a single water molecule (Table 2) was found in the S6R′ position inside the β-cage, in agreement with experimental work by Pissis and Daoukaki-Diamanti,[20] who found that water molecules in the β-cages of Na-13X were most strongly adsorbed and therefore most difficult to remove from the zeolite upon dehydration. When considering the adsorption energies (Table 2), we find that there is a small energy advantage of approximately 0.3 eV per water molecule for the siliceous zeolite framework to adsorb/retain some water molecules within its crystal structure, which is due to bridging hydrogen-bonding interactions of the water molecules with framework oxygens. In the S6R′ position, the water molecule coordinates by one of its hydrogens to three framework oxygens, while its other hydrogen and the oxygen ion are pointing towards the center of the β-cage. This position is the mirror image of the water molecule in the larger S6R site, but the increased stability (by 0.08 eV) is due to the shorter O(3)···H (2.27–2.30 Å) distances compared to those in the S6R adsorption site. We therefore suggest that upon dehydration, some of the residual water will be located in the β-cages of zeolite A.

On the introduction of a second water molecule into the zeolite, we find that only when both water molecules are located in the S8R position are there any intermolecular interactions between the water molecules (Fig. 2(d)). The net effect is that the average adsorption energy per water molecule

Table 1 Potential parameters used in this work

Species	Charge/e	Core–shell interaction/eV Å^{-2}	Species	Charge/e
O (core)	0.86902		Ba	2.0
O (shell)	−2.86902	74.92	Sr	2.0
Ow (core)	1.25000		Ca	2.0
Ow (shell)	−2.0500	209.449602	Cd	2.0
H	0.40000		Cs	1.0
Si	4.0		Na	1.0
Al	3.0			
Lennard–Jones potential parameters				
Ion Pair	A/eV Å^{12}	B/eV Å^{6}		References
Ow–Ow	39344.98	42.15		47
Buckingham potential (short-range cutoff: 18.5 Å)				
	A/eV	ρ/Å	C/eV Å^{6}	
O–O	22764.00	0.1490	27.88	38, 39
O–Ow	22764.00	0.1490	28.92	47
Si–O	1283.907	0.32052	10.66158	40
Si–Ow	562.032	0.32052	10.66158	this work
Al–O	1460.30	0.29912	0.0	39
Al–Ow	584.1107	0.29912	0.0	this work
Ba–O	905.700	0.3976	0.0	42
Ba–Ow	362.265	0.3976	0.0	this work
Sr–O	959.100	0.3721	0.0	42
Sr–Ow	383.64	0.3721	0.0	this work
Ca–O	1090.400	0.3437	0.0	42
Ca–Ow	436.16	0.3437	0.0	this work
Cd–O	1064.900	0.3389	0.0	28
Cd–Ow	425.96	0.3389	0.0	this work
Cs–O	1065.320	0.3911	0.0	44
Cs–Ow	426.130	0.3911	0.0	this work
Na–O	5836.814	0.2387	0.0	45
Na–Ow	4088.384	0.2387	0.0	this work
Morse potential				
	D/eV	a/Å^{-1}	r_0/Å	
H–Ow	6.203713	2.22003	0.92376	47
Three-body potential				
	k/eV rad^{-2}	Θ_0		
O_{shell}–Si–O_{shell}	2.09724	108.693195		40
O_{shell}–Al–O_{shell}	2.09724	109.470000		41
H–O_{shell}–H	4.19980	109.470000		47
Intra-molecular Coulombic subtraction (%)				
H–H	50			47
Ow–H	50			47

is increased by 0.26 eV compared to the adsorption energy of a single molecule, due to intermolecular hydrogen-bonding (Ow···H is 2.22 Å). In the more spacious locations of the α- and β-cages, the water molecules adsorb to the internal zeolite surfaces, but they do not interact with each other.

Adsorption of water in zeolite CaNa-A

We next investigated hydration of the NaCa-A structure, in order to investigate whether the potential model was capable of reproducing the experimental structure adequately, which would give us confidence in the accuracy of our subsequent calculations of cation exchange. We added 24 water molecules to the structure of dehydrated zeolite CaNa-A, randomly distributed throughout the framework, followed by energy minimisation and removal of water molecules at high energy positions. As a result, we obtained a low energy CaNa-A structure, containing eight water molecules per unit cell. Comparing the lattice energy of this (partially) hydrated structure (−5500.1 eV) with that of the dehydrated structure (−5421.9 eV)[28] and eight isolated water molecules (−9.1 eV each)[47] we find an adsorption energy for the water in the zeolite of −0.68 eV per water molecule. The lattice vectors (a = 24.646 Å) are in good agreement with experimental parameters of a dehydrated CaNa-A zeolite (a = 24.486 Å),[54] giving an increase in cell volume of only 0.24%, which may be due to the presence of the eight water molecules in the unit cell.

The water molecules in the energy minimised CaNa-A structure are all situated near the framework, where they form interactions with both framework and extra-framework Na and Ca cations. The water molecules are mainly located in the α-cages (Fig. 3), near S8R windows where they coordinate by

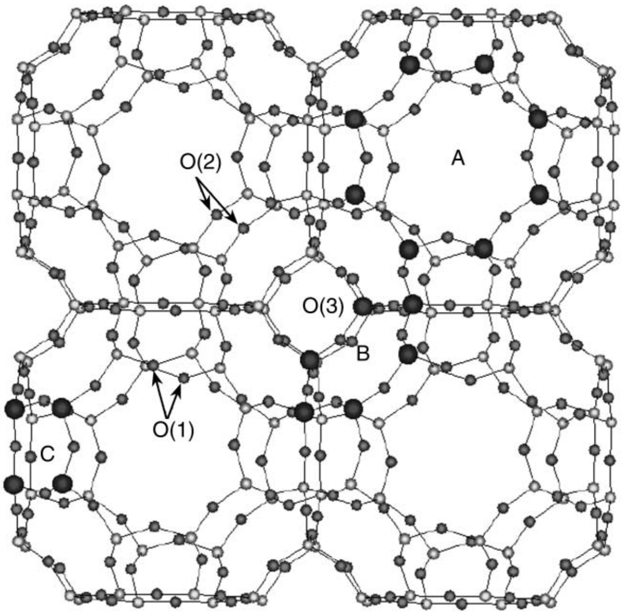

Fig. 1 The siliceous structure of dehydrated zeolite A, identifying O(1), O(2) and O(3) oxygen atoms and showing the eight-ring (A), six-ring (B) and four-ring (C) in big, black spheres (Si = pale grey, O = dark grey).

their oxygen atoms to framework silicon or aluminium ions (typically Si–O_w = 1.86 Å, Al–O_w = 2.00 Å) and form hydrogen-bonding interactions with framework oxygens (typically H···O(1) ~ 1.9 Å and H···O(2) ~ 1.85 Å). In addition, most of the water molecules can approach the extra-framework cations closely enough to interact with them as well (*e.g.* Ca–O_w = 2.4 Å, Na–O_w = 2.6 Å).

The effect of the water molecules on the cation positions is dependent on the location of the cation (in the α- or β-cage). The calcium ions in the α-cages move further into the cage, away from their position near the plane of the six-ring windows, shown by the calcium–oxygen distances Ca–O(2) = 2.76–2.88 Å and Ca–O(3) = 2.36–2.38 Å, compared to Ca–O(2) = 2.70–2.80 Å and Ca–O(3) = 2.30–2.35 Å in the dehydrated zeolite CaNa-A.[28] The sodium ions show the same trend upon hydration, moving away from the six-ring window further into the α-cage with Na–O distances increasing by 0.02–0.10 Å. In the β-cage on the other hand, the calcium ion moves towards the plane of the six-ring window, which expands to accommodate the calcium ion in its new adsorption position, with the result that Ca–O distances decrease only very little (~0.02 Å) upon hydration of the CaNa-A zeolite.

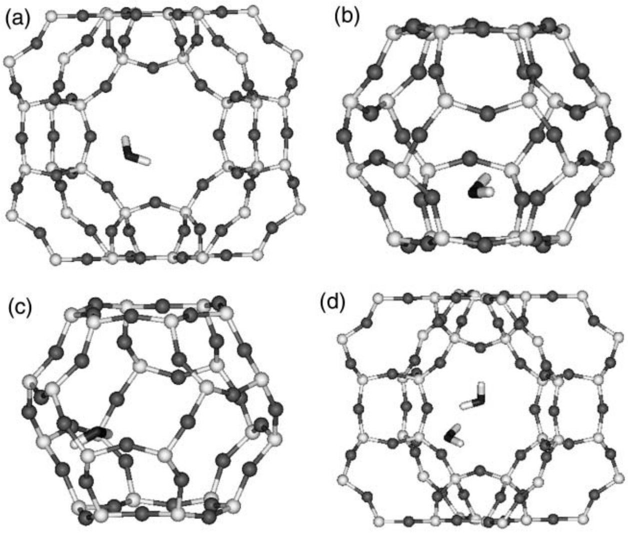

Fig. 2 Minimum energy adsorption positions for water molecules in the siliceous zeolite A structure: a single molecule at (a) the S8R site, (b) the S6R position, (c) inside the β-cage in the S6R′ site and (d) two molecules in the S8R site (Si = pale grey, $O_{lattice}$ = dark grey, O_{water} = black, H = white).

Table 2 The calculated adsorption energies per water molecule in siliceous zeolite A (where the calculated self-energy of an isolated water molecule is −9.1 eV)

Adsorption energies of water in siliceous zeolite A/eV	
Location	$E_{adsorption}/H_2O$
S8R	−0.300
S6R	−0.305
S6R′	−0.384

The good agreement of our calculated zeolite structures with experimental findings gives us confidence that the interactions between water, zeolite framework and extra-framework cations are modelled adequately by the potential model and we next study the cation locations in more detail in the siliceous zeolite A, to investigate whether we can correctly calculate the relative stabilities of the various sites in the lattice for a host of different cations. We have chosen to concentrate on the purely siliceous structure in this, our first simulation study of ion exchange in hydrated zeolite A, because we can then study each cation in isolation and compare directly with results of our study of cations in the dehydrated siliceous zeolite[28] and hence quantitatively evaluate the (de)stabilising effect of water on the cations in their possible locations.

Location of extra-framework cations in siliceous zeolite A

We studied the effect of water on the adsorption positions and relative stabilities of the following range of cationic species: Ca^{2+}, Na^+, Cs^+, Ba^{2+}, Cd^{2+} and Sr^{2+}. A large number of different configurations were studied where clusters of water molecules (ranging from one to eight molecules) were added around the cations in four different adsorption sites, namely the S6R (α-cage), S8R (8-ring window), 4R (4-ring window) and S6R′ (β-cage) sites. The starting positions of the water molecules were at realistic distances from the zeolite framework while the cation–water distances were obtained from experimental results, where available, or from the summation of the individual ionic radii (Table 3).

Adsorption of calcium. We discuss the relative stabilities of the various calcium positions in some detail as our previous calculations on dehydrated zeolite A identified the α-cage as its

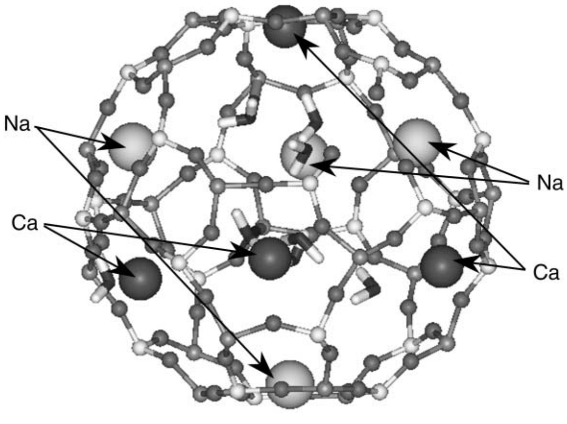

Fig. 3 α-Cage of the hydrated CaNa-A structure, showing Na^+ and Ca^{2+} cations and water molecules (Si = white, Al = pale grey, $O_{lattice}$ = dark grey, O_{water} = black, H = white).

Table 3 Experimental and theoretical cation–water distances

Cation–O_{water} distances/Å		
Cation	Distance	Reference
Caesium	3.09	9
Sodium	2.4–2.9(6)	58, 59
Barium	2.79	60
Strontium	2.62	60
Calcium	2.4(6)	58
Cadmium	2.28(6)	61

energetically preferred position, which did not agree with experimental findings by Adams and Haselden[10] who located calcium in the β-cage. We are therefore interested to see whether the inclusion of water in the calculations makes a difference to the relative stabilities of the calcium ion in the different positions. Calcium is calculated to be stable in all four adsorption positions under various states of hydration. However, we found that a maximum number of five water molecules could be coordinated to the calcium ion, after which additional water molecules moved away to empty S6R or S8R adsorption sites. Comparison of the energies of clusters, consisting of the calcium ion and a cumulative number of water molecules, showed that these additional water molecules do not contribute to the overall stability of the calcium ion in its adsorption positions but that the lowest energy location is due to stabilisation of the calcium ion through interactions with its maximum number of coordinated water molecules and framework oxygens. Table 4 shows the defect energies for incorporation of the clusters of calcium ion with water molecules in the four different adsorption sites (compared to the empty framework), together with the stabilisation energy, which we define as the energy difference between the framework with the hydrated calcium cluster on the one hand and the hydrated framework without the calcium ion on the other, which is the sum of the energies of the dehydrated framework and the individual water molecules in the zeolite, depending on their location, plus the calcium ion in the dehydrated framework on the other:

$$E_{\text{stabilisation}} = E(\text{Ca}(\text{H}_2\text{O})^{2+}_{n(\text{zeolite})}) - [E(\text{Ca}^{2+}_{\text{zeolite}}) + nE(\text{H}_2\text{O}_{\text{zeolite}})] \qquad (1)$$

For example, the defect energy of a calcium ion in the S6R site of dehydrated siliceous zeolite A was calculated at −10.63 eV (compared to the dehydrated framework without calcium present)[28] and the energies of the individual water molecules are 3 × −9.405 eV (energy of a water molecule adsorbed in the S6R window) and 1 × −9.484 eV for the water molecule inside the β-cage (Table 2), the sum of which equals −48.329 eV. The stabilisation energy for the hydrated calcium ion is then −2.68 eV for adsorption at the S6R position (Table 4).

In the S6R adsorption site the calcium ion was sevenfold-coordinated in its most stable configuration to three framework oxygens (Ca–O(3) = 2.57 Å) and four water molecules (Fig. 4a). Three of the water molecules were located inside the α-cage (Ca–O_w = 2.33 Å) and the fourth water in the β-cage, perpendicular to the plane of the S6R containing the calcium ion (Ca–O_w = 2.63 Å). Each of the water molecules inside the α-cage were stabilised by a single hydrogen-bond interaction with one of the framework oxygens in an S6R adsorption site (H···O(2) = 2.12 Å), while the water molecule inside the β-cage was too far removed from the zeolite framework to interact with it.

Table 4 Defect and stabilisation energies of calcium clusters in siliceous zeolite A

Defect and stabilisation energies of hydrated calcium ions $\text{Ca(H}_2\text{O)}_n^{2+}$ in siliceous zeolite A			
Site	$n_{\text{water molecules}}$	E_{defect}/eV	$E_{\text{stabilisation}}$/eV
S6R	4	−51.01	−2.68
S6R′	4	−50.89	−2.93
S8R	5	−61.09	−2.15
4R	5	−61.10	−2.18

At the S6R′ position in the β-cage, the most stable calcium cluster again consisted of the calcium ion coordinated to four surrounding water molecules (Fig. 4b). The defect energy of this location at −50.89 eV is similar to the S6R site (51.01 eV), but the stabilisation energy of the hydrated cluster is now −2.93 eV, more exothermic than at the S6R site (−2.68 eV). Hence, in a zeolite with residual water molecules the β-cage is the preferred location for the calcium cluster rather than the α-cage. The calcium ion is situated near the centre of the β-cage (~0.5 Å from the centre of the cage). The four water molecules stabilising the calcium ion in its adsorption position are arranged around the ion in tetrahedral coordination (Ca–O_w = 2.13, 2.22, 2.23 and 2.24 Å). Each water molecule is located near a six-ring window, interacting by its hydrogens with three to four framework oxygens (H···O(2) and H···O(3) range between 1.80 and 2.27 Å).

For the S8R adsorption site we calculated approximately twelve different configurations concentrating on a calcium hydration state of four to six water molecules as experimentally calcium ions are often hydrated by six water molecules [$\text{Ca(H}_2\text{O)}_6^{2+}$]. In addition, the S8R adsorption site, with the two α-cages on each side of the eight-ring window is an ideal site for cations to retain most of their water coordination. We found, on energetic grounds, that a maximum number of five

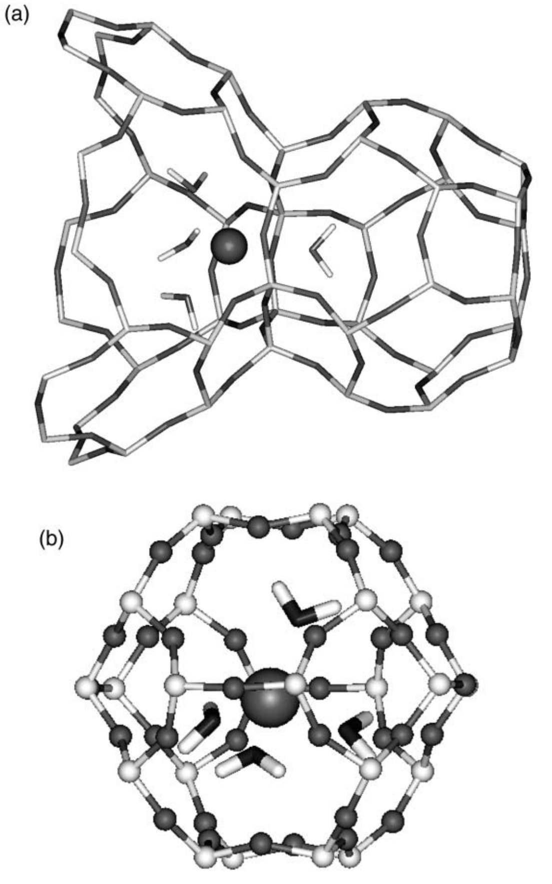

Fig. 4 Ca^{2+} adsorption in (a) the S6R site, sevenfold-coordinated by three framework oxygens and four water molecules' oxygens and (b) the S6R′ adsorption site, fourfold-coordinated by four water molecules (Ca = sphere, Si = pale grey, O_{lattice} = dark grey, O_{water} = black, H = white).

water molecules could be coordinated to the calcium ion in the S8R position, which also interacted with three framework oxygen ions (Ca–O(1) = 2.71, 2.80 Å, Ca–O(2) = 2.75). It is perhaps interesting to note that a two-fold coordination of Ca^{2+} together with five coordinated water molecules is a common feature of many natural minerals. The five coordinating water molecules are divided over the two α-cages on either side of the eight-ring window ($Ca–O_w$ = 2.20, 2.33, 2.44, 2.47 and 2.57 Å). The stabilisation energy (−2.15 eV) showed that this position is not as favourable as either the S6R or S6R′ locations for the calcium ion.

We finally investigated the 4R location, where we again calculated a maximum number of five coordinating water molecules surrounding the calcium ion, which also interacted with framework oxygen ions in the four-ring (Ca–O(1) = 3.13 Å, Ca–O(3) = 3.15 Å). The defect energy at this position (−61.104 eV) is marginally more favourable than the S8R location (−61.088 eV), mainly due to the location of four of the water molecules, which have formed either two (near an S6R) or four (near an S8R) strong interactions with framework oxygen atoms (H···O(1) and H···O(2) = 2.02 Å). The fifth water molecule is too far removed from the zeolite framework and only interacts with the calcium ion ($Ca–O_w$ = 2.34 Å). The stabilisation energy, calculated at −2.18 eV, is also comparable with the S8R site and both are less favourable locations for the calcium ion than the S6R′ site.

In previous work on the dehydrated zeolite A, we calculated the preferred location of the calcium ion to be in the α-cage at the S6R position, even though crystallographic structure refinements of a dehydrated Ca_5Na_2-A crystal by Adams and Haselden[10] showed that the calcium ions are located in the β-cage at the S6R′ adsorption sites. However, our present calculations show that the addition of water has a large stabilising effect on calcium ions in the S6R′ sites, which has now become the preferred location. We therefore suggest that in the experimental crystal analysed by Adams and Haselden[10] the residual water molecules (∼4 water molecules per full unit cell) are located inside the β-cages, where they stabilise the calcium ions, in agreement with experimental work by Pissis and Daoukaki-Diamanti,[20] who identified the most immobile water species to be inside β-cages of zeolite Na-13X, and our above calculations of both the hydrated calcium clusters and the adsorption of water in the cation-free framework.

In addition to calculating the optimum number of water molecules in the calcium ion clusters, we also investigated the effect on the stabilisation energy of sequential removal of water molecules from the S6R′ calcium cluster. We found that after removal of one water molecule the calcium ion was still very stable in its adsorption position inside the β-cage although the stabilisation energy had decreased to −2.73 eV, indicating that this fourth water molecule contributed ∼0.2 eV to the stability of the calcium ion in its adsorption site. However, removal of a second water molecule corresponded to a reduction in stabilisation energy in the S6R′ adsorption site of ∼1.0 eV, now making it a less favourable adsorption site than the S6R positon in the α-cage. We therefore suggest that at this stage of dehydration the energy gradient between the S6R and S6R′ sites is such that the calcium ion will migrate from its S6R′ position, through a six-ring window into the α-cage and settle in its S6R adsorption position, which we calculated to be the favoured location in dehydrated siliceous zeolite A.[28]

Adsorption of caesium. We next investigated the effect of water on the location of caesium ions in the zeolite lattice, for which experimental results are also available for comparison.[9] Addition of a single water molecule near the caesium ion in the S8R adsorption led to a stabilisation energy of −0.28 eV, compared to the unhydrated ion and water molecule adsorbed in the zeolite. The caesium ion is located in the α-cage (0.25 Å), where it is ninefold-coordinated by weak interactions to eight framework oxygen atoms (Cs–O(1) = 4.05 Å, Cs–O(2) = 4.15–4.19 Å) and a stronger interaction to the water molecule ($Cs–O_w$ = 3.13 Å). The water molecule was stabilised by two bridging hydrogen-bonding interactions with framework oxygen atoms belonging to a six-ring (H···O(3) = 1.96 Å).

When caesium is coordinated to four water molecules, the stabilisation energy increases to −1.6 eV for the most favourable position, shown in Fig. 5(a). The caesium ion is located slightly off-centre above an S8R window with Cs–O distances ranging from 4.70 to 5.05 Å, which are too long to stabilise the cation in its adsorption position. However, the distances between the caesium ion and the four coordinating water molecules are 3.03–3.32 Å, which agree with the sum of the corresponding ionic radii (3.09 Å).[9] Each of the water molecules (one in the eight-ring and the other three in the plane of three separate six-rings) are further interacting with the zeolite framework (H···O distances = 1.96–2.14 Å).

We identified a second stable fourfold-coordinated caesium adsorption site with a stabilisation energy of −1.3 eV (Fig. 5(b)). Here, the caesium ion has moved farther inside the α-cage surrounded by four water molecules at distances of 3.13–3.38 Å, which adsorption position is similar to the site documented by Maxwell and Baks[55] and Ahn and Iton,[56] who referred to this adsorption site as the 12th adsorption site for caesium. From their experiments Ahn and Iton concluded that this 12th adsorption position only comes into existence at high concentrations of molecular water, while upon dehydration this is the first adsorption site to lose its water molecules, which causes the caesium ion to migrate to a neighbouring S8R or S6R adsorption position. The caesium adsorption/exchange behaviour in this particular adsorption position therefore corresponds to a mechanism governed by zeroth order kinetics, as the lifetime of caesium ions in this site is independent of its steady-state population, which means that the lifetime of caesium ions is determined by other factors, which do not involve the caesium ion directly, *e.g.* the presence of water in the α-cage.[56]

Generally, we find that the introduction of more water molecules in the cluster causes the caesium ion to move away

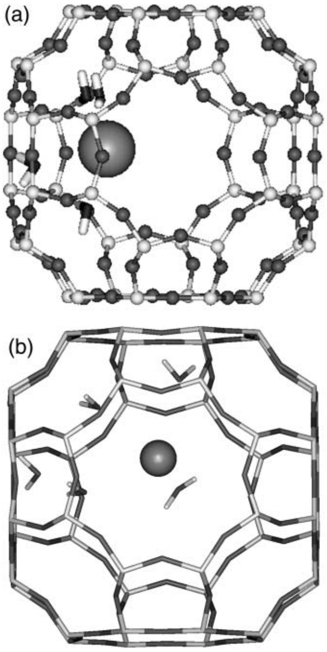

Fig. 5 Adsorption positions of fourfold-coordinated Cs^+ ions: (a) the most stable position in the α-cage above a S8R window and (b) less favourable, far inside the α-cage, where the fifth water molecule does not interact with the Cs^+ ion (Cs = sphere, Si = pale grey, $O_{lattice}$ = dark grey, O_{water} = black, H = white).

from the siliceous zeolite framework, losing all ionic interactions with the lattice oxygens in favour of coordinating with the surrounding water molecule(s) (Cs–O_w = 3.03–3.60 Å). Vance and Seff[9] refined and subsequently compared the adsorption locations for caesium ions in hydrated and (vacuum-)dehydrated crystal structures of Cs_7Na_5-A and to some extent their observations confirmed our calculated results, as they found all S8R-sites occupied by caesium ions, which did not appear to have any direct ionic interactions with the zeolite framework, in agreement with our calculations. However, our calculated Cs–O distances (>4.5 Å) do not agree with their experimental data, *e.g.* Cs–O(1) = 3.40 Å and Cs–O(2) = 3.58 Å. In addition, Vance and Seff found that the remainder of the caesium ions were identified in the S6R adsorptions sites,[9] which location, however, is not directly comparable to our stable adsorption positions in the α-cages.

In addition to calcium and caesium, we also investigated the preferred locations in the siliceous zeolite A framework of other monovalent and divalent cations, namely Na^+, Ba^{2+}, Cd^{2+} and Sr^{2+}, which we compared to the Ca^{2+} and Cs^+ results. Generally, the cadmium and strontium ions behave in a similar fashion to the calcium ion, while the larger barium ion follows the behaviour of the caesium ion, *e.g.* neither of these two cations had stable adsorption positions in the S6R or S6R′ sites, migrating instead to neighbouring S8R adsorption sites. The calculated distances between cations and water molecules agreed with experimental values (Table 3). Table 5 shows the preferred locations for all cations together with the optimum number of coordinating water molecules in the clusters.

Location of Na^+ cations. The calculated locations of the sodium ions differed from those of calcium as far as the relative stabilities of the S6R and S6R′ adsorption sites are concerned. In the S6R′ and S8R positions the sodium ions only coordinate to one water molecule, while any additional water molecules move away to interact with the zeolite lattice. The stabilisation energies for these clusters are calculated at −0.99 and −1.06 eV respectively (Table 6), while an identical Na–H_2O cluster at the S6R position in the α-cage has a stabilisation energy of −0.87 eV, less than either the 8-ring or β-cage locations. However, when more water molecules are added to the cluster in the S6R position, the water molecules remain in the cluster and the optimum number of water molecules coordinated to the sodium ion is calculated at four. Addition of a fifth water molecule to the sodium cluster has no effect on the stabilisation energy. The sodium cluster with four water molecules in the α-cage is now highly stable in comparison to the other adsorption sites (S6R′ and S8R) with a calculated stabilisation energy of −1.62 eV (Table 6). The sodium ion is sixfold-coordinated by the four water molecules (Na–O_w = 2.29 and 2.41 Å) and two framework oxygens (Na–O(3) = 2.40 and 2.42 Å). Three of the water molecules are located inside the α-cage and are stabilised by their interactions with the framework (H···O(2) = 2.17 Å), while the fourth water molecule is located inside the β-cage, perpendicular to the six-ring window where the sodium ion was located. The preferred adsorption by the sodium ion clusters at the S6R position is in agreement with experimental work by Vance and Seff,[9] who found in their crystallographic study of a hydrated Cs_7Na_5-A crystal that all sodium ions were located in the S6R adsorptions sites. They measured Na^+–O(3) distances of 2.42 Å, in good agreement with our values.

Table 5 Cation locations in siliceous zeolite A

Lowest energy cation locations in siliceous zeolite A

Cation	No. of water molecules	Preferred site
Na^+	4	S6R
Cs^+	4	S8R
Ca^{2+}	4	S6R′
Ba^{2+}	5	S8R
Cd^{2+}	5	S6R′
Sr^{2+}	5	S6R′

Table 6 Defect and stabilisation energies of sodium clusters in siliceous zeolite A

Defect and stabilisation energies of hydrated sodium ions $Na(H_2O)_n{}^{2+}$ in siliceous zeolite A

Site	$n_{\text{water molecules}}$	E_{defect}/eV	$E_{\text{stabilisation}}$/eV
S6R	4	−43.33	−1.62
S6R′	1	−13.63	−0.99
S8R	1	−14.25	−1.06

Conclusions

We have employed atomistic simulation techniques to model the effects of hydration on the structures of siliceous zeolite A and CaNa-A, and on the adsorption behaviour of the extra-framework cations calcium, caesium, sodium, barium, cadmium and strontium in the siliceous structure. As a result we can draw the following conclusions:

Our calculations identified the β-cage as the energetically most favourable adsorption site (S6R′) for water molecules, in agreement with experimental evidence by Pissis and Daoukaki-Diamanti,[20] who found that water molecules in the β-cages of Na-13X were most strongly adsorbed and therefore the most difficult to remove from the zeolite upon dehydration. We therefore suggest that upon dehydration, residual water will be located in the β-cages of zeolite A.

The calculated structural parameters of the partially hydrated CaNa-A structure agree well with the experimental values obtained by Jang *et al.*[54] for a dehydrated CaNa-A zeolite and Adams and Haselden[10] for a dehydrated Ca_5Na_2-A structure, containing approximately four water molecules per full unit cell. The average adsorption energy for the water molecules in CaNa-A was calculated at −0.68 eV, due to interactions between the water molecules' oxygen ions to framework silicon and aluminium ions and extra-framework cations, together with hydrogen-bonding interactions to framework oxygen ions.

The energetically most favourable adsorption sites for the calcium ions in the hydrated siliceous zeolite A were identified as the β-cages (S6R′ positions), in agreement with crystallographic data by Adams and Haselden,[10] who identified the adsorption positions for calcium in the S6R′ sites, while the sodium cations occupied the S6R adsorption sites inside the larger α-cages, which positions were also confirmed by our calculations. The cation locations are governed by the residual water molecules left in the dehydrated zeolite structure. Some of this residual water is located inside the β-cages where they interact with the calcium cations, causing them to move inside the β-cages. However, our calculations showed that it takes approximately three water molecules inside the β-cage for the S6R′-site to become energetically more stable than the S6R adsorption site for calcium, which is quite feasible as Gramlich and Meier,[57] for example, used X-ray measurements to identify an average of 5.5 water molecules inside the β-cages and 22.9 water molecules in the α-cages of a fully hydrated Na-4A structure. The sodium cations do not retain the water molecules as strongly as the calcium cations, which is why the sodium ions are less stabilised in the β-cages, where they lose their water molecules. In the S6R position in the α-cage, however, the sodium ions do retain up to five water molecules in their cluster and this is now the energetically preferred position, in agreement with experimental findings by Vance and Seff.[9]

The results of our calculations show the importance of including the effects of hydration when studying ion-exchange in zeolites. Even dehydrated zeolites retain some water adsorbed within the lattice and we have shown that even a small number of water molecules can influence the preferred adsorption positions of the extra-framework cations. The positions of the extra-framework cations will, of course, be affected by the presence of aluminium and hence, further work will extend these present calculations to the investigation of aluminated zeolite A lattices, where more than one type of cation is present in the structure, as well as Molecular Dynamics simulations of diffusion of a range of cations through hydrated zeolites, in order to obtain activation energies and diffusion pathways.

References

1 B. J. Alloway, *Heavy Metals in Soils*, Blackie and Son Ltd., Glasgow and London, 1990.
2 L. L. Ames Jr., *Am. Mineral.*, 1960, **45**, 689.
3 J. E. Fergusson, *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*, Pergamon Press plc, Oxford, 1991, ch. 8 and 9.
4 S. Kesraoul-Ouki, C. Cheeseman and R. Perry, *Environ. Sci. Technol.*, 1993, **27**, 1108.
5 M. Adabbo, D. Caputo, B. de Gennaro, M. Pansini and C. Colella, *Microporous Mesoporous Mater.*, 1999, **28**, 315.
6 S. M. DePaoli and J. J. Perona, *AIChE J.*, 1996, **42**, 3434.
7 P. Attewell, *Ground Pollution: Environment, Geology, Engineering and Law Report*, E and FN Spon, 1993.
8 I. R. Phillips, *J. Soil Contam.*, 1998, **7**, 191.
9 T. B. Vance jr. and K. Seff, *J. Phys. Chem.*, 1975, **79**, 2163.
10 J. M. Adams and D. A. Haselden, *J. Solid State Chem.*, 1984, **51**, 83.
11 J. R. Agger, N. Pervaiz, A. K. Cheetham and M. W. Anderson, *J. Am. Chem. Soc.*, 1998, **120**, 10754.
12 R. G. Bell, R. A. Jackson and C. R. A. Catlow, *Zeolites*, 1992, **12**, 870.
13 J. Lignieres and J. M. Newsam, *Microporous Mesoporous Mater.*, 1999, **28**, 305.
14 S. Sugiyama, S. Yamamoto, O. Matsuoka, H. Nozoye, J. Yu, G. Zhu, S. Qiu and I. Terasaki, *Microporous Mesoporous Mater.*, 1999, **28**, 1.
15 H. Upadek, B. Kottwitz and B. Schreck, *Tenside, Surfactants, Deterg.*, 1996, **33**, 385.
16 P. J. Davis, H. van Bekkum and E. N. Coker, *J. Chem. Educ.*, 1999, **76**, 469.
17 D. M. Ruthven, *3rd FEZA workshop lecture notes*, Manchester, 6–9 April, 1997.
18 L. T. Markovska, V. D. Meshko and R. T. Kiprijanova, *Korean J. Chem. Eng.*, 1999, **16**, 285.
19 G. H. Thompson, J. M. Murray and J. P. H. Fee, *Ir. J. Med. Sci.*, 1996, **165**, 306.
20 P. Pissis and D. Daoukaki-Diamanti, *J. Phys. Chem. Solids*, 1993, **54**, 701.
21 G. Artioli, J. V. Smith, A. Kvick, J. J. Pluth and K. Stahl, in *Zeolites*, ed. B. Dram, S. Hocevar and S. Paovnik, Elsevier, Amsterdam, 1985, p. 249.
22 L. Leherte, J.-M. Andre, E. G. Derouane and D. P. Vercauteren, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1959.
23 T. Armbruster and M. E. Gunter, *Am. Mineral.*, 1991, **76**, 1872.
24 R. L. Ward and H. L. McKague, *J. Phys. Chem.*, 1994, **98**, 1232.
25 B. Winkler, *Phys. Chem. Miner.*, 1996, **23**, 310.
26 A. Dyer and H. Faghihian, *Microporous Mesoporous Mater.*, 1998, **21**, 39.
27 N. Almora-Barrios, A. Gomez, A. R. Ruiz-Salvador, M. Mistry and D. W. Lewis, *Chem. Commun.*, 2001, 531.
28 F. M. Higgins, G. W. Watson and S. C. Parker, *J. Phys. Chem. B*, 1997, **101**, 9964.
29 S. C. Parker and G. D. Price, *Adv. Solid State Chem.*, 1989, **1**, 295.
30 A. R. Ruiz-Salvador, D. W. Lewis, J. Rubayo-Soneira, G. Rodriguez-Fuentes, L. R. Sierra and C. R. A. Catlow, *J. Phys. Chem. B*, 1998, **102**, 8417.
31 M. Leslie, SERC Daresbury Report DL/SCI/TM31T, 1982.
32 J. H. Harding, Technical Report AERE R 13217, Harwell, 1988.
33 N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.*, 1938, **284**, 431.
34 A. M. Stoneham and J. H. Harding, *Ann. Rev. Phys Chem*, 1989, **1**, 295.
35 M. Cherry, M. S. Islam and C. R. A. Catlow, *J. Solid State Chem.*, 1995, **118**, 125.
36 M. S. Islam and L. J. Winch, *Phys. Rev. B: Condens. Matter*, 1995, **52**, 10510.
37 J. H. Harding, *Water Chemistry of Nuclear Reactor Systems 7*, BNES, London, 1996, vol. 1, p. 309.
38 C. R. A. Catlow, *Proc. Royal Soc. London, Ser. A*, 1977, **353**, 533.
39 R. James, DPhil Thesis, Oxford University, Oxford, 1979.
40 M. J. Sanders, M. Leslie and C. R. A. Catlow, *J. Chem. Soc., Chem. Commun.*, 1984, 1271.
41 R. A. Jackson and C. R. A. Catlow, *Mol. Simul.*, 1988, **1**, 207.
42 G. V. Lewis and C. R. A. Catlow, *J. Phys. C: Solid State Phys.*, 1985, **18**, 1149.
43 J. Purton and C. R. A. Catlow, *Am. Mineral.*, 1990, **75**, 1268.
44 S. C. Parker, PhD Thesis, University of London, London, 1983
45 J. E. Post and C. W. Burnham, *Am. Mineral.*, 1986, **71**, 142.
46 P. J. Lawrence, PhD Thesis, University of Bath, Bath, 1992.
47 N. H. de Leeuw and S. C. Parker, *Phys. Rev. B*, 1998, **58**, 13901.
48 K. P. Schroder, J. Sauer, M. Leslie and C. R. A. Catlow, *Chem. Phys. Lett.*, 1992, **188**, 320.
49 W. M. Meier, D. H. Olsen and Ch. Baerlocher, *Atlas of the Zeolite Structure Types*, Elsevier, London, 1996.
50 R. M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London, 1982.
51 B. Beagley and J. O. Titiloye, *Struct. Chem.*, 1992, **3**, 429.
52 A. Dyer, *An Introduction to Zeolite Molecular Sieves*, John Wiley and Sons Ltd., Chichester, 1988.
53 D. W. Breck, *Zeolite Molecular Sieves*, Wiley, London, 1974.
54 S. B. Jang, S. H. Song and Y. Kim, *Bull. Korean Chem. Soc.*, 1995, **16**, 1163.
55 I. E. Maxwell and A. Baks, *Adv. Chem. Ser.*, 1973, **121**, 87.
56 M. K. Ahn and L. E. Iton, *J. Phys. Chem.*, 1991, **95**, 4496.
57 V. Gramlich and W. M. Meier, *Z. Kristallogr.*, 1971, **133**, 134.
58 R. T. Forbes, P. York, V. Fawcett and L. Shields, *Pharmacol. Res.*, 1992, **9**, 1428.
59 R. L. Firor and K. Seff, *J. Phys. Chem.*, 1978, **82**, 1650.
60 I. Persson, *J. Phys. Sci.*, 1995, **50**, 21.
61 K. A. Blackwell, B. F. Anderson and E. N. Baker, *Acta Crystallogr., Sect. D*, 1994, **50**, 263.