# A molecular dynamics study of the swelling patterns of Na/Cs-montmorillonites and the hydration of interlayer cations

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We report on a molecular dynamics study of the swelling patterns of an Na-rich/Cs-poor montomorillonite and a Cs-montomorillonite. The recently developed CLAYFF force field is used to predict the basal spacing as a function of the water content in the interlayer. The simulations reproduce the swelling patterns of the Na and Cs-montomorillonite, suggesting a mechanism of its hydration different from that of the montomorillonite. In addition, we find that the differences in size and hydration energy of Na and Cs ions have strong implications for the structure and the internal energy of interlayer water. In particular, our results indicate that the hydrate difference in the presence of coexistent Na and Cs has a larger influence on the behavior of a clay–water system. For Na-rich/Cs-poor montomorillonite, the hydration energy values of Na ions and water molecules each have a dramatic increase compared with those in Na-montomorillonite on the interlayer spacing, and the hydration energy values of Cs ions and water molecules decrease somewhat compared with those in Cs-montomorillonite.

**Keywords:** montmorillonite, molecular dynamics simulation, swelling, hydration energy

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## 1. Introduction

The study of the physical and chemical properties of smectite clay minerals is of importance in several areas of fundamental and applied research.[1–6] Their stabilities in aqueous environments have been the subject of a large body of environmental work. Smectite clay minerals are important in a number of geological processes and industrial applications such as catalytic activity, adsorbents in environmental engineering, and waste disposal.[7–12] For example, smectites have been widely used as the barrier materials to fix radioactive nuclides in nuclear waste disposal. In many cases, the capacity of clay to incorporate water or other cations into its structure is of central interest.

Montmorillonite is a 2:1 clay mineral, consisting of two tetrahedral sheets separated by an octahedral sheet. Tetrahedral substitution of Si by Al in two tetrahedral sheets and/or octahedral substitution of Al by Mg in a central octahedral sheet makes the clay platelets negatively charged, which are compensated by interlayer ions. These isomorphic substitutions in octachedral and/or tetrahedral sheets can, for example, yield an excess of negative charge, which is normally compensated with the adsorption of cations onto the surface of the clay to preserve global electroneutrality. Water and other polar solvents can enter into interlayer regions and cause clay-swelling, and water is found to be able to form integer-number molecular layer in smectite hydrate.

As is well known, molecular dynamics (MD) simulation has been widely employed to study the clay–fluid systems and many simulation results are in good agreement with experimental results.[13,14] Although simulations of montmorillonite to $Na^+$ or $K^+$ have been conducted,[15–20] no simulation study has taken into consideration the questions of how and to what extent the presence of $Cs^+$ cations affect the swelling pattern of a natural Na-rich montmorillonite and why the swelling patterns of Na-rich/Cs-poor or Cs-rich montmorillonites are very different from those of Na-saturated montmorillonite. In previous simulations[21–25] with a Cs-rich Wyoming-type montmorillonite, containing $Na^+$ and $K^+$ in the interlayer spaces, the layer spacings and the adsorption of cations were observed experimentally to be very different from those typically for an Na-saturated montmorillonite. Experimental studies have shown that the adsorption rate decreases in the presence of coexistent $Na^+$ and $K^+$ ions.

In order to study this difference, we focus on the simulations of the hydration of a Wyoming-type montmorillonite, containing both $Na^+$ and $Cs^+$ cations or saturated with $Cs^+$ cations in the same interlayer spaces, over a broad range of water content, as described in Section 2. In Section 3, the swelling behaviors of the Na-rich/Cs-poor montmorillonite are compared with those of Na-saturated and Cs-saturated montmorillonites. Moreover, we present a detailed analysis of the interactions between interlayer cations and water (water and water, cations and cations, cation and clay oxygen), which provides additional information necessary for a better understanding of the hydration process and the dehydration process in montmorillonite.

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## 2. Simulation detail

The model clay structure we used in this paper is a Wyoming-like montmorillonite with the unit cell formula $Na_2Cs_1[Al_{14}Mg_2][Si_{31}Al]\ O_{80}(OH)_{16}$. To model a montmorillonite particle, three-dimensional periodic boundary conditions are applied to a simulation box composed of $4(2\times2\times1)$ unit cells, having horizontal dimensions of $Lx \times Ly$ ($\sim 5$ Å$^2\times \sim 7$ Å$^2$, 1 Å = 0.1 nm) and representing halves of two montmorillonite layers with an interlayer space in between.

All molecular dynamics simulations are carried out by using the LAMMPS package,[26] and the recently developed CLAYFF force field[27] is used to describe the interatomic interactions. The CLAYFF has been shown to be highly effective in simulating the hydrated and multicomponent mineral systems and their interfaces with aqueous solutions. The interatomic potential in the CLAYFF force field is derived from parametrization incorporating structural and spectroscopic data for a variety of simply hydrated compounds. In order to permit the simulation of a disordered clay system, all atoms are represented as point charges and allow complete translational freedom within this force field framework. Metal–oxygen interactions are based on a simple Lennard–Jone (6-12) potential combined with electrostatics. The empirical parameters are optimized on the basis of known mineral structures, and the partial atomic charges are derived from periodic density functional theory (DFT) quantum chemical calculations of simple oxide, hydroxide, and oxyhydroxide model compounds.[27] Oxygen and hydroxyl charges vary with nearest-neighbor cation substitution. The bond stretch and angle bend terms with flexibility of the OH are represented in the clay lattice as harmonic terms. For the water behavior, the flexible version of the single point charge (SPC) model is used.[28] Compared with the water models (e.g., TIP4P, BJH), the SPC model is relatively simple in having partial charges centred directly on each of three atoms, and the short-range interactions represented by a simple Lennard–Jones term. The simulation is carried out for 1 ns at 300 K and 1 atm (1 atm = $1.01325\times10^5$ Pa) by using an isobaric-isothermal (NPT) ensemble in which the temperature and pressure are maintained via a Nose–Hoover thermobraostat.

All the simulations are first run for a total of $2\times10^5$ time steps to reach equilibrium configurations before a statistical average is taken. Once the equilibrium is achieved, production runs of $10^5$ time steps in total are performed with averages accumulated in blocks of $10^5$ time steps.[29] We chose to output the atomic positions every 2.0 ps during production runs. From these data, radial distribution functions and atomic density profiles are calculated.

## 3. Results and discussion

### 3.1. Swelling pattern and interlayer structures

Calculated layer spacings for Na-, Na+/Cs-, and Cs-montmorillonites with the same mineral chemical formula are given each as a function of water content in Fig. 1. The Na-montmorillonite simulated curves compared with experimental measurements[30] are very similar. Comparing the curves in Fig. 1, we see that the presence of the Cs ion has a dramatic effect on the interlayer spacing. They can differ by as small as 2 Å for a given water content. Taking into account that Cs ions are larger than Na ions, these results indicate that the size of the cation has a larger influence on the behavior of the clay–water system. In Ref. [8] it is shown that for Na- and Ca-montmorillonites, their valences have larger influences on the behavior of clay–water system. Figure 1 indicates that the Na-montmorillonite exhibits an overall smaller interlayer space than the Na+/Cs- and Cs-montmorillonites as a function of water content, and the predicted basal spacing and trend of Na+/Cs-montmorillonite are similar to those of the Cs-montmorillonite for three types of montmorillonites. In addition, our simulation summarizes the basal spacing values of dry montmorillonite and the plateaus from both simulations and measurements in the literature. For the dry state (there exist no water molecules in the interlayer), our simulations yield $d$-spacing $D = 10.07$ Å for Na-montmorillonite, $D = 10.64$ Å for Cs-montmorillonite, and $D = 10.72$ Å for Na+/Cs-montmorillonite. The experimental values that have been reported by Boek *et al.*[31] for the dry state of two $Na^+$-montmorillonites are both $D = 10.17$ Å similar to ours.

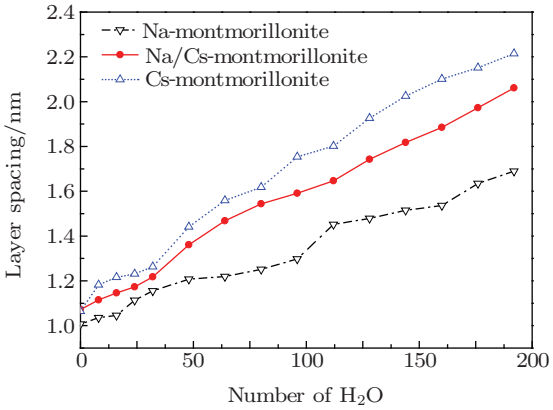



**Fig. 1.** (color online) Simulated layer spacings of the Na-, Na-rich/Cs-poor, and Cs-montmorillonite clays versus water content.

We present in Fig. 2 a detailed description of the structure of the Na+/Cs-montmorillonite. This figure gives a clear insight into the position of the ions, water molecules within the clay spacing and depicts the density of the Na+/Cs-montmorillonite along an axis perpendicular to the clay sheet. Our simulations for Cs-Wyoming montmorillonite indicate

that the Cs cations are surrounded by water molecules for most water content values. As illustrated in Fig. 2 the Cs cations are mostly distributed in the central part of the interlayer, where they are fully surrounded by water molecules. Figure 2 displays the density profiles of the water oxygens and the cations for three values of the water content values, namely, $N_w = 24$, $N_w = 64$, and $N_w = 128$. Note that for $N_w = 24$ the interlayer develops only one layer of Cs, whereas two layers of Cs appear for $N_w = 64$. For the larger value of water content, i.e., $N_w = 128$, the density profile of the water oxygens exhibits four pesks indicating the formation of four layers of water. In particular, our results indicate that the Cs cations have a larger influence on the behavior of clay–water system in the Na+/Cs-montmorillonite.

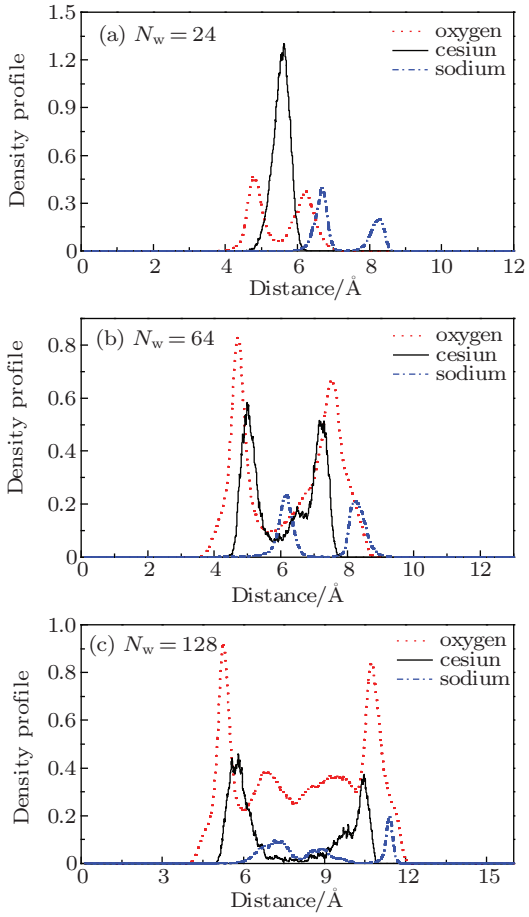



**Fig. 2.** (color online) Density profiles for water oxygens and cations at water content value $N_w = 24$ (a), 64 (b), and 128 (c).

### 3.2. Structure of interlayer water

To allow a more detailed analysis of the effect of interlayer cations on interlayer water, Figs. 3 and 4 compare the water structures of three-hydrates of Na-, Na+Cs-, and Cs-montmorillonites, which are represented by the water oxygen–water oxygen (O–O) radial distribution functions (RDFs). The strong dependence of water structure on hydration ability of interlayer cation can be well seen, especially in the one hydrate state, owing to the different positions of the first-neighbor peaks of the O–O RDFs. For the Na-montmorillonite, the first-neighbor peaks are centred near 2.74 Å in the three-hydrates. For the Na+Cs-montmorillonite, the first-neighbor peaks are centred near 2.73 Å in the three-hydrates. For the Cs-montmorillonite, the first-neighbor peaks are centred near 2.76 Å in the three-hydrates.

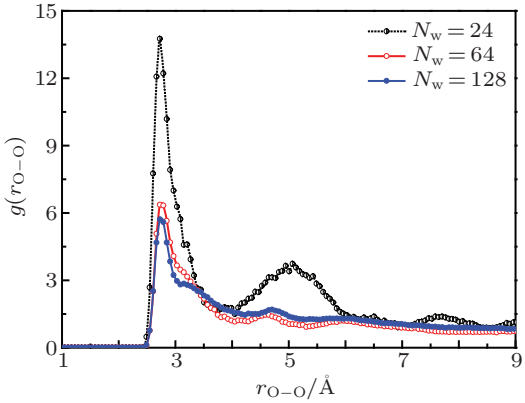



**Fig. 3.** (color online) O–O RDFs in the hydrate states for Na-montmorillonite at the water content values of 24, 64, and 128.

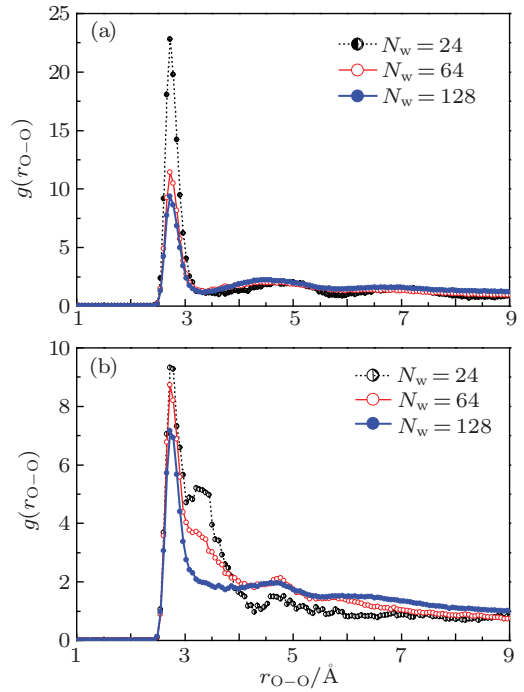



**Fig. 4.** (color online) O–O RDFs in the hydrate states for Na/Cs-montmorillonite (a) and Cs-montmorillonite (b) at the water content values of 24, 64, and 128.

### 3.3. Interaction between interlayer cations and water

As a prerequisite, such a detailed analysis requires the interlayer cation–water oxygen RDFs, which are presented in Figs. 5, 6, and 7 for the examples of Na-, Cs-, and Na+Cs-montmorillonites. For the Na-montmorillonite, the first-neighbor peaks are centred near 2.34 Å (Fig. 5) in these

three-hydrates. For the Cs-montmorillonite, the first-neighbor peak shifts to 3.56 Å in one-hydrate, but is centred near 3.62 Å in two- and three-hydrates (Fig. 6). It is apparent that the shift in one-neighbor peak occurs because all water molecules are in the hydration shells of Cs cation in this state, and their hydrate energy values are very smaller than those of Na cations. These results indicate that the valences of the cations and their sizes more greatly affect the behaviors of clay–water systems.

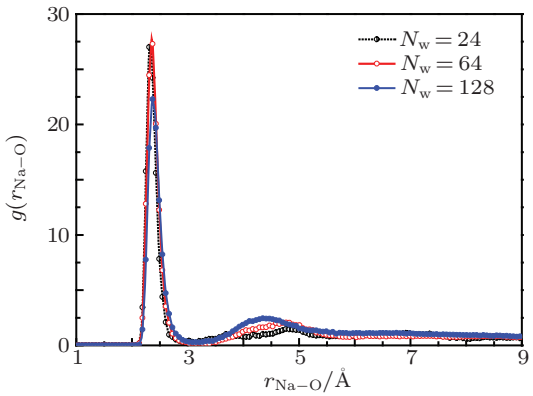



**Fig. 5.** (color online) RDFs between ions and water oxygen atoms for Na-montmorillomite at water content value $N_w = 24$, 64, and 128.

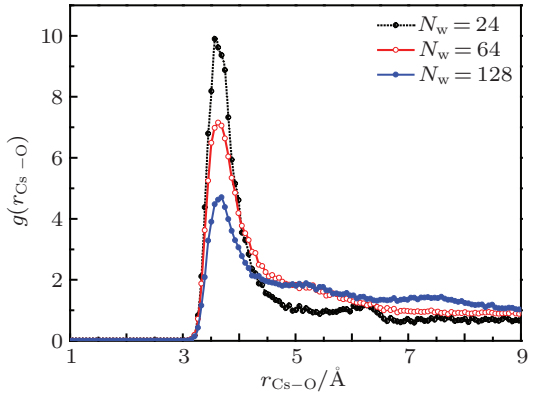



**Fig. 6.** (color online) RDFs between ions and water oxygen atoms for the Cs-montmorillomite at water content value $N_w = 24$, 64, and 128.

In Fig. 7, the first-neighbor peaks are centred near 2.31 Å in the three hydrates for Na ions. For Cs ions, the locations of the first maxima are all centred near 3.63 Å. The locations of the first maxima in these RDFs ($\sim$ 2.31 Å for Na and $\sim$ 3.63 Å for Cs) are slightly larger than the first peaks of Na- and Cs-montmorillonite. Considering the fact that Na ions and Cs ions have the same charge quantity, these results indicate that the Coulombic interaction between the cations has an effect on the behaviors of clay–water systems. These results show that when hydrate is within clays, $Na^+$ behaves as in bulk water. Similar results to ours were obtained for the hydrated $Na^+$-montmorillonite system using Monte Carlo simulations.[32] Interestingly, the hydration behaviors of $Na^+$ and $Cs^+$ within confined environments are shown to be critical for the conductivity properties of these materials. Finally, compared with the big alkali cations, $Cs^+$ has lower hydration energy, which explains the greater distance of the first hydration sphere.

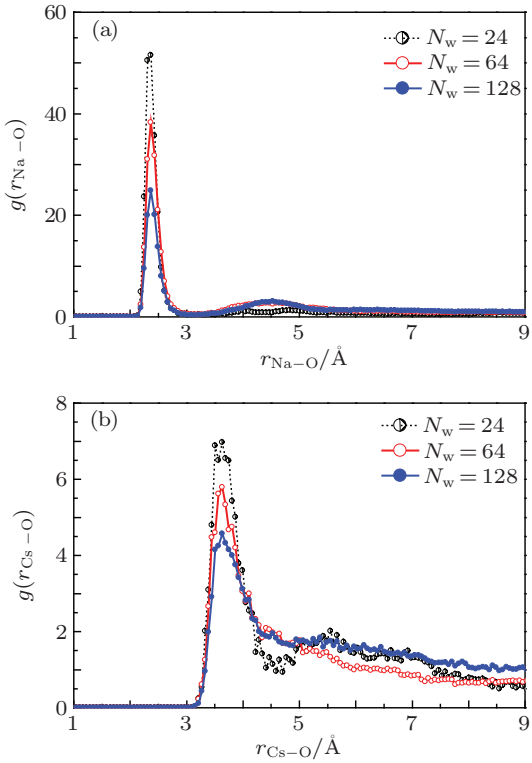



**Fig. 7.** (color online) RDFs between ions and water oxygen atoms for Na/Cs-montmorillomite at water content value $N_w = 24$, 64, and 128.

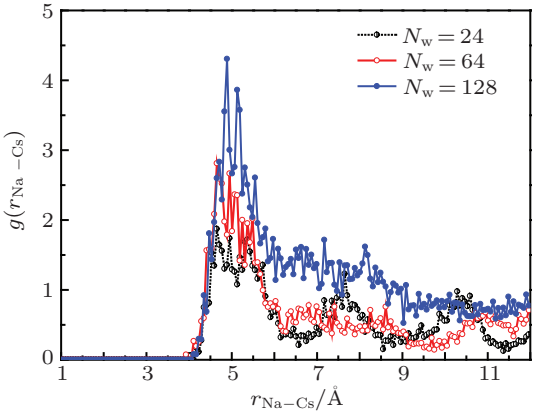



**Fig. 8.** (color online) RDFs between sodium and cesium atoms for Na/Cs-montmorillomite at water content value $N_w$=24, 64, and 128.

As is well known, the interaction of the clay cations with their interlay cations depends on non-bonding electrostatic and van der Waals potentials. As seen in Fig. 8, The RDF between the Na cations and the Cs clearly shows the interaction. By contrast, we can see that this structure tends to appear with the increase of water content. This can be explained as follows. The Na cations interact weakly with the

Cs cations in interlayer spacings. However, in the case of hydrated clay, the cations are solvated by water and are more likely to diffuse within the clay galleries. As interlayer water content increases, in the two and three-hydrate states of Na-/Cs-montmorillonites, these peaks broaden and become similar to those in bulk liquid.

## 4. Conclusions

In this work we perform a molecular dynamics computer simulation of $Na^+$-, Na+Cs-, and $Cs^+$-saturated montmorillonites using the recently developed CLAYFF force field. First, we present the swelling patterns of $Na^+$-, Na+Cs-, and $Cs^+$-montmorillonites and compared them with previous experimental and theoretic results. We find that Ca-montmorillonite exhibits less swelling than Na- and K-montmorillonites for a given water content. Second, we compare K-saturated clays and Na-, Ca-saturated clays, and find that the K, Ca cations each have a large influence on the swelling, with respect to that predicted for the Na cation. These simulations clearly show that the cations are solvated by water in the present work. In a future investigation, we plan to compute the elastic properties and the diffusion coefficients of the water molecules and cations for these systems.

The results of the present study show that the higher the hydration energy of the interlayer cation, the greater the difference is. Furthermore, the hydration energy of the Ca cation is higher than that of the Na cation, especially the K cation. Furthermore, for the dehydrated clays, the comparison of RDF between the cations and the clay oxygen atoms (Fig. 7) shows that the K cations interact strongly with the clay sheet. However, for the hydrated clays, Fig. 7 shows clearly that the Ca cations interact strongly with the clay sheet.

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