Clay Swelling

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A Thermodynamic Understanding of Clay-Swelling Inhibition by Potassium Ions**

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Smectites are important in geological processes and have industrial and engineering applications.[1–3] They consist of negatively charged clay platelets and interlayer counterions. Water can enter the interlayer space and force the clay platelets apart, causing clay swelling.[2,4] Generally, this swelling behavior can be divided into two types: intracrystalline swelling, with a limited amount of adsorbed water, and osmotic swelling, which involves a much larger amount of water. This unique property has resulted in numerous studies because of its direct applicability in civil and petroleum engineering.[3,5] It has been found, for instance, that K-smectites do not expand to the osmotic regime and form crystalline hydrates even in aqueous suspension.[6,7] Thus, the K^+ ion can be used as a swelling inhibitor in drilling mud to prevent the well-bore collapse typically caused by the macroscopic swelling of Na-smectites.[7] However, the fundamental mechanisms of the inhibition of clay swelling by K^+ ions are not clear,[8–10] and the striking stability of the single-layer K-hydrate cannot yet be explained.[10,11]

Herein, we employ molecular simulations to study the thermodynamic constraints imposed by K^+ ions on clay-swelling inhibition, in comparison with the contrasting case of Na^+ ions. We find that the single-layer hydrate of K-smectites actually corresponds to the global minimum of the swelling energy curve and that expansion to the osmotic regime is, therefore, energetically unfavorable. In contrast, the double-layer state of Na-smectites corresponds to the global minimum of the energy curve, and osmotic swelling is easy to achieve. Furthermore, we examine the microstructure of the single-layer K-hydrate and find, for the first time, that the K^+ ions are all tightly confined in coordination cages above surface hexagons, which leads to this surprising stability.

We used Arizona montmorillonite as the smectite model.[12] Constant number pressure temperature (NPT) molecular dynamics simulations were performed using the LAMMPS code[13] to mimic the experimental environments (298 K, 1 atm). Clayff, which incorporates the simple point charge (SPC) water model, was used as the force field.[14] Details are given in the Supporting Information.

It has been shown that the energy contribution to free energy dominates clay swelling and that the entropy term plays only a secondary role.[15–17] The local minima of the swelling energy curve correspond to stable states, namely the single-, double-, or triple-layer hydrates. Hence, the relative stabilities of different states can be determined from Equation (1):[15,16]

$$Q = \langle U(N)\rangle - \langle U(N^0)\rangle - (N-N^0)U_{\mathrm{bulk}} \quad (1)$$

$\langle U(N)\rangle$ is the average potential energy of the hydrate with water content N, N^0 is the water content of the reference state, and U_{bulk} is the internal energy of bulk water. In this study, we selected the state with 425 milligrams of water per gram of clay as the reference. Q is often referred to as the "immersion energy", although it is difficult to compare the calculated results directly with experimentally measured data, owing to the formation of mixed-layer hydrates and external surface contributions.[15] The energy term can also be expressed as the "hydration energy" [Eq. (2)], where $\langle U(0)\rangle$ is the average potential energy of the dry clay.[15]

$$\Delta U = (\langle U(\mathrm{N})\rangle - \langle U(0)\rangle)/N \quad (2)$$

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The hydration energy is an integral quantity and can be compared with the calorimetry data renormalized by adding the condensation heat of water.[9,18]

Table 1 shows an encouraging agreement between the simulated and experimental basal spacings. Figures 1 and 2 display the calculated hydration and immersion energies,

Table 1: A comparison of simulated basal spacings and measured ranges.

	Sim. [Å]	Exp. [Å]
Single-layer (K)	12.49	11.8–12.6[11,19,21,22]
Double-layer (K)	15.61	15.2–16.0[11,19,21]
Single-layer (Na)	12.19	12.2–12.6[19,21–24]
Double-layer (Na)	15.17	15.0–15.55[19,21–24]
Triple-layer (Na)	18.24	18.1–19.0[24]

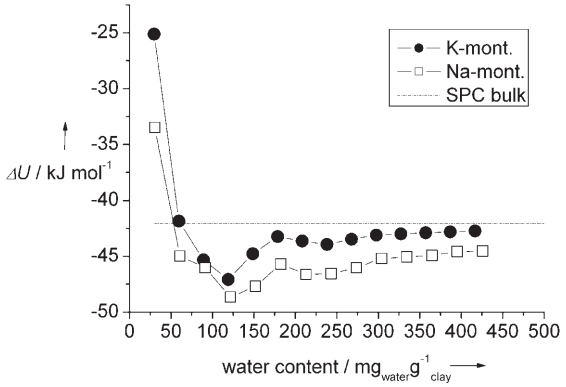

Figure 1. Hydration energy ΔU of K- and Na-montmorillonite.

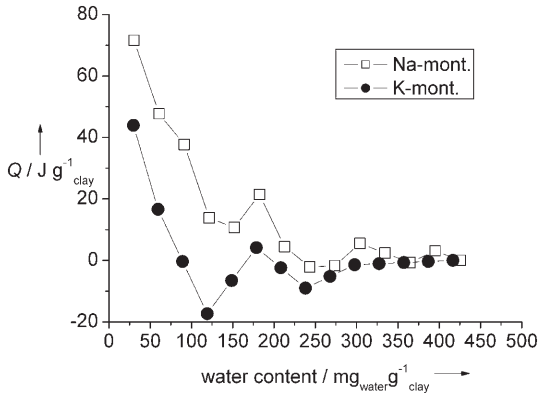

Figure 2. Swelling immersion energy Q of K- and Na-montmorillonite.

respectively. The simulated hydration energy of single-layer K-hydrate is $-47.0\ kJ\,mol^{-1}$ (approximately 120 milligrams of water per gram of clay), similar to the experimental value of $-45\ kJ\,mol^{-1}$ (approximately 100 milligrams of water per gram of clay).[9,19] The simulated value of single-layer Na-hydrate ($-48.6\ kJ\,mol^{-1}$) falls within the experimental range (-52 to $-48\ kJ\,mol^{-1}$).[4,20] These findings confirm that our simulations can reproduce both basal spacings and calorimetry data and thus suggest the reliability of our subsequent analyses.

Two local minima occur on the hydration energy curve for Na-montmorillonite, with the one with lower water content being the global minimum. Three local minima appear on the immersion energy curve, of which the double-layer state, which is similar to the triple-layer state in energy, is the global minimum. This result is exactly consistent with the experiments: Na-smectites prefer expanded states (double-layer, triple-layer, and fully expanded) to a single-layer hydrate.[6,7] The swelling energy can, therefore, reveal the relative stabilities of the different hydrate states. For K-montmorillonite, the swelling immersion energy curve presents two local minima, which correspond to single- and double-layer states, respectively. The single-layer state is the global minimum, with an energy much lower than that of the double-layer state. It is, therefore, more stable than the double-layer state. There is no local minimum at higher water contents; therefore, no triple-layer K-hydrate is formed even under aqueous conditions.[9]

The hydration energy approaches that of bulk water as the water content increases (Figure 1);[8,15] therefore, the hydration energy curve allows us to study the hydration potential at relatively high water contents. Thus, when the water content of Na-montmorillonite exceeds 370 milligrams of water per gram of clay (i.e. the triple-layer state), its hydration energy is still much lower than that of bulk water, which indicates that further swelling is still strongly preferred. For K-montmorillonite, however, when the water content is higher than the range of the double-layer hydrate, the hydration energy is very close to that of bulk water; therefore, its osmotic swelling is inhibited energetically. This means that K-hydrates never expand fully, even in aqueous suspension, whereas Na-hydrates do.

The interlayer structure and dynamic behavior of the single-layer K-hydrate were also investigated. The water molecules form a single layer and the K^+ ions bind to the clay surfaces (Figure 3a). A detailed analysis shows that all the K^+ ions are centered above the adjacent six-membered rings and present a cage-like coordination structure in which each K^+ ion is coordinated to six oxygen atoms of the hexagonal ring and five oxygen atoms from water (Figure 3b). Interestingly, two neighboring ions can share a water molecule. To study the mobility of the ions, a long simulation of 3500 ps was run. No macroscopic diffusion can be identified in the resulting mean square displacements (MSD; Figure 4).[25] The movement trajectories of the ions clearly show that every ion is restricted within a very limited space above the hexagon and that their actual motions are below the detectable limits of both length and time (Figure 5).[25] In other words, the K^+ ions are trapped and immobile within the coordination cages. We repeated the simulation with different initial states and always obtained the same coordination structure, which is similar to one of the patterns found on an open mica surface but without the reported mobility.[26] The fixed ions effectively screen the negative charges of the clay sheets so that further swelling is inhibited, just as neutral clay minerals (e.g. pyrophyllite) never swell. This microscopic mechanism verifies previous suggestions,[8,27] and clarifies the inherent "hydrophobicity" of K^+ ions.[28] The stable cage-like coordination structure indicates that K^+ ions strongly prefer binding to the clay

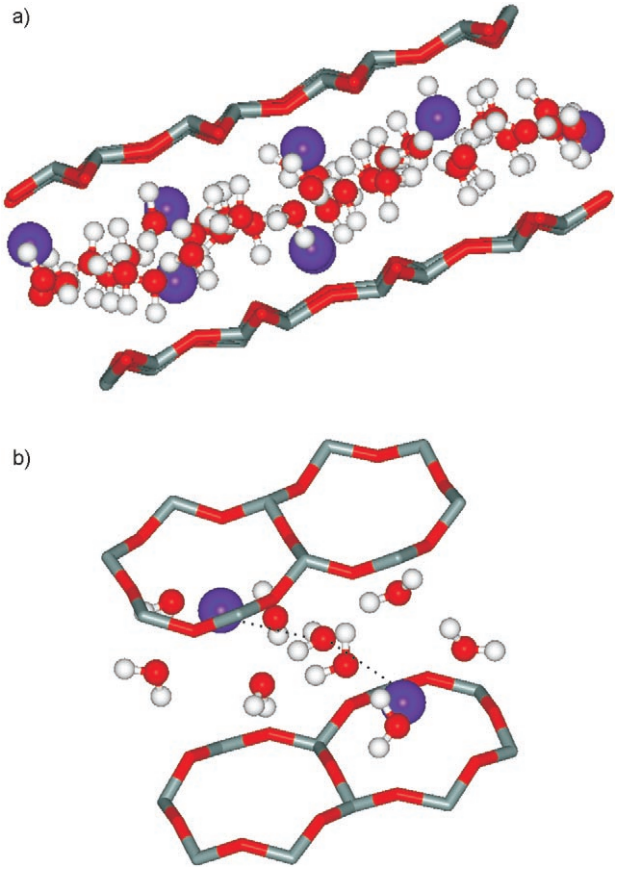

Figure 3. a) A snapshot of the equilibrated single-layer K-hydrate. b) An amplified snapshot of the cage-like coordination structures of two K^+ ions; dotted lines denote the shared water molecule. Sticks: clay framework, blue spheres: K, red spheres: water O, white spheres: water H.

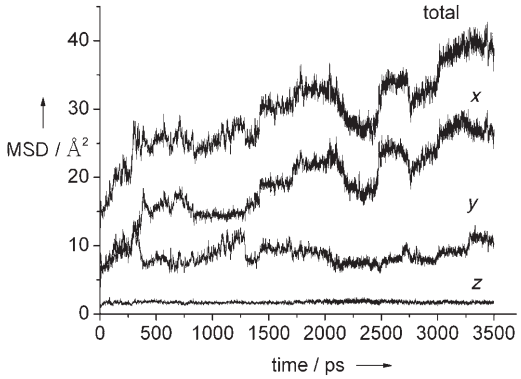

Figure 4. Mean square displacements (MSD) of K^+ ions during a simulation of 3500 ps in a single-layer K-hydrate. The *x*, *y*, and *z* components, and the total are plotted.

rather than being solvated, which results in the surprising stability of the single-layer hydrate.

In summary, we have presented a fundamental understanding of the inhibition of clay swelling by K^+ ions. The most stable single-layer state is found to correspond to the global minimum of the swelling energy curve, and the osmotic swelling is inhibited energetically. We have also found a novel microstructure of this single-layer K-hydrate that is responsible for the surprising stability: the K^+ ions are all fixed in coordination cages composed of surface oxygen atoms and water molecules.

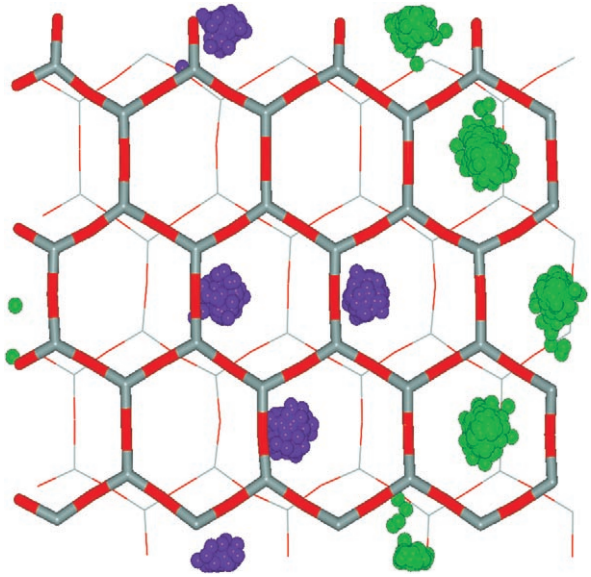

Figure 5. Trajectories of K^+ ions after 1000 ps in the simulation of a single-layer K-hydrate. The stick and line frameworks represent the upper and lower clay surfaces, respectively. The green and blue spheres represent K^+ ions close to the upper and lower surfaces, respectively. Each "cluster" represents the sampled trajectories of a single ion. The motions are so restricted that the ions can be viewed as being stationary.

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