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Driving force for the swelling of montmorillonite as affected by surface charge and exchangeable cations: A molecular dynamic study

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ABSTRACT

Swelling of montmorillonite (MMT) is a nonnegligible factor in many industrial processes owing to its great ability to absorb water in interlayer space. It is not easy to determine whether the exchangeable cations or the MMT layers interacts much stronger with water molecules to provide the dominant driving force for the swelling of MMT. In this work, driving force for the swelling of montmorillonite as affected by surface charge and exchangeable cations has been investigated through molecular dynamics simulations (MDs). The adsorption energy between water molecules and MMT layers and between interlayer cations and water molecules was calculated to qualitatively characterize the driving force for the swelling of MMT, and higher negative adsorption energy means greater driving force. It is found that the adsorption energy between interlayer cations and water molecules are far higher than that between MMT layers and water molecules. Thus, it is the exchangeable cations that provide the dominant driving force for MMT to swell. Besides, it is observed that interlayer cations with stronger hydration ability (Mg > Ca > Na > K) have more negative adsorption energy to water molecules, which indicates that the stronger the hydration ability of exchangeable cations the greater contribution they make to the total driving force for the swelling of MMT.

Introduction

Montmorillonite is a typical clay mineral with one alumina octahedral sheet sandwiched by two silica tetrahedron sheets [1]. Isomorphous substitutions in the crystal structure of the smectite clay are pervasive in a natural state, such as substitution of Al^{3+} in octahedral sites by Mg^{2+} and Si^{4+} by Al^{3+} in tetrahedral sites, and thus result in negatively charged layers [2]. Exchangeable cations, such as Na^{+}, K^{+}, Ca^{2+}, or Mg^{2+}, are introduced in the MMT interlayer space to compensate the negative charge [3]. When exposed to the water, MMT can absorb enough water to enlarge its volume greatly owing to the presence of interlayer cations and negatively charged layers [4,5]. Swelling of MMT is a ubiquitous phenomenon and plays an important role in various industrial processes or fundamental research activities. In the pharmaceutical field, the swelling and adsorption properties of MMT promote drug delivery systems to improve the pharmaceutical disadvantages of drugs, such as low solubility and poor pharmacokinetic properties [6]. In plate-boundary faults, swelling of smectite produces high pressure and exerts a key influence on the development of decollement fold [7].Besides, the swelling of MMT can be applied to the exfoliation of MMT and then used as two dimensional materials, and show excellent properties [8–10].On the other hand, in the oilfield, swelling of MMT leads wellbore instability problems and causes an adverse influence on drilling operations when using water-based drilling fluids [11]. Understanding the MMT swelling is thus of great importance for a better application of montmorillonite in many fields.

Many researches have investigated the swelling of MMTs by different means to understand and determine their swelling properties. Ferrage et al applied XRD to investigate the interactions between cations and water molecules in MMT layers and determined the MMT interlayer structure for 0–3 planes of interlayer H_2O over a limited RH range [12]. Salles et al studied the specific surface area evolution during the hydration process by the experimental adsorption isotherms of swelling solids and discriminated the influence of the cations [13]. However, there is no experimental technique to offer the possibility to unambiguously discriminate the driving force for the swelling of MMT. Meanwhile, it is inferred that MMT layers with negative charge also give rise to the swelling of MMT [14]. Thus, it is difficult for experimental method to determine whether the interlayer cations or the negatively charged layers provide the driving force for the swelling of

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MMT. Molecular simulation, as a powerful tool for theoretical research, can provide an insight into structure and properties of the bulk system in microscopic aspect based on the numerical integration of Newton's equation of motion and the basic principle of statistical mechanics [15]. This method allows to observe the swelling of MMT in a molecular level and to estimate the hydration energy, interlayer spacing and so on [16]. Boek et al. applied Monte Carlo simulation to study a series of Na-MMTs with different water molecules, which showed that the interlayer spacing was a function of water content and it increased with the increase in water molecules, in qualitative agreement with experimental data [17]. Yi et al. applied MDs to investigate the surface wettability of MMT (0 0 1) surface and discovered the dominant role exchangeable cations play in determining the surface wettability behaviors [18]. Zhang et al. studied the swelling properties, hydration behaviors and mobility of the interlayer species of (Na_x, Ca_y)-MMTs with different water contents through MDs and obtained predicted results [19]. Yi et al. applied molecular dynamic simulations to investigate the interactions between water molecules and MMT to reveal the thickness of hydration shell on MMT surface [20]. Cygan et al. explained MDs could be used to the study about layered minerals from the theoretical level [21]. As a result, molecular dynamic simulation is a valuable tool to describe the interactions of clay-water-cations systems.

Many researches have investigated the influence of exchangeable cations on the swelling of MMT by molecular simulation technique [22–24]. Young and Smith explored the crystalline swelling and hydration characteristics of Na-, Cs-, Sr-MMTs by molecular dynamic simulation and revealed that interlayer spacing for the three MMTs mainly depended on the size and charge of the exchangeable cations in the interlayer space [25]. Ferrage et al. held similar views and applauded that the valence and hydration properties of interlayer cations have a considerable influence on the swelling of the crystal structure [26]. It is universal acknowledged that interlayer cations play an important role in the swelling of MMT. Nevertheless, comprehensive study of the driving force for the swelling of MMT as affected by surface charge and exchangeable cations is still lack. Considering that MD is suitable for the study of interactions among clay, cations and water, the driving force for the swelling of MMT effected by surface charge and exchangeable cations has been investigated through MD method in this work. The objective is to reveal whether the charged MMT layers or the exchangeable cations that dominate the driving force for the swelling of MMT.

Simulation details

The atomic structure model of montmorillonite (MMT) was constructed using Material Studio 8.0. The space group generally used to represent MMT was C2/m [27]. The fundamental cell parameters used in our simulations were originated from empirical models introduced by Boek [23]: a = 0.520 nm, b = 0.897 nm, and the c value depends on the water content in the interlayer [28], with $\alpha = \gamma = 90.000^{\circ}$, $\beta = 98.866^{\circ}$. As shown in Fig. 1, the Na-MMT surface model comprises of two layers and each layer possesses 4 × 4 unit cells. Meanwhile, net layer charge per formula unit (ξ) is in the range of 2/16–10/16 in accordance with the actual fact that natural MMT surface charge (ξ ~ 0.2–0.6). For example, when 2 isomorphous substitutions (one substitution of Al^{3+} in octahedral sites by Mg^{2+} and Si^{4+} by Al^{3+} in tetrahedral sites) are introduced into the MMT layer surface composed of 16unit cells, the ξ of this MMT layer surface equals to 2/16. MMT surface models were built with different surface charge and isomorphous substitutions were randomly distributed following the Lowenstein rule [29]. The negatively charged MMT layer surface compensated by Na^{+} was named as Na-MMT, and Na-, K-, Mg- and Ca-MMT surface models were constructed separately to study the effect of cations types on the driving force for the swelling of MMT. Finally, the hydrated models of MMT consisting of 1, 2, 3 layers of water molecules were built through sorption module, respectively.

All simulation work in this paper was accomplished based on the Forcite module. The Geometry Optimization task was carried out on Na-, K-, Mg- and Ca-MMTs systems and each system consisted of a series of simulations with surface charge varying from 2/16 to 10/16, respectively. Optimizing cell was chosen and all the molecules were allowed to move. Interatomic interactions were described by the CLAYFF force field, which has turned out to be suitable for simulation of hydrated, multicomponent mineral systems and their interfaces with aqueous solution [30]. All atoms are regarded as point charges and are allowed complete translational freedom within this force field framework [31]. The single point charge (SPC) water model is incorporated to CLAYFF force field and used to simulate the water-water interaction [32]. The short-range van der Waals interaction was calculated based on atom-based method, and the long-range Electrostatic interaction was calculated by the Ewald summation method.

After all simulation work, the resulted equilibrium configurations of MMT-water structures were obtained. XRD powder diffraction was applied to acquire the interlayer spacing of MMT by the Reflex/Powder Diffraction module. The interlayer spacing was calculated according to Bragg equation:

$$2d\sin\theta = n\lambda \quad (1)$$

where d is interlayer spacing, n is the class of diffraction peak, n = 1, 2, 3…, λ is the wavelength of copper, $\lambda = 0.154$ nm.

Finally, the Forcite module was used to calculate the energy among MMT surface, interlayer cations, water molecules. The adsorption energies of MMT/Water, Cations/Water and C-MMT/Water were calculated to analyze the interaction among water molecules, MMT surface and exchangeable cations, which are defined by Eqs. (2)–(4), respectively. Theη was applied to assess the contribution of cationic hydration to the total driving force for the swelling of MMT, which is defined by Eq. (5).

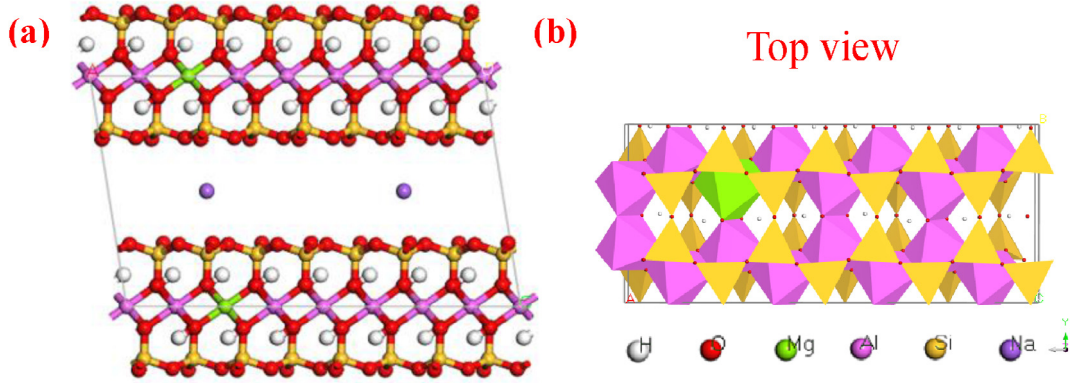

Fig. 1. Supercell model of Na-MMT.

$$\Delta E_{MMT/Water} = E_{MMT/Water} - (E_{MMT} + E_{Water}) \quad (2)$$

$$\Delta E_{Cations/Water} = E_{Cations/Water} - (E_{Cations} + E_{Water}) \quad (3)$$

$$\Delta E_{C-MMT/Water} = E_{C-MMT/Water} - (E_{C-MMT} + E_{Water}) = \Delta E_{MMT/Water} + \Delta E_{Cations/Water} \quad (4)$$

$$\eta = \Delta E_{Cations/Water}/\Delta E_{C-MMT/Water}\Delta 100\% \quad (5)$$

where the $\Delta E_{MMT/Water}$ is the adsorption energy between MMT (exclude the exchangeable cations) and water molecules, and the $\Delta E_{Cations/Water}$ equals the adsorption energy between exchangeable cations and water molecules (also called hydration energy). $\Delta E_{C-MMT/Water}$ means the total adsorption energy between MMT (include the exchangeable cations) and water molecules. $E_{MMT/Water}$ and $E_{Cations/Water}$ reflect the energy of MMT-water system and cations-water system. The E_{MMT}, E_{Water} and $E_{Cations}$ mean the energy of MMT surface, water molecules and exchangeable cations, respectively. And η represents the percentage of cationic hydration energy ($\Delta E_{Cations/Water}$) to the total adsorption energy ($\Delta E_{C-MMT/Water}$) in the swelling of MMT.

Results and discussion

Swelling process of montmorillonite

In order to investigate the swelling process of MMT, the models are constructed by introducing 32, 64, 96 water molecules into the MMT interlayer space according to previous research [33]. As shown in Fig. 2, when 32 water molecules are absorbed into the Na-MMT interlayer, one layer of water appears between MMT layers. And two or three layers of water formed when introduced 64 or 96 water molecules into the Na-MMT interlayer space. The layer spacings are calculated by Eq. (1) and the results of d are 1.24, 1.54, 1.78 nm, respectively. It is apparent that the layer spacing (d) experiences an increase with the increase of water and meanwhile the similar conclusion could be drawn from K, Mg, Ca-MMT. Considering that the simulated results agree well with the practical results, it is reasonable to investigate the driving force for the swelling of MMT by using these models.

Swelling of montmorillonite affected by surface charge

To further understand the effect of surface charge on the driving force for the swelling of MMT, the interactions between MMT surface and water molecules have been investigated. In this section, 32, 64 or 96 water molecules are introduced to Na, K, Mg, Ca-MMT interlayers with surface charge in the range of 2/16–10/16. Adsorption energies of MMT/Water and Cations/Water are calculated to assess the interactions among MMT surface, cations and water molecules. According to Fig. 3, when 2 isomorphous substitutions occur on Ca-MMT composed of 16unit cell (ξ = 2/16), the adsorption energy ($\Delta E_{Ca/H2O}$) between

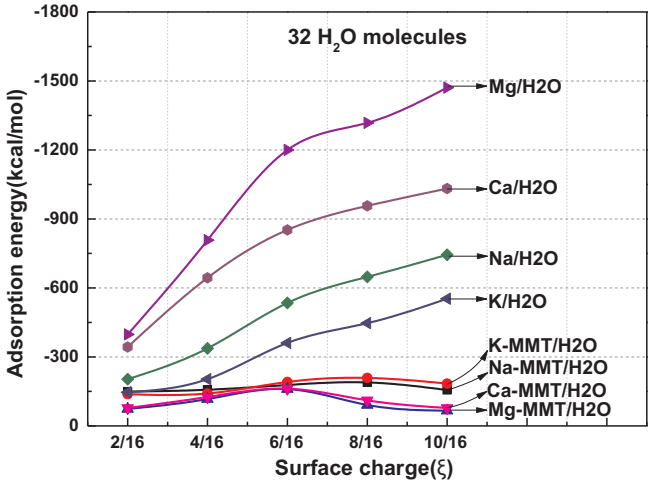

Fig. 3. Adsorption energy of MMT/Water and Cations/Water on Na, K, Mg, Ca-MMT with 32 water molecules in the interlayer and different surface charge.

Ca^{2+} and water molecules is −343.5 kcal/mol, while the adsorption energy is −644.1 kcal/mol when ξ = 4/16. And Ca^{2+} in the interlayer have much more negative adsorption energy to water molecules with the increase of surface charge. The similar results can be also obtained by Na-, K-, Mg-MMTs, which can be ascribed to the increase of interlayer cations. The number of interlayer cations increase correspondingly with the increase of surface charge, and more interlayer cations mean more adsorption energy to water molecules.

When it comes to the adsorption energy ($\Delta E_{MMT/Water}$) between MMT (exclude the exchangeable cations) and water molecules, it is clear from the Fig. 3 that adsorption energy ($\Delta E_{MMT/Water}$) shows signs of leveling off, to some extent, with the increase of surface charge. Figs. 4 and 5 display MMT layers have a slowly increasing negative adsorption energy to water molecules. With the increase of surface charge, MMT layers have more isomorphous substitution sites, making them easier to adsorb water than before. On the other hand, it is observed that the hydration energy of water molecules by MMT decreased when the surface charge exceeded 6/16, shown in Fig. 3. Interlayer cations could have a priority to surface charge and thus water molecules, in a lower water content, tend to interact with interlayer cations firstly. Compared to MMT layers with negative surface charge, exchangeable cations always have more negative adsorption energy to water molecules in the same conditions. It is concluded that exchangeable cations make greater contribution to the total driving force for the swelling of MMT.

Finally, the total adsorption energy between MMT (include the exchangeable cations) and water molecules can be calculated with Eq. (4). It is observed that the negative adsorption energy between MMT and water molecules is markedly increasing with the increase of surface

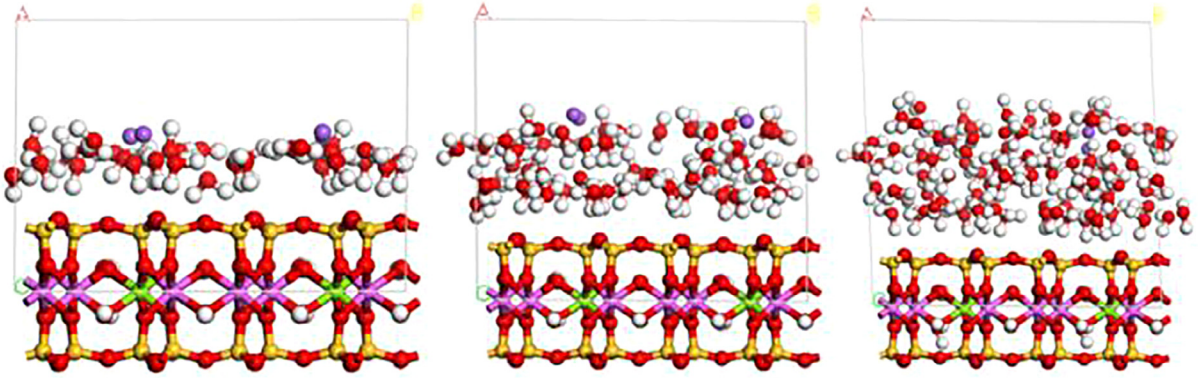

Fig. 2. Sodium montmorillonite absorbed 32, 64, 96 water molecules in the interlayer.

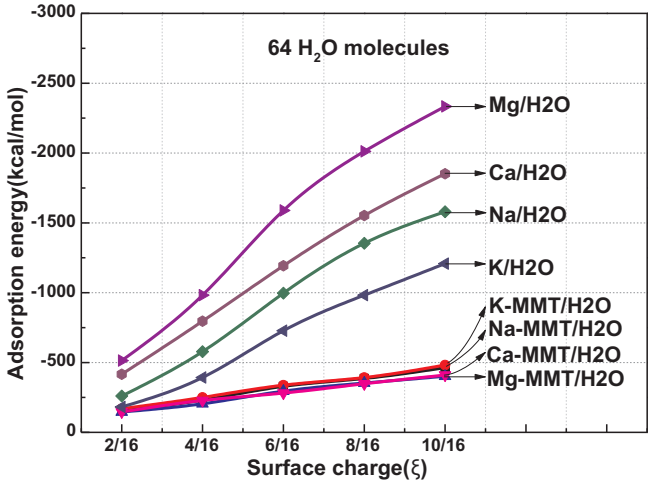

Fig. 4. Adsorption energy of MMT/Water and Cations/Water on Na, K, Mg, Ca-MMT with 64 water molecules in the interlayer and different surface charge.

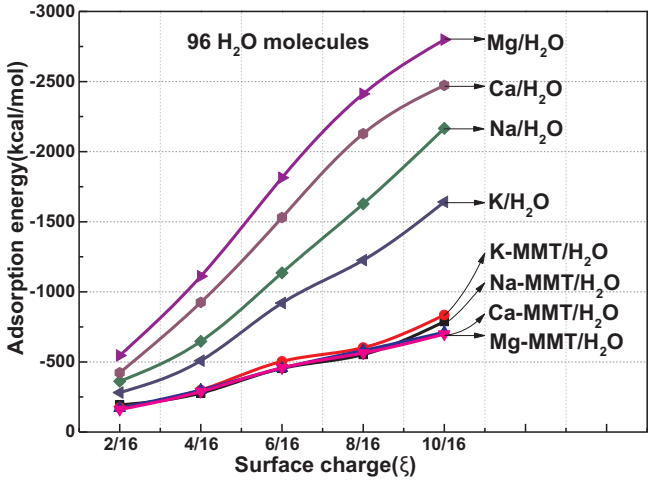

Fig. 5. Adsorption energy of MMT/Water and Cations/Water on Na, K, Mg, Ca-MMT with 96 water molecules in the interlayer and different surface charge.

charge, which is similar to the increase of negative adsorption energy between exchangeable cations and water molecules. As a result, surface charge mainly impacts the number of interlayer cations and thus exerts a positive influence on the driving force for the swelling of MMT.

Swelling of montmorillonite affected by exchangeable cations

To further understand the contribution of the exchangeable cations to the driving force for the swelling of MMT, MMT models with different cations (Mg-, Ca-, Na-, K-MMT) have been simulated. Adsorption energies of Cations/Water and C-MMT/Water are calculated based on Eqs. (3) and (4) and the percentage of cationic hydration energy ($\Delta E_{Cations/Water}$) to the adsorption energy ($\Delta E_{C-MMT/Water}$) is calculated according to Eq. (5), which are shown in Figs. 6–8. When MMTs (Mg-, Ca-, Na-, K-MMT) with certain surface charge are introduced into the same number of water molecules, it is noted that Mg has the most negative adsorption energy to water molecules in comparison with that of Na/H_2O, K/H_2O, Mg/H_2O and Ca/H_2O, followed by Ca, Na and K. The order of Mg > Ca > Na > K is consistent with the cationic hydration ability, and thus the cationic hydration ability is in direct ratio to the negative adsorption energy between exchangeable cations and water molecules. Besides, Fig. 6 shows that when ξ = 6/16, the adsorption energy between K and water molecules accounts for 65.4% to the total adsorption energy, while the percentage is 75.0, 83.7, 88.2 when

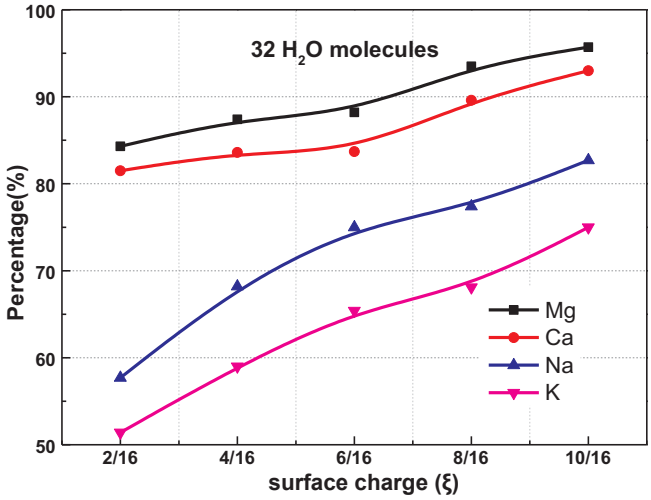

Fig. 6. $\Delta E_{Cations/Water}$ as a percentage of $\Delta E_{C-MMT/Water}$ on Na, K, Mg, Ca-MMT with 32 water molecules in the interlayer and different surface charge.

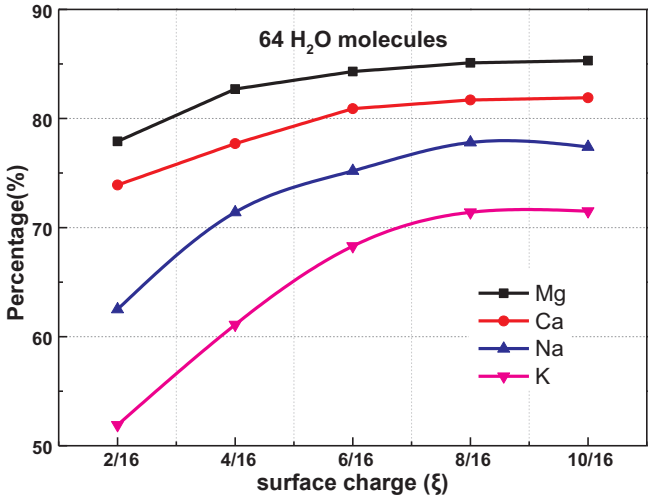

Fig. 7. $\Delta E_{Cations/Water}$ as a percentage of $\Delta E_{C-MMT/Water}$ on Na, K, Mg, Ca-MMT with 64 water molecules in the interlayer and different surface charge.

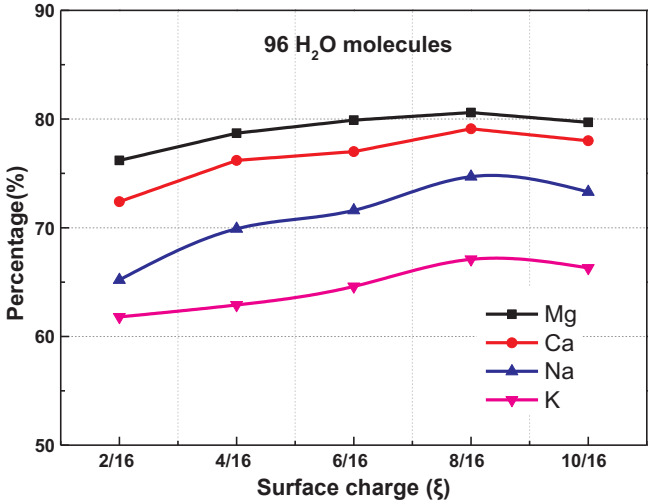

Fig. 8. $\Delta E_{Cations/Water}$ as a percentage of $\Delta E_{C-MMT/Water}$ on Na, K, Mg, Ca-MMT with 96 water molecules in the interlayer and different surface charge.

cations are Na, Ca, Mg, respectively. Mg has the strongest hydration ability and its hydration energy has the largest proportion of total adsorption energies no matter that surface charge and interlayer water content. Therefore, the stronger the cations hydration ability is, the greater contribution made by exchangeable cations to the total driving force for the swelling of MMT.

With the increase of water molecules in the interlayer, the negative adsorption energy between exchangeable cations and water molecules rises dramatically, as shown in Figs. 3–5. On the other hand, Figs. 6–8 reveal that the contribution made by exchangeable cations experience a decrease with the increase of water molecules in the interlayers. For example, under the circumstance of $\xi = 6/16$, the adsorption energy ($\Delta E_{Ca/H_2O}$) between Ca^{2+} and water molecules is -852.7, -1193.3, -1530.5 kcal/mol, and the percentage of $\Delta E_{Ca/H_2O}$ to $\Delta E_{Ca-MMT/H_2O}$ is 83.7, 80.9, 77.0 when 32, 64, 96 water molecules are introduced to MMT interlayer, respectively. Therefore, the higher water content makes exchangeable cations have a stronger driving force for the swelling of MMT, but it causes adverse effect on the contribution of cations to the total driving force.

Finally, as shown in Figs. 6–8, with the increase of surface charge, exchangeable cations play an increasingly important role in the contribution to the total driving force for the swelling of MMT. Even if surface charge is the lowest ($\xi = 2/16$), the adsorption energy between K^+ and water molecules is still more than the half of total adsorption energy between MMT and water molecules. It confirms that exchangeable cations have a stronger affinity to water molecules than negatively charged MMT surface layers. Thus, it is exchangeable cations that provide the dominant driving force for the swelling of MMT.

Conclusion

1. In contrast to MMT layers with negative surface charges, exchangeable cations have a much stronger affinity to water molecules and thus provide the dominant driving force for the swelling of MMT.
2. With the increase of surface charge, the number of exchangeable cations increases correspondingly, and meantime the contribution of exchangeable cations is increasing in the total driving force for the swelling of MMT.
3. The stronger the hydration ability of the exchangeable cations, the greater contribution they make to the total driving force for the swelling of MMT.

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