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Adsorption of Ions at the Interface of Clay Minerals and Aqueous Solutions

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Abstract

Adsorption of ions at the interface of clay minerals and aqueous solutions plays a critical role in a wide spectrum of colloidal, chemical, physical, and geological processes. Owing to the particular complexity of related systems and the femtosecond scale of related processes, the direct experimental observations often become a challenging task. As a contrast, computer simulations have proven to be a competent and powerful approach therein and already realized fruitful and significant contributions. In this chapter, we attempt to draw a relatively comprehensive picture of the interfacial adsorption of ions mainly within the context of computer simulations. As elaborated, quantum mechanics (QM) and molecular dynamics (MD), two popular simulation techniques currently used, have respective advantages, and with their collaborative efforts, we are striding toward the in-depth and systematic understanding of adsorption configuration, distribution, stability, reaction thermodynamics and mechanism, dynamics, diffusivity as well as electric double layer and other fundamental issues that are closely associated with the adsorption of ions at the interface of clay minerals and aqueous solutions. In addition, we demonstrate that investigation of the interfacial adsorption of ions greatly helps to unravel the origin and mechanism of ion-specific effects, whose importance has been explicitly suggested to be no less than Gregor Mendel's work to genetics.

Keywords: interfacial adsorption, clay mineral, molecular dynamics, quantum mechanics, ion-specific effects

1. Introduction

Adsorption of ions at the interface of clay minerals and aqueous solutions is ubiquitous and plays a pivotal role in a wide spectrum of colloidal, chemical, physical, and geological processes, such as the transport and bioavailability of ions, nutrients and contaminants [1–3]. Owing to the large surface area, low permeability and high retention capability, clay minerals show outstanding adsorption performances for metal ions, organic matters and other substances that further control the transport and bioavailability of metal ions, nutrients, and contaminants; on the other hand, the surface properties of clay minerals are affected significantly by these adsorbents that may result in the aggregation, dissociation of clay minerals, and/or chemical reactions at the interface of clay minerals and aqueous solutions [4–7].

To date, it remains challenging for experimental techniques to observe the interfacial processes of clay minerals and aqueous solutions because of the complexity of related systems (involving aqueous solutions, ions, counterions, and clay minerals that may have the various surface structures and even mixtures) and the promptness of related processes (generally on the femtosecond scale). Computational simulations, which can provide the otherwise inaccessible details such as adsorption configuration, distribution, stability, reaction thermodynamics and mechanism, dynamics, diffusivity as well as other fundamental issues such as electric double layer began to emerge as a powerful research tool to complement the experimental results. In the recent few decades, we have witnessed the unprecedented advances of computer simulations within this context. Quantum mechanical (QM) methods are highly precise and it proves that the MP2 or MP2:DFT schemes can reproduce the reaction barriers with near chemical accuracy [8, 9]. Although QM methods are qualified for predicting reaction mechanism, thermodynamics, spectroscopic data, and other information, they are computationally costly and thereby restricted mainly for the treatment of relatively small systems. To overcome this disadvantage, Morokuma and collaborators [10] developed an ONIOM scheme that divides the systems into several layers. For the ONIOM scheme, each layer can freely choose the desired functional and basis set, and in many cases, molecular mechanics (MM) is employed for the low-level region, which is also referred to as the so-called QM/MM methodology. In this way, systems up to thousands of atoms become within the power of computer simulations. Classical molecular dynamics (MD) based on Newton's second law or the equation of motion ($F = m \times a$, where " F ," " m ," and " a " refer to the exerted force, mass, and acceleration, respectively) is ready to describe 10,000 atoms that approach the real systems; in the meanwhile, dynamic information on the femtosecond scale such as structural evolution, interaction, and diffusion can be monitored *in situ*. One of the representative achievements of MD simulations is toward the understanding of protein folding [11]. For complicated systems, computer simulations can consider the various influencing factors one by one (e.g., pH, substituent effect, temperature, pressure, water content, etc.), which often seem impossible to handle experimentally; in addition, QM and MD methods have their respective merits: QM is accurate, while MD provides dynamic information. *Ab initio* molecular dynamics (AIMD) has revolutionized the field of computer simulations by unifying molecular dynamics and electronic structure theories, allowing the colloidal, chemical, physical, or/and geological processes to be *in situ*

monitored in an accurate and unbiased way. That is, AIMD integrates the merits of QM and MD methods by providing accurate and dynamic information within one simulation task.

Recently, these simulation techniques have been used in our group to tackle the adsorption behavior and mechanism of ions onto clay minerals, in the absence or the presence of aqueous solutions [12–16]. According to the QM-calculated results [12–14], metal ions such as K^+ and Ca^{2+} construct strong ionic bonds with the oxygen (O) atoms of hexagonal rings at the tetrahedral SiO_4 sheet of clay minerals, whereas OH^- deprotonates the clay minerals by depriving protons from the bridging O atoms and thus enhance the densities of negative charges of clay minerals. The presence of water molecules displaces metal ions from the center of the hexagonal rings [15]. Our MD simulations [15, 16] indicate that whether for metal ions or anions, adsorbed species can be classified into inner and outer-sphere modes: inner-sphere ions form direct interactions with the surfaces of clay minerals, while outer-sphere ones are separated by only one intermediate water molecule. In this chapter, we are aiming to draw a relatively comprehensive picture of the adsorption of ions at the interface of clay minerals and aqueous solutions, and hence, the discussions will not be limited to the computational results obtained from our group. Related results from other groups obtained thus far can also be included, and here, examples are given: Greathouse and Cygan [17] used MD simulations and found that $[UO_2(H_2O)_5]^{2+}$ should be the major species for UO_2^{2+} adsorption onto the clay minerals of 2:1 layer type such as beidellite and montmorillonite and pyrophyllite. Yang et al. [18] continued the studies and demonstrated that the U^{6+} center and the O atoms from the hydration shell are the competitive binding sites during the interaction of $[UO_2(H_2O)_5]^{2+}$ with montmorillonite, and the adsorbed species using the U^{6+} center and coupled-water O atoms as the binding sites correspond, respectively, to the inner and outer-sphere modes.

In consequence, this chapter focuses on the studies of adsorption of metal ions and anions at the interface of clay minerals and salt solutions, with inclusion of both QM and MD results. To broaden the horizon, the underlying ion-specific effects and the removal of heavy metal ions and anions are discussed as well. As aforementioned, the adsorption of metal ions onto clay minerals can exert a positive influence for a wide range of colloidal, chemical, physical, and geological processes [1–3]; on the other hand, the adsorption of heavy metal ions and certain anions is known to cause contamination to soils that further results in the serious environmental pollutions and threatens the health of human beings. Biochar, produced by the pyrolysis of biomass, has proven to be effective to improve soil properties, remediate soils with heavy metal and organic pollutants and increase crop biomass [19]. With use of density functional calculations, we have demonstrated that biochar is potential to remediate soils with anionic pollutants [20], in addition to heavy metal ions that are known to us all.

The scientific status of ion-specific effects has been well established, and Kunz et al. [21] explicitly suggested that the importance of ion-specific effects should be no less than Gregor Mendel's work to genetics. As a matter of fact, ion-specific effects occur ubiquitously and play a vital role during a wide range of interfacial processes of clay minerals and salt solutions, and a number of these processes can be associated closely with the adsorption processes. We have

clearly demonstrated the presence of Hofmeister series for both metal ions [12, 22–24] and anions [14, 16] during the adsorption of ions onto clay minerals and the resulting aggregation of clay minerals; in addition, mechanism of ion-specific effects was explored and for metal ions, it can be ascribed to the difference of polarization effects responding to the electric field of colloidal particles [12].

2. QM calculations

Isomorphous substitutions occur in almost all types of clay minerals, especially 2:1 layer type such as mica, montmorillonite, and pyrophyllite. A plethora of negative charges are thus created that determine the adsorption properties for ions. First principles density functional theory (DFT) calculations of pyrophyllite and montmorillonite have been carried out by Vamsee et al. [25], with consideration of octahedral $\text{Mg}^{2+}/\text{Al}^{3+}$ substitutions. The octahedral $\text{Mg}^{2+}/\text{Al}^{3+}$ substitutions lead to the enrichment of negatively charges at the interlayer, which then strongly bind counterbalancing ions such as Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} . For montmorillonite, it shows that the interlayer distance varies in a nearly direct proportion to the radius of intercalated counterions (**Figure 1**). Compaction of the interlayer space triggers the Li^+ ions to migrate into the tetrahedral sheet and be closely coordinated with the basal O atoms of the tetrahedral sheet. The electron densities on these basal O atoms are increased mainly as a result of isomorphous substitutions at the octahedral sheet instead of associated counterions. The authors also point out that inclusion of dispersion corrections is necessary in order to achieve satisfying agreements with the experimental results with respect to lattice parameters and bulk modulus.

Shi et al. [26] study the adsorption of Na^+ , NH_4^+ and protonated formamide (FAH) ions onto the dry and hydrated montmorillonite surfaces at various interlayer distances. Complex interactions that vary with the identity of counterions, volume, and interlayer space are detected among the counterions, lower and upper montmorillonite surfaces, such as ionic bonding, H-bonding, electrostatic attraction and repulsion as well as vdW forces. Na^+ ions form direct ionic bonds with the surfaces of montmorillonite by situating at approximately the center of six O atoms of hexagonal rings with the shortest Na-O distances of ca. 2.46 Å, whereas NH_4^+ and FAH ions construct strong H bonds with the surfaces of montmorillonite, with the shortest H-bond distance being equal to 2.31 and 2.13 Å, respectively. Different from Na^+ ions that have been trapped by one of montmorillonite surfaces, NH_4^+ and FAH ions construct strong interactions with both montmorillonite surfaces through forceful H bonds. The expansion energy potentials near the equilibrium interlayer distances are described by the nearly quadratic functions, and at larger interlayer distances, the attraction interactions among the counterions, lower and upper surfaces turn to be predominant and the energy potentials approach the constant values.

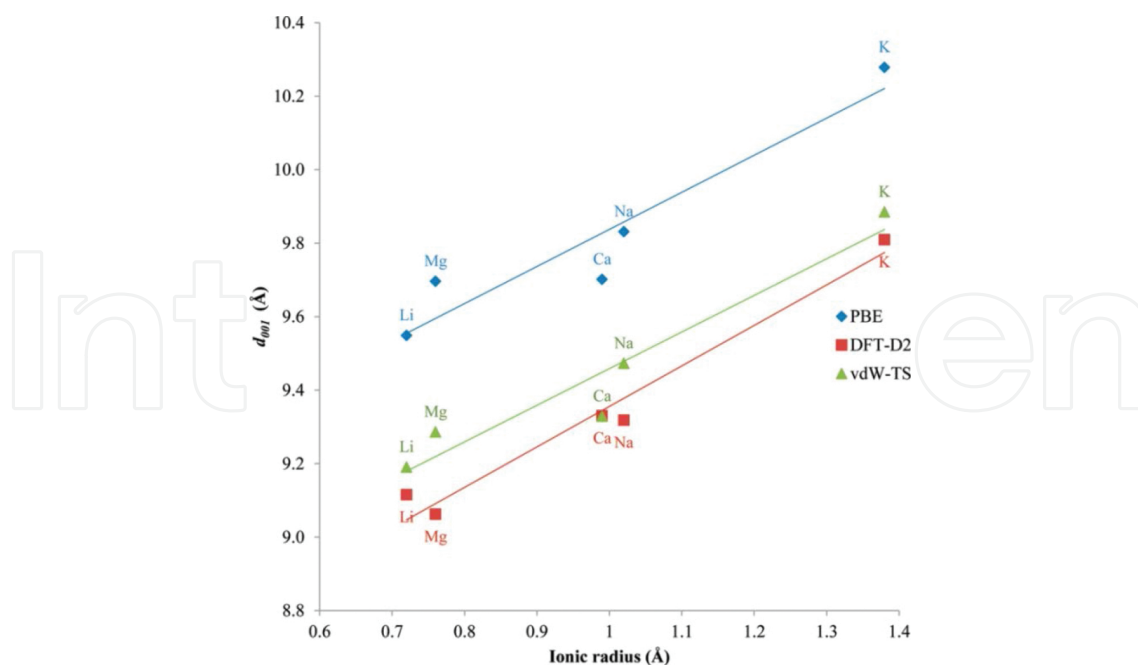


Figure 1. The interlayer distance (d_{001}) versus the ionic radius of counterions for montmorillonite with octahedral $\text{Mg}^{2+}/\text{Al}^{3+}$ substitutions.

Isomorphous substitutions and resulting effects on the adsorption of ions have been studied by several different groups [27–32]. When montmorillonite is acid treated, the adsorption of protons (H^+) takes place at the interlayer, and these protons act as counterions and can be exchangeable. Owing to the acidic treatment, the lattice Al atoms of montmorillonite undergo the rapid autotransformation and migrate to the ion-exchanged sites at the surfaces of clay minerals, at a comparable rate for lattice Al atoms at the octahedral and tetrahedral sheets [27]. At the same time, the cation-exchange capacity of montmorillonite declines significantly. The effects of isomorphous substitutions on the Brønsted acid sites are demonstrated by Claudia and Esther [28]. It shows that isomorphous substitutions of the octahedral $\text{Mg}^{2+}/\text{Al}^{3+}$ sites result in stronger acidities than those of tetrahedral $\text{Al}^{3+}/\text{Si}^{4+}$ sites, which further lead to the more effective protonation of probe molecules such as methylamine, ammonia, and pyridine and acetonitrile in the former case. The interaction strengths of probe molecules abide by the same sequence for both octahedral $\text{Mg}^{2+}/\text{Al}^{3+}$ and tetrahedral $\text{Al}^{3+}/\text{Si}^{4+}$ substitutions, as methylamine > ammonia > pyridine > acetonitrile, which seems to be not directly related to the proton affinities of probe molecules. The $\text{Al}^{3+}/\text{Si}^{4+}$ substitutions lead to substantial alterations to the atomic arrangements along the c-axis direct and charge distribution at montmorillonite surfaces, and counterions interact with the internal surfaces by forming a specific configuration associated with the six O atoms of hexagonal rings at the tetrahedral SiO_4 surface [29]. Counterions with smaller radii or/and higher charges are likely to lead to strong binding with the internal surfaces of clay minerals. This is apparent because metal ions with smaller size are more apt to enter into the hexagonal rings and/or metal ions with higher charges are beneficial for stronger electrostatic interactions. The $\text{Mg}^{2+}/\text{Al}^{3+}$ substitutions

cause the vicinities to be the most negative charged and thus can qualitatively predict the most possible sites for the adsorption of counterions [30]. The adsorption energetics of metal ions on the layer surfaces are found to be linearly correlated with the inverse cation-substitution distances (**Figure 2**), further substantializing the negative point-like character of $\text{Mg}^{2+}/\text{Al}^{3+}$ substitutions. The change of different adsorption sites causes remarkable differences in the adsorption energetics, up to 126 kJ/mol. Adsorption of Na^+ ions on montmorillonite surfaces is somewhat preferential when Na^+ ions are located in proximity to the $\text{Mg}^{2+}/\text{Al}^{3+}$ rather than $\text{Al}^{3+}/\text{Si}^{4+}$ substitution sites, and the energy difference reaches approximately 15 kJ/mol [31]. Three different types of isomorphous substitutions (tetrahedral, octahedral and both) have been calculated by Mignon et al. [32], and it clearly indicates the distinct adsorption behaviors for the various metal ions: K^+ ions remain closely bound to the surfaces of each type of isomorphous substitution (i.e., inner-sphere) and this is consistent with the role as a good swelling inhibitor; Li^+ ions are preferential for hydration and coordinates to four water molecules in all types of substitutions (i.e., outer-sphere), except the emergence of inner-sphere species in the case of isomorphous substitutions at both tetrahedral and octahedral sites; Na^+ ions display an intermediate adsorption behavior, bound to the surface in the case of tetrahedral substitution (i.e., inner-sphere) while hydrated in the case of octahedral substitution (i.e., outer-sphere). It is due to that the binding energies of alkali ions with water molecules decrease in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ while with the surfaces of clay minerals change in the reverse order ($\text{K}^+ > \text{Na}^+ > \text{Li}^+$).

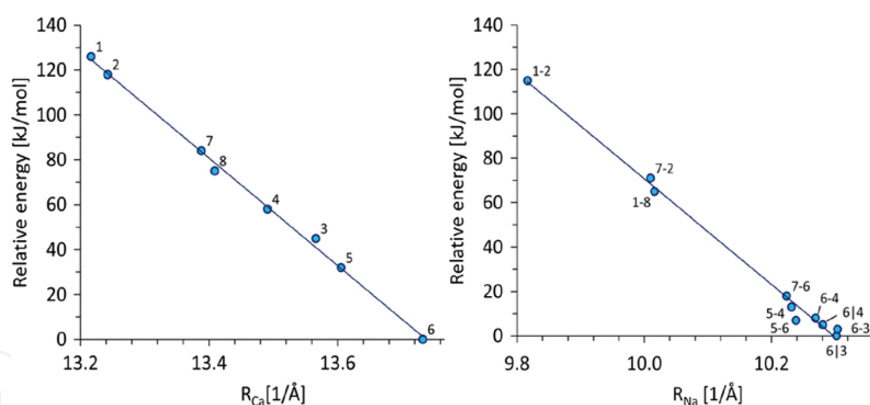


Figure 2. Correlation of the relative adsorption energetics for Ca^{2+} (up) and Na^+ (bottom) ions with the sum of inverse cation-substitution distances (R_M , $M = \text{Ca}, \text{Na}$). Details for the R_M calculations can be found in the supplementary information of Ref. [30].

With isomorphous substitutions, counterions are strongly adsorbed onto the surface of clay minerals, and the hydration of counterions occurs facilely in humid environments, carrying the water molecules into the interlayer space and causing the swelling or collapse of the lamina structures [33–42]. It is apparently seen that the interactions among counterions, water molecules, and surfaces in the adsorption processes of metal ions are of great scientific importance. Periodic DFT calculations have been performed to investigate the hydration of Ca^{2+} ions in the interlayer space of montmorillonite [43]. The hydration of metal ions is

significantly affected by the interior surfaces of clay minerals that possess a plethora of negative charges. The hydration structures of Ca^{2+} ions in the interlayer space are distinct from those in gas phase, especially at higher water loadings. Nonetheless, at all water contents, Ca^{2+} ions are closely bound to one of the interior surfaces of montmorillonite and the hydrated Ca^{2+} ions in the interlayer space of montmorillonite have a tendency to construct a H-bond (HB) network that links the upper and lower surfaces, which is achieved as long as the number of water molecules (N) reaches three ($N = 3$). In gas phase, Ca^{2+} ions tend to form direct bonds with as many as water molecules until the first shell has been saturated ($N \geq 6$).

The distribution and migration of actinide compounds in the environmental circumstances are within the context of risk assessment for long-time radioactive waste repositories. Alena et al. [44] perform the periodic DFT calculations on the adsorption of uranyl (UO_2^{2+}) on solvated (110) and (010) edge surfaces of pyrophyllite. The bidentate adsorption configurations on the various partially deprotonated sites of pyrophyllite (i.e., octahedral $\text{Al}(\text{O},\text{OH})$, tetrahedral $\text{Si}(\text{O},\text{OH})$, and mixed AlO-SiO). It shows that the preferred sites for adsorption of UO_2^{2+} are different for (110) and (010) edge surfaces, respectively, as the octahedral $\text{Al}(\text{O},\text{OH})$ and mixed AlO-SiO sites. The authors of the same group [45] further show that structural parameters of uranyl adsorption complexes are essentially determined by the surface chemical groups that construct the local adsorption sites rather than type of clay minerals, and relatively slight effects on structural parameters are exerted even if substituted cations occur at the adsorption sites. Adsorption of uranyl can induce the hydrolysis of -AlOH and result in the formation of uranyl mono-hydroxide. The frayed edge sites formed in micaceous clays are indicated to have a crucial role with respect to the long-term stability of radioisotopes of Cs on the topsoil surfaces [46].

It is known to us that clay minerals have outstanding adsorption performances for metal ions, including heavy metal ions that may rigorously pollute the environmental circumstances and further the health of human beings. On the other hand, anions such as Cr(VI)-oxo and phosphate are also widely spread in soil systems as metal ions that can result in environmental pollutions [47–49]. There are obviously fewer computational reports on the adsorption of anions on clay minerals in contrast to the extensive studies on metal ions. DFT calculations are performed by Zhu et al. [50] to investigate the adsorption of As(V)- and As(III)-oxo anions and related reactions on Mn(II) and Mn(IV) sites of birnessite. It shows that whether on Mn(II) or Mn(IV) site, the adsorption of As(V)- rather than As(III)-oxo complexes is more thermodynamically favorable and thereby the oxidation of As(III) is expected to be inhibited due to the blocking of adsorption sites by As(V)-oxo complexes. For kaolinite surface, the adsorption of SiO(OH)_3^- takes place primarily on the Al-terminated (001) surfaces, similar to the situation of Si(OH)_4 adsorption. The various adsorption configurations of Si(OH)_4 and SiO(OH)_3^- on the Si- and Al-terminated. Owing the more reactive nature of unbounded O atom, SiO(OH)_3^- forms stronger electrostatic interactions than Si(OH)_4 and result in more stable adsorption configurations [51]. As a result of SiO(OH)_3^- adsorption, the surfaces of kaolinite become more hydrophilic and carry more negative charges, which may significantly facilitate the dispersion of kaolinite particles in aqueous solutions.

Nowadays, biochar has been listed as one of the most concerned materials due to the high capacity for ion adsorption and facile recyclability, showing excellent performances to remove heavy metal ions from clay minerals and remediate soil ecosystems [52–55]. It is essential to acquire an in-depth mechanistic understanding of ion adsorption on biochar. However, biochar has no specific structures and it is suggested to use other carbon-based materials for prototypes. Graphene is a two-dimensional honeycomb structure composed by sp^2 -hybridized carbon atoms; that is, it is similar to other carbon-based materials such as biochar in that all of them are polycyclic aromatic hydrocarbons, mainly built upon the structural unit of benzene ring. Accordingly, grapheme can be an idea model for comprehension of ion adsorption on carbon-based materials. Colherinhas et al. [56] conduct DFT calculations and indicate that the adsorption strength of metal ions on grapheme is closely associated with the radius and charge of metal ions. The adsorption configurations with the highest stability correspond to the hollow site (*H*-site) where metal ions are situated at the center of an aromatic ring, as a result of maximizing the cation– π interactions [57]. As indicated by Addition of water molecules may significantly weaken the binding between metal ions on grapheme [58]. Different from metal ions, halide ions are electron-rich and can be adsorbed on graphene that are generally used as electron donors? Zhu et al. [20] and Shi et al. [59] clearly show that halide ions are potentially adsorbed on graphene, where halide ions are electron donors while graphene turn to be electron acceptors. Zhu et al. [20] demonstrate the binding strengths of metal ions on pristine graphene are stronger than the halide ion when they are adsorbed; however, the edge-fluorination alters the adsorption priority of metal ions versus halide ions and the adsorption strengths of metal ions/anions change in direct/reverse proportion with increase in functionalization degrees. In consequence, the preferential adsorption and selective removal of certain metal ions or anions can be facilely realized by choice of an appropriate functionalization degree. It is suggested by us that the binding strengths of hydrated ions should be calculated as follows:

$$E_b = E_{GN-ion-nW} - (E_{GN} + E_{ion-nW}) \quad (1)$$

where E_{GN} , E_{ion-nW} , and $E_{GN-ion-nW}$ are the energies of graphene, hydrated ions, and hydrated ions interacting with graphene, respectively, and n refers to the number of water molecules.

That is, the hydrated ions are treated as a whole instead of separately. Because of the different adsorption configurations of hydrated halide ions and metal ions that water molecules around form H-bonds with halide ions and at the same time interact with graphene through their O atoms, while metal ions construct direct ionic bonds with the O atoms of water molecules, and hence, only the H atoms of water molecules can be available to interact with graphene. It shows that in the case of edge fluorination, the binding energies of halide ions remain substantial while those of metal ions decline apparently, and the change trends are opposite in the case of pristine graphene.

3. MD simulations

As claimed by MD simulations, the adsorption of ions (whether metal ions or anions) onto the basal surfaces of clay minerals can proceed via two potential modes, respectively as the inner-sphere species that form direct interactions with the surfaces of clay minerals and the outer-sphere species that are separated from the surfaces by only one intermediate water molecule [15, 16, 60–72]. With regard to the inner-sphere metal ions, direct bonds are constructed with the surface of clay minerals, while forceful and complicated H-bond networks are detected in the case of anions such as halide ions (X^-) and hydroxide ion (OH^-) [16]. The adsorption behaviors and performances of metal ions are largely associated with the identity of clay minerals because their surface properties may vary significantly. With regard to regular clay minerals (with no isomorphous substitutions or defect sites), a majority of metal ions are found to adsorb primarily as the outer-sphere surface complexes, and to the best of our knowledge, only the weakly solvated alkali metals (K^+ , Rb^+ , and Cs^+) are inclined to form mainly the inner-sphere surface complexes [73, 74].

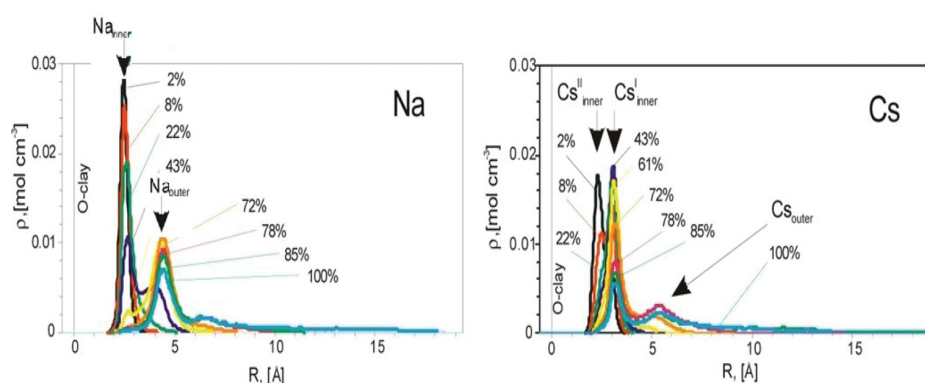


Figure 3. Na^+ and Cs^+ density distributions at the external surface of montmorillonite as the function of relative humidity (RH). Black arrows show position of inner-sphere and outer-sphere ion complexes [69].

The mechanism of metal ions adsorbed onto the montmorillonite surfaces has been extensively investigated by MD simulations. Churakov [69] studies the Na^+ and Cs^+ migration on the external surfaces of montmorillonite under partially saturated and saturated conditions and demonstrates that the surface complexation of Na^+ ions is driven substantially by the availability of water molecules. The density distributions of Na^+ and Cs^+ normal to the external surfaces are displayed in **Figure 3**. Under saturated conditions, Na^+ ions are adsorbed principally as the outer-sphere surface complexes, and when the relative humidity (RH) declines and falls within the range of 43–61%, the thickness of water film reduces from two to one layer, which causes Na^+ ions to approach the surfaces of montmorillonite and construct the so-called inner-sphere surface complexes; meanwhile, the coordination number of water molecules with Na^+ ions shows an obvious decrease and as a compensation, the surface O atoms become part of the Na^+ coordination shell. Rather than, Cs^+ ions display a distinct adsorption behavior: They form both outer and inner-sphere surface complexes under saturated conditions and are presented exclusively as the inner-sphere surface complexes when

the RH decreases below 60%. The adsorption differences between Cs^+ and Na^+ ions are assumed to be due to their different ionic sizes that can result in the obviously different strengths of ion–water and ion–surface interactions. Marry et al. [64] compare the dynamic properties of Na^+ and Cs^+ ions in the monohydrated montmorillonite interlayers. The distribution of Li^+ , Na^+ , and K^+ ions on montmorillonite surfaces is also investigated by the combination of MD and Monte Carlo (MC) simulations [65–68], which are in agreement with the results of spectroscopic observations [70–80].

Hydration occurs readily for metal ions at the interfaces of clay minerals and aqueous solutions. Water molecules can become an essential portion of coordination for metal ions. Greathouse and Cygan [17] perform a systematic MD study and show that $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ should be the major species for uranyl adsorption onto the surface of clay minerals of 2:1 layer type. There is no adsorption near the surface of pyrophyllite, while the adsorption behaviors are similar on the surfaces of beidellite and montmorillonite. Ologomeric uranyl complexes are observed at dense solutions, particularly near the surfaces of pyrophyllite and montmorillonite instead of beidellite. Subsequently, Yang et al. [18] demonstrate that the U^{6+} center and the O atoms used to form the hydration shell are the two competitive binding sites during the interaction of $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ with montmorillonite, and the adsorbed species using the U^{6+} center and coupled-water O atoms as the binding sites correspond, respectively to the inner and outer-sphere modes. In addition, the work of adhesion between the uranyl species and montmorillonite surfaces is evaluated and can reach 2.348 J/m^2 , larger than the value between two montmorillonite sheets. Vasconcelos et al. [81] study the interactions between aqueous metal ions (Cs^+ , Na^+ , Pb^{2+} , and Cd^{2+}) and the basal surfaces of kaolinite, showing that Cs^+ ions can form strong inner-sphere complexes at the ditrigonal cavities of the tetrahedral SiO_4 surface (**Figure 4**). The outer-sphere Cs^+ ions are also present while highly mobile indicating the occurrence of weak adsorption. For Na^+ ions, only a small portion is adsorbed directly on the tetrahedral SiO_4 surface as inner-sphere complexes that are not clearly defined sites and very weak outer-sphere complexes predominate instead. The inner-sphere complexes of Pb^{2+} and Cd^{2+} do not occur on the tetrahedral SiO_4 surface, and only the outer-sphere mode is resulted from the adsorption of these two heavy metal ions; however, the corresponding outer-sphere surface complexes are apparently stronger than the outer-sphere Na^+ ions due to the apparently enhanced interactions of Pb^{2+} and Cd^{2+} versus Na^+ with surrounding water molecules. Sakuma et al. [82] investigate the distribution and dynamics of monovalent cations (Li^+ , Na^+ , K^+ , Cs^+) on muscovite surfaces and show that hydrated Li^+ ions close to muscovite surfaces form two types of inner-sphere complexes and one type of outer-sphere complex. The two types of inner-sphere Li^+ complexes are respectively situated at the cavity and rim of the ditrigonal rings of muscovite. Na^+ , K^+ , Cs^+ , and H_3O^+ form stable inner-sphere complexes on muscovite surfaces. Adsorbed Li^+ , Na^+ , K^+ , and H_3O^+ species have resembling coordination conditions with water molecules, while Cs^+ ions have an obviously lower binding number with water molecules. Steele and collaborators [83] investigate the interactions of the (001) surface of muscovite with toxic divalent metal ions (Cu^{2+} , Zn^{2+} , and Cd^{2+}) and find that none of them

can form strong bonds with the regular surface of muscovite, which is similar to the scenarios of Pb^{2+} and Na^+ ions discussed earlier.

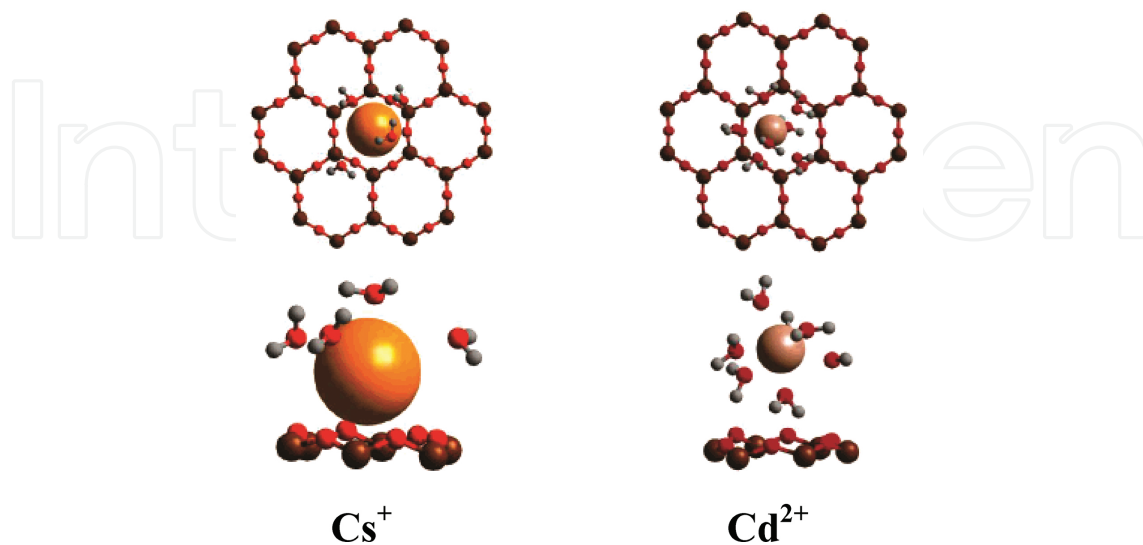


Figure 4. Representative Cs^+ and Cd^{2+} adsorption complexes [81].

MD simulations can also provide the dynamic and diffusion information for up to real systems that seems challenging to acquire by the structural optimization tasks using QM-based methods. As indicated by the time-evolution trajectories, the inner-sphere Cs^+ ions have little mobility and are kept rather stable at the hexagonal cavities of the tetrahedral SiO_4 surface of regular kaolinite, whereas the outer-sphere Cs^+ ions are liable to migrate on the tetrahedral SiO_4 surface. The trajectories of outer-sphere Na^+ ions are quite diffusive and resemble those of outer-sphere Cs^+ ions. Although more focused at the adsorption sites than the outer-sphere species, the inner-sphere Na^+ ions that are asymmetrical with respect to the hexagonal rings are not stable enough to maintain at the adsorption sites during the MD simulations, which is quite different from the case of inner-sphere Cs^+ ions. Such discrepancy should be caused by the radius difference between these two alkali ions that result in the remarkable variations of ion-surface and ion-water interactions. As aforementioned, Cd^{2+} and Pb^{2+} ions that fall above the hexagonal cavities of the tetrahedral SiO_4 surface are exclusively outer-sphere adsorbed while their stabilities are apparently higher than those of other outer-sphere ions.

The diffusional dynamics of interlayer species such as Cs^+ ions and water molecules increases within the content of interlayer water molecules and with the distance from clay surfaces [84]. The mobility of ions in the water films on the external surfaces of clay minerals is similar to that at the surface of a water-saturated pore, as long as the thickness of water film is more than two layers. At the lower water pressure (i.e., thinner water films), the mobility of metal ions shows a dramatic decrease, and this is associated with the change in the surface complexation behaviors [85–89]. Zhang et al. [85] investigate the mobility of Na^+ and Ca^{2+} ions in the interlayer of montmorillonite, showing that the self-diffusion coefficient of

Ca^{2+} is lower than that of Na^+ due to the much more stable and larger hydration shell for Ca^{2+} versus Na^+ ions. In Na montmorillonite with high water contents, the interlayer Na^+ ions can displace in a relatively free way, while when Na^+ and Ca^{2+} ions coexist in the interlayer of montmorillonite, the moving regions of Na^+ ions have apparently been restricted by the hydration shell of Ca^{2+} ions as well as the interlayer spatial confinement, and as a result, the mobility of Na^+ ions in (Na, Ca)-montmorillonite is obviously inferior to that of Na-montmorillonite.

A number of factors can exert potential influences on the adsorption of metal ions onto clay minerals, such as isomorphous substitutions, temperature, water pressure, and counterions. It seems almost impractical for experimental operations to adjust one factor and at the same time keep all the others constant, while molecular simulations can easily realize such tasks. Below, we will analyze these factors one by one.

(1) Isomorphous substitutions, which are a general phenomenon for clay minerals of 2:1 layer type such as mica and montmorillonite [81, 84, 86–90]. Ngouana et al. [84] investigate the effects of substitutional disorder on the mobility of aqueous solvated species within the montmorillonite interlayers using the differently distributed $\text{Al}^{3+}/\text{Si}^{4+}$ and $\text{Mg}^{2+}/\text{Al}^{3+}$ substitutions, concluding that the specific localization of isomorphous substitutions has only a minor effect on the thermodynamic, structural, and transport properties. Liu et al. [91] use three montmorillonite models with different layer charges in the octahedral and tetrahedral sheets to study the thermodynamics and structural properties of Cs smectites, with use of the advanced CLAYFF force field [92]. All these smectites are found to swell in a similar way, with production of consistent swelling plateaus and energetic profiles. This indicates that the layer-charge distribution affects very slightly on the swelling behaviors of Cs smectites. Both ionic species and water molecules within the interlayer exhibit pronounced confining effects and correspond to obviously slower diffusivities than the corresponding bulk species, and smectite with the highest octahedral charges results in the lowest mobility of Cs^+ ions confined in the interlayer pores, whether at high or at low water contents. The layer charges can significantly affect the distribution of Cs^+ ions in the interlayer pores: inner-sphere Cs^+ ions in the interlayer pores of smectite can be adsorbed on the hexagonal (H-site) and triangular (T-site) sites, with the H-site being energetically preferential, (**Figure 5**). The relative stabilities of different adsorption sites may show variations, and the preference sequence is as tetrahedrally substituted H-site > nonsubstituted H-site > tetrahedrally substituted T-site > nonsubstituted T-site, while no conspicuous adsorption preference is detected for the various octahedral substitutions. MC is combined with MD demonstrating that the layer-charge location has a pronounced effect on the interlayer structure [93]. The full hydration of Ca^{2+} and Mg^{2+} ions is accompanied with the interlayer expansion into the 2W state. All layer charges in beidellite are created in the tetrahedral sheet, and metal ions remain adsorbed to the surfaces as the inner-sphere complexes at much higher water contents than in the case of montmorillonite, which may be caused by strong ion-surface interactions. For montmorillonite, the layer charges are exclusively assigned to the octahedral sheet, and all metal ions have been completely hydrated as the outer-sphere complexes even at low water content (2W state).

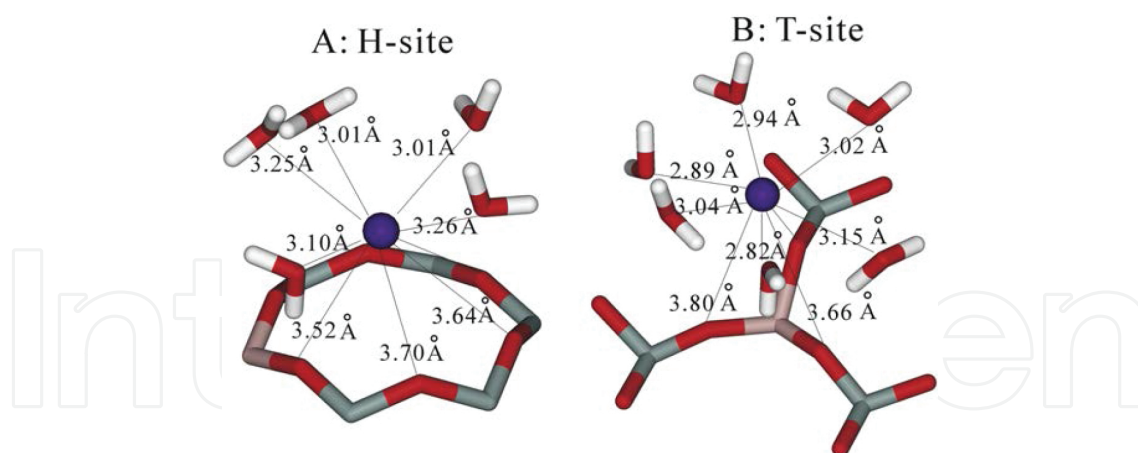


Figure 5. Two predominant coordination environments for the inner-sphere Cs⁺ ions confined in the interlayer pores of smectite: (A) hexagonal site (H-site) and (B) triangular site (T-site) [91].

(2) Temperature: Malikova et al. [94] study the effect of temperature fluctuations (0~150°C) on the adsorption of metal ions in the interlayer of montmorillonite. The diffusion coefficients for Na⁺ and Cs⁺ ions increase by an order of magnitude over the covered temperature range, and the clear differences at these temperatures indicate that Na⁺ and Cs⁺ ions have different modes of diffusion in the monohydrated montmorillonite: at both low and high temperatures, Cs⁺ ions exhibit a site-to-site diffusion mode that allows the coordination to six surface O atoms of the tetrahedral SiO₄ surface of clay minerals, while no definitely preferential sites are present for the adsorption of Na⁺ ions, even at low temperatures. Water phase behaves similarly in Na- and Cs-montmorillonites, and a rapid transition from the surface to bulk dynamics has been detected in the case of Na-montmorillonite. Zheng and Zaoui [95] further state that the size and mass of hydrated metal ions play a crucial role on their diffusion behaviors. The hydration number of metal ions shows a gradual decrease with the increase of temperatures, and at relatively high temperatures, more water molecules from the hydrates of metal ions are released that elevates the amount of free water molecules into aqueous solutions and enhances the mobility of metal ions to a certain degree.

(3) Defect sites. Defect sites are ubiquitous in all types of clay minerals and play a vital role during the adsorption and reaction processes [15, 83, 96–98]. Li et al. [15] perform a systematic investigation on the adsorption behavior, stability, and mechanism of metal ions on the defective clay minerals, showing that the adsorption quantities and stabilities of metal ions on kaolinite can be fundamentally promoted by the occurrence of defect sites. In the case of regular kaolinite, Na⁺ ions are adsorbed mainly as the outer-sphere species and only at dense solutions, the inner-sphere Na⁺ ions can be detected sporadically. The presence of defect sites reverses the adsorption preference of outer versus inner-sphere Na⁺ ions and causes the inner-sphere mode to be predominant for defective models with the various sizes. Pb²⁺ ions on regular kaolinite exist exclusively as the outer-sphere species, and the presence of defect sites causes the emergence of a small quantity of the inner-sphere species and the outer-sphere Pb²⁺ ions govern the adsorption processes consistently. As indicated in **Figure 6**, the adsorption configurations

of metal ions are significantly altered by the presence of defect sites, while the change of defect sizes or contents causes very limited influences. In the case of Si_4 (a large defect site with 10 lattice Si atoms having been leached), the inner-sphere Pb^{2+} ions are nonexistent because no direct interactions with kaolinite surfaces can be detected, while interestingly, a very small number of Pb^{2+} ions have distances from kaolinite surfaces that can be ascribed to the inner-sphere species. After structural analyses, we show that these Pb^{2+} ions are associated with the water molecules that enter into the cavities of Si_4 and accordingly are nominated as quasi inner-sphere species. Defect sites improve the numbers and stabilities of both inner and outer-sphere adsorption, and the inner-sphere Pb^{2+} ions occur only at defect sites that reinforce the ion-surface interactions, which also evidences the vital role of defect sites during the adsorption processes. The MD simulated results satisfactorily negotiate the experimental “conflicts” that some consider only the weak adsorption of metal ions on kaolinite surfaces, while others insist the presence of strong adsorption (i.e., inner-sphere species)—actually, structural differences such as the presence or absence of defect sites can cause the inconsistency in different experimental observations. Steele et al. [83] study the interactions of Cu^{2+} , Zn^{2+} , and Cd^{2+} with the regular surface of muscovite and the surface containing defect sites. The results indicate that no strong bonds have formed between regular surface and any of the three heavy metal ions. However, Cu^{2+} and Zn^{2+} ions can be strongly attached on the surface with defect sites, while Cd^{2+} ions will not bind directly to either regular surface or defective surface and instead, persist to exist exclusively as the outer-sphere complexes in defective surface as in the case regular surface.

(4) Water content. The dynamics of the interlayer species in clays is critically dependent on the water content in the system [84]. Zheng and Zaoui [99] compare the diffusion behaviors of counterions in montmorillonite at the one-, two-, and three-layer hydrated states, and the results show that the diffusion coefficients of counterions increase in a reverse proportion to the quantity of water content, corroborating that water content within the interlayer of clay minerals plays a very important role on the diffusion behavior of counterions. As discussed earlier, Churakov [69] demonstrate that the distribution of Na^+ ions on montmorillonite surfaces is strongly dependent on the relative humidity (RH): At relatively high RH, Na^+ ions form exclusively the outer-sphere complexes, and inner-sphere Na^+ surface complexes will be constructed. With the addition of water molecules, the inner-sphere Na^+ surface complexes that have formed at low RH will be reversibly transformed to the outer-sphere species, while K^+ ions show a distinct response to the increase of RH: K^+ ions at low RH form stable inner-sphere surface complexes and with increase of RH, remain tightly attached to the surface as inner-sphere species [100]. Zhang et al. [85] investigate the swelling properties, hydration behaviors, and mobility of interlayer ions (Na^+ and Cs^+) in montmorillonite at different water contents. It indicates that both Na^+ and Ca^{2+} ions are apt to construct the inner-sphere surface complexes at low water contents and the outer-sphere complexes at high water contents. The coordination numbers of water molecules in the first hydration shell of Na^+ and Ca^{2+} ions show a gradual increase as the water content increases, while the contribution of surface O atoms presents an opposite tendency. The

transitions from the inner-sphere surface complexes to outer-sphere complexes occur approximately at the water content of $170 \text{ mg}_{\text{water}}/\text{g}_{\text{clay}}$ that correspond to the swelling processes of (Na, Ca)-montmorillonite from the monolayer hydrated to bilayer hydrated states.

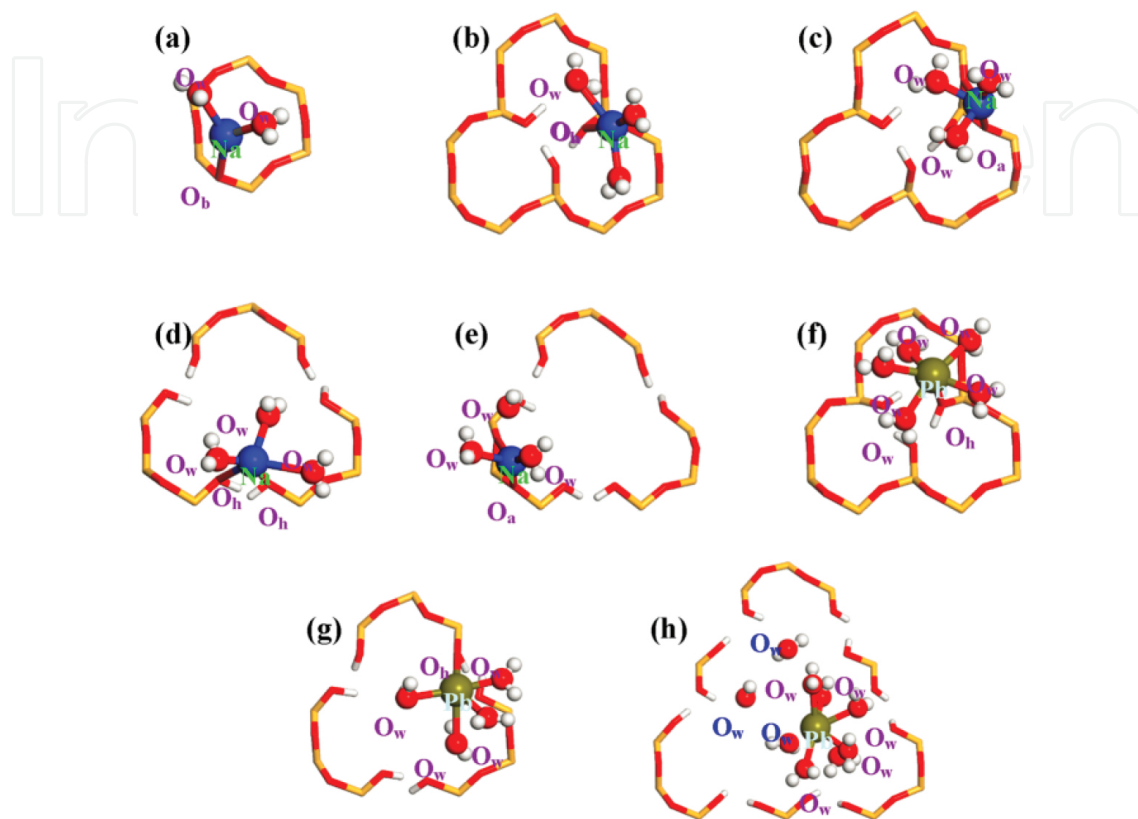


Figure 6. Local structures of inner-sphere Na⁺ and Pb²⁺ ions adsorbed on the tetrahedral SiO₄ surface of regular (Si₀) and defective kaolinite (Si₁, Si₂ and Si₄): (a) for Si₀(Na⁺), (a–c) for Si₁(Na⁺), (a, d, e) for Si₂(Na⁺) as well as (f) for Si₁(Pb²⁺), (g) for Si₂(Pb²⁺) and (h) for Si₄(Pb²⁺), respectively. Note that Si₄(Pb²⁺) is for quasi inner-sphere Pb²⁺ ions adsorbed on the water molecules that enter into the silanol cavities of Si₄ [15].

(5) Counterion. Metal ions and anions in aqueous solutions are referred to each other as “counterion.” It indicates that the distribution and stability of metal ions adsorbed onto the surface of clay minerals are affected substantially by different counterions such as the various halide ions ($A^- = F^-, Cl^-, I^-$) [16]. However, the adsorption modes of metal ions seem not affected by the choice of counterions; for example, inner-sphere (mainly) and outer-sphere adsorbed for Na⁺ ions and exclusively outer-sphere adsorbed for Pb²⁺ ions for all halide ions as counterions. Na⁺ ions in dilute NaOH solutions are adsorbed only at tetrahedral SiO₄ surface, in line with the scenarios of halide ion solutions, while when the NaOH concentration increases to around 0.48 mol/L, a portion of Na⁺ ions begin to emerge at the octahedral AlO₆ surface. For all halide ions as counterions, the local structures of adsorbed metal ions are similar, and when changing to the OH⁻ ion, several other structures will be generated for metal ions that are coordinated with OH⁻ ions. The OH⁻ ions can even drag metal ions toward the octahedral AlO₆ surface. Different from halide ions, OH⁻ can act not only as H-bond acceptor but also H-

bond donor, in a similar way as water molecules. In consequence, OH^- is capable of constructing forceful H-bond networks together with water molecules in aqueous solutions, which results in the distinct counterion effects as compared to halide ions. The stabilities of adsorbed Na^+ ions are affected by counterions and decrease in the order $\text{OH}^- > \text{F}^- > \text{Cl}^- > \text{I}^-$. The adsorption quantities and affinities of Cu^{2+} ions on clay soils are experimentally observed to be dependent on the choice of anions [101], which are consistent with the simulated results of counterion effects.

The diffusion coefficients of metal ions (D_M) in dilute solutions seem insensitive to the change of counterions; for example, the inner-sphere D_{Na^+} values are very close to each other when the counterion is I^- , Cl^- , F^- , or OH^- . However, the D_M values are significantly affected by counterions in dense solutions; for example, for the adsorption of 0.96 mol/L NaA solutions ($\text{A}^- = \text{F}^-$, Cl^- , I^- , OH^-) on the tetrahedral SiO_4 surface of kaolinite, the inner-sphere diffusion coefficients of Na^+ ions vary dramatically and decrease in the order $0.74 \pm 0.06 (\text{I}^-) > 0.67 \pm 0.04 (\text{Cl}^-) > 0.42 \pm 0.06 (\text{F}^-) > 0.28 \pm 0.03 (\text{OH}^-)$, with units being $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$. Both inner and outer-sphere diffusion coefficients of metal ions show a gradual increase with salt concentrations suggesting the enhancement of mobility of adsorbed metal ions. The outer-sphere Pb^{2+} rather than Na^+ complexes have different coefficients and thus correspond to higher stability, which is due to the stronger interactions of Pb^{2+} ions with surrounding water molecules.

Although obviously less attention has been given, anions are clearly shown to be capably adsorbed onto the surface of clay minerals as in the case of metal ions [16]. Anions construct only H-bonds with the surface clay minerals while form stable inner and outer-sphere complexes, even if when the metal ions of constituent electrolytes correspond solely to the outer-sphere adsorption mode; for example, F^- in PbF_2 where Pb^{2+} ions are presented exclusively as outer-sphere complexes. Albeit forming only H-bonds with the surface of clay minerals, adsorbed anions have surprisingly high stabilities that are comparable to those of metal ions. In the case of F^- and OH^- ions, an appreciable amount show even superior stabilities suggesting the formation of especially stable anion-mineral complexes. All anions can form mono-dispersive inner and outer-sphere complexes at the octahedral AlO_6 surface, and OH^- ions can form several new adsorption structures that are absence for halide ions, forming OH^- clusters at the octahedral AlO_6 surface as well as Na^+ and OH^- pairs at both tetrahedral SiO_4 and octahedral AlO_6 surfaces. Adsorbed anions have comparable diffusion coefficients with metal ions and depend significantly on the choice of metal ions, with those from PbA_2 instead of NaA solutions responding more sluggishly to the change of salt concentrations.

4. Concluding remarks

With the advent of computer simulations, probing the complicated and prompt adsorption processes of ions at the interface of clay minerals and aqueous solutions becomes viable that complement the experimental observations. In the recent three decades, computer performances have improved unprecedentedly and sophisticated computational techniques (including

methodologies and software) have emerged consecutively, which make computer simulations grow into an independent discipline. Nowadays, two types of computational simulations are popular in the studies of the adsorption processes of ions at the interface of clay minerals and aqueous solutions: QM methods accurately predict the adsorption behavior, reaction thermodynamics and mechanism, whereas MD methods provide the dynamic information for up to real systems on the femtosecond scale. With these computational techniques, a plethora of important details regarding to the adsorption configuration, distribution, stability, reaction thermodynamics and mechanism, dynamics, diffusivity as well as electric double layer and other fundamental issues have been brought to us, as has been elaborated in the chapter.

Ion-specific effects, also known as Hofmeister effects, are detected over 130 years ago when Hofmeister [102] finds a series of salt ions have consistent effects on the solubility and stability of proteins. Recently, ion-specific effects have experienced a renaissance and as suggested by Kunz et al. [21], the importance of ion-specific effects should be no less than Gregor Mendel's work to genetics. As a matter of fact, ion-specific effects control a wide spectrum of chemical, physical, biological, and colloidal processes, such as the interfacial tension of electrolyte solutions [103], chemical reaction rate [104, 105], protein conformation and stability [106–108], colloidal interaction [107] and even mudslides [109]. Ion-specific effects continue to defy all-encompassing theories [110]. Ionic size [111], hydration [111, 112], dispersion force [113–115] and surface charge [116, 117] are successively proposed to interpret the mechanism of ion-specific effects. Recently, our group [23, 118] reveals that the polarization effect could be the driving force of ion-specific effects for the adsorption of different metal ions onto the surface of clay minerals. With use of DFT calculations, we [12] have clearly shown that the polarization effect increases in a direct proportion with the negative charge of clay minerals and should be the driving force for the aggregation of colloidal soil particles. The aggregation mechanisms of colloidal soil particles with one- and bi-components are given and can be easily extended to more complicated colloidal soil particles. For the bi-component colloidal soil particles, the colloidal soil particles with more negative charges shows the larger polarization effect to metal ions and hence binds metal ions firstly and tightly, which then attract the colloidal soil particles with fewer negative charges. The aggregation processes are cycled and finished this way, and in consequence, the polarization effect is assumed to be responsible for the underlying ion-specific effects.

Although the aggregation of colloidal soil particles (usually carrying abundant negative charges) is dominated by metal ions [22], anions are found to also play a significant role and have clear Hofmeister series, as $\text{H}_2\text{PO}_4^- < \text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{HPO}_4^{2-} < \text{PO}_4^{3-}$ [14]. The DFT calculations indicate that interaction energies of anions with metal ions and proton affinities of anions are two influencing factors for such anion specificities. OH^- can facilely deprive protons from the bridging O atoms and increase the negative charges of colloidal soil particles, which further result in the significant retardation of the aggregation processes. The MD simulations demonstrate that clear anion-specific effects are manifested during the adsorption of anions at the interface of clay minerals and aqueous solutions that abide by the sequence of $\text{OH}^- > \text{F}^- > \text{Cl}^- > \text{I}^-$ [16]. Accordingly, computer simulations have contributed remarkably to the mechanistic understanding of ion-specific effects.

As commented by Nostro and Ninham [119], “if we had to sum up in a line or two what we have learned over the past decade, we could say this: previously biologists and physical chemists lived in parallel universes, almost disjunct.” Ion-specific effects may probably be the bridge that connects soil science with other disciplines such as biology, chemistry, and physics, and the progresses made therein are likely to bring about revolutionary breakthroughs in colloidal and soil sciences. It is just in time that we are lucky to encounter the renaissance of ion-specific effects [120], and computer simulations are destined to play a critical role within the context.

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