

# Computer Simulations to Predict the Adsorption and Cation Exchange at Mineral Surfaces

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**Abstract:** Computer simulations play a critical role in geochemical science. In this work, density functional theory calculations were employed to address some critical issues that are the adsorption of metal ions and cation exchange at clay surfaces. Data showed that the adsorption strengths of metal ions at clay surfaces were enhanced pronouncedly due to the increase of surface charges, while for specific clay particles (with determined surface charges), the adsorption strengths greatly declined with more loading of metal ions. Metal ions adsorbed at clay surfaces can be inter-exchanged, and the exchange difficulty significantly relied on the identity of metal ions and the type of clay minerals. The Hofmeister effects abided by the sequences of  $Cs^+ > K^+ > Na^+ > Li^+$  on montmorillonite, and kaolinite whereas of  $Na^+ > Li^+ > Cs^+ \geq K^+$  on beidellite. Based on the cation exchange studies, mechanism of cation exchange at clay surfaces has been proposed. The cation exchange equilibrium constants were calculated for the various alkali ions at the surfaces of different clay minerals, which are in accord with the experimental observations.

## 1 INTRODUCTION

Adsorption of metal ions at the interface of clay minerals and aqueous solutions largely controls the distribution, transport, and bioavailability of nutrients, water, and contaminants. It has been acknowledged as a critical topic for a number of disciplines such as chemical, environmental and geological sciences (Sposito et al., 1999; Dahn et al., 2003). Cation exchange is closely associated with adsorption. Heavy (e.g.,  $Pb^{2+}$ ) and radioactive (e.g.,  $Pb^{2+}$ ) metal ions adsorbed at clay surfaces can be exchanged with regular metal ions (e.g.,  $K^+$ ), which further remediates the polluted geological resources (Loganathan and Kalinichev, 2017).

Computer simulations have gained a great deal of valuable information such as adsorption configurations, microscopic interactions, dynamics, and diffusion that are otherwise inaccessible. Zhang et al. (Zhang et al., 2017) used first-principles molecular dynamics simulations and found that  $Ni^{2+}$  forms three different complexes with the edge structures of montmorillonite. They were respectively the monodentate binding at the  $\equiv SiO$

site, bidentate binding at the  $\equiv Al(OH)_2$  site and tetradentate binding at the octahedral vacancy with  $Ni^{2+}$  fitting well into the clay lattice. The tetradentate complex is significantly preferred and can be deprotonated at normal conditions ( $pK_a = 8.4$ ) while the other less stable complexes are obviously more difficult to be deprotonated owing to the extremely high  $pK_a$  values. Wang et al. (Wang et al., 2017) demonstrated that six factors affected the adsorption of  $K^+$  at clay surfaces. The quantity of negative charges is the most critical to decide the adsorption performances while the other factors under certain circumstances can also play an important role. Clay minerals generally carry an abundance of negative charges that result in strong surface electric fields (Kumar et al., 2016; Calarge et al., 2013). In presence of strong electric fields, metal ions are inner-sphere adsorbed at the interface of clay minerals and aqueous solution, which resemble closely the adsorption configurations under dry conditions (Zhang et al., 2017; Wang et al., 2017; Tian et al., 2015).

The previous studies (Wang et al., 2017; Li et al., 2017) showed that density functional theory

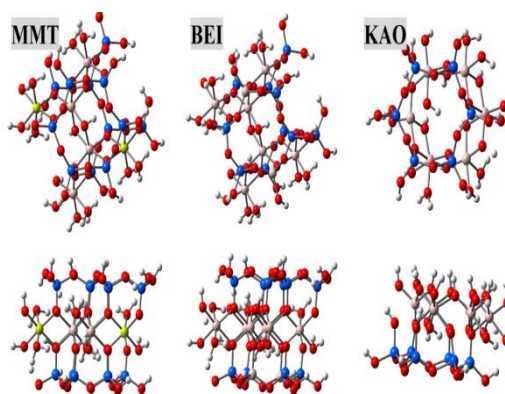
calculations were presently employed to study the adsorption of  $K^+$  ions at montmorillonite surfaces. In addition to the adsorption of a single  $K^+$  ion at clay minerals with different negative charges as reported previously (Wang et al., 2017; Li et al., 2017), disparate numbers of  $K^+$  ions ( $n = 1\sim 3$ ) were considered to inspect the correlation between the adsorption performances vs. the number of metal ions. As observed experimentally, more than one metal ion should be bound onto clay surfaces at the same time. A portion of these adsorbed metal ions can be exchanged and the exchange degree should depend on the identities of two metal ions involved in the exchange processes. The second issue of this work was to address the exchange thermodynamics among the various alkali ions on three clay surfaces (montmorillonite, kaolinite, and beidellite). Then the mechanism of cation exchange at clay surfaces was tentatively proposed. Finally, the cation exchange equilibrium constants for the various alkali ions at clay surfaces were calculated and compare with the experimental results.

## 2 COMPUTATIONAL SECTION

First-principles density functional theory calculations were performed using Gaussian09 software packages (Frisch et al., 2013). Figure 1 showed the models for montmorillonite, kaolinite, and beidellite. Almost all clay minerals were characterized by an abundance of surface charges (Kumar et al., 2016; Calarge et al., 2013). Clay minerals presently used were endowed with -2 charges, unless otherwise noted. As suggested (Wang et al., 2017), metal ions were adsorbed on the external surfaces of clay minerals. In line with previous literatures (Tian et al., 2015; Jia et al., 2018), the hexagonal rings of silica surfaces along with adsorbed metal ions were selected as the high-level region that was handled at the B3LYP/6-31+G(d,p) level of theory, while the rest of models were treated as the low-level region and simulated by the B3LYP/3-21G method. Owing to the significance of relativistic effects, the inner and valence electrons of Cs were described by the LanL2DZ effective core potential and LanL2DZ basis set, respectively.

## 3 RESULTS AND DISCUSSION

### 3.1 $K^+$ adsorption onto Montmorillonite Surfaces



Top (upper panel) and side (lower panel) views of models are shown, and Si, Al, Mg, O and H are presented in blue, pink, yellow, red and white balls, respectively.

Figure 1: Models of montmorillonite (MMT), beidellite (BEI) and kaolinite (KAO).

With the increase of negative charges in montmorillonite caused by more  $Mg^{2+}/Al^{3+}$  substitutions, the distances of  $K^+$  to the adjacent surface-O atoms ( $O_S$ ) showed a gradual reduction, consistent with the previous results (Wang et al., 2017; Tian et al., 2015). For  $\sigma$  (the number of negative charges) = 1, 2, 3, the distances of  $K^+$  to three closet  $O_S$  atoms were averaged at 2.734, 2.684 and 2.657 Å, suggesting that there were stronger interactions between metal ions and clay surfaces due to the increase of negative charges. The interaction energies between  $K^+$  and the montmorillonite models were calculated to be -522.5, -739.6 and -976.8 kJ/mol, respectively, and the adsorption performances of metal ions were substantially enhanced at clay surfaces with more negative charges (Wang et al., 2017; Tian et al., 2015). It demonstrated that the quantity of negative charges plays a critical role during the adsorption of metal ions (Wang et al., 2017; Li et al., 2017).

Figure 2 depicted the adsorption configurations of one, two and three  $K^+$  ions onto the surfaces of montmorillonite with two  $Mg^{2+}/Al^{3+}$  substitutions (Calarge et al., 2013). Compared with the first  $K^+$  ion ( $n = 1$ ), the adsorption strengths of subsequent  $K^+$  ions considerably reduced, and the interactions

energies between the first, second and third  $K^+$  ions and the montmorillonite surfaces amounted to -739.6, -379.6 and -131.4 kJ/mol, respectively. It clearly indicates that for given clay particles, the latter adsorbed metal ions are more facile to be detached from their surfaces and as the desorption process continues, metal ions are getting more and more difficult to desorb.

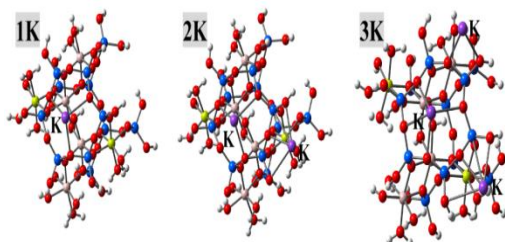


Figure 2: Structures for the adsorption of one, two and three  $K^+$  ions at montmorillonite surfaces.

Si, Al, Mg, O, K and H are presented in blue, pink, yellow, red, purple and white balls, respectively.

### 3.2 Cation Exchange Thermodynamics and Mechanism

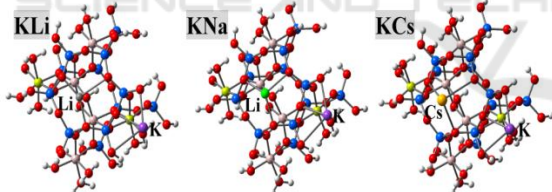
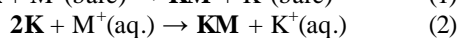


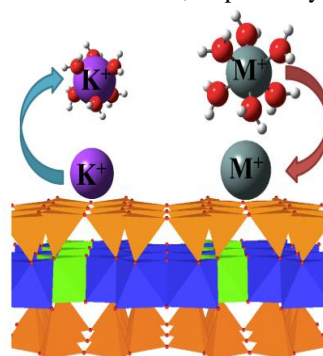
Figure 3: Structures for the adsorption of  $Li^+$ ,  $Na^+$  and  $Cs^+$  at  $K^+$ -montmorillonite surfaces

Si, Al, Mg, O, K, Li, Na, Cs and H are presented in blue, pink, yellow, red, purple, grey, green, orange and white balls, respectively.

Figure 3 showed the structures of **2K** (Figure 2) exchanged by one other alkali ion  $M^+ = Li^+, Na^+, Cs^+$ . The adsorption configurations of different alkali ions at clay surfaces resembled closely each other. Two different mechanisms for cation exchange were given,



where bare and aqution in parentheses manifest the bare and aqueous conditions, respectively.



Scheme 1: Mechanism posed for cation exchange ( $M^+/K^+$ ) at clay surfaces.

The cation exchange energies were calculated and are presented in Table 1. When the bare metal ions were used (eq. 1), the cation exchange energies were -176.4, -96.4 and 81.7 kJ/mol for  $Li^+$ ,  $Na^+$  and  $Cs^+$ , respectively. The Hofmeister sequence based on the bare metal ions was presented as  $Li^+ > Na^+ > K^+ > Cs^+$ , apparently differing from the experimental observations (Tian et al., 2015). When the aqueous species were used (eq. 2), the cation exchange energies amounted to 14.3, 5.1 and -13.3 kJ/mol for  $Li^+$ ,  $Na^+$  and  $Cs^+$ , respectively, where a consistent Hofmeister series with the experimental observations ( $Cs^+ > K^+ > Na^+ > Li^+$ ) was attained. Consequently, the mechanism for cation exchange at clay surfaces should comply with eq. 2 and was further sketched in Scheme 1, which got support from the recent molecular dynamics simulations (Loganathan and Kalinichev, 2017) and the following discussions.

The cation exchange energies ( $M^+/K^+$ ) at the surfaces of beidellite and kaolinite were also calculated (Table 1). The Hofmeister sequences followed as  $Na^+ > Li^+ > Cs^+ \geq K^+$  and  $Cs^+ > K^+ > Na^+ > Li^+$  for beidellite and kaolinite, respectively. Accordingly, disparate clay minerals may correspond to distinct Hofmeister series and cation exchange phenomena. The Hofmeister sequences during ion exchange and clay aggregation were known to be affected by a number of factors (Tian et al., 2015; Li et al., 2017; Jia et al., 2018), and the experimental verifications on these calculated results are anticipated in the near future.

Table 1: Cation exchange energies ( $\Delta E_{ex}$ ) and cation exchange equilibrium constants ( $K_{ex}$ ) for different  $K^+$ -clays <sup>a, b</sup>.

	montmorillonite		beidellite		kaolinite	
	$\Delta E_{ex}$	$K_{ex}$	$\Delta E_{ex}$	$K_{ex}$	$\Delta E_{ex}$	$K_{ex}$
$Li^+$	14.3 (-176.4)	0.0031 ( $8.0 \times 10^{30}$ )	-1.8	2.0	17.8	0.00076
$Na^+$	5.1 (-96.4)	0.13 ( $7.8 \times 10^{16}$ )	-3.5	4.1	7.5	0.048
$Cs^+$	-13.3 (81.7)	217.8 ( $4.9 \times 10^{-15}$ )	-0.8	1.4	-13.6	244.9

<sup>a</sup> Energy units in kJ/mol;

<sup>b</sup> Data using bare metal ions are shown in parentheses.

### 3.3 Cation Exchange Equilibrium Constants

It is difficult for experimentalists to refer to and make comparisons with the calculated cation exchange energies. However, the cation exchange equilibrium constants ( $K_{ex}$ ) can provide a good platform to bridge the computational and experimental results. The cation exchange equilibrium constants ( $K_{ex}$ ) and cation exchange free energies ( $\Delta G_{ex}$ ) can be correlated by the Arrhenius equation [3], i.e.,

$$\Delta G_{ex} = -RT \ln K_{ex} \quad (3)$$

where  $R$  and  $T$  stand for gas constant and temperature, respectively.

$$\begin{aligned} \text{We know that } \Delta G_{ex} &= \Delta H_{ex} - T\Delta S_{ex} \\ &= \Delta E_{ex} + p\Delta V_{ex} - T\Delta S_{ex} \end{aligned} \quad (4)$$

where  $H$ ,  $S$ ,  $p$ , and  $V$  are enthalpy, entropy, pressure, and volume, respectively.

For cation exchange at clay surfaces, the volumes of clays remained essentially invariable ( $\Delta V_{ex} \cong 0$ ), and because the clay structures prior and posterior to cation exchange (Figures 2 and 3) closely resembled each other, the entropic effects can almost be neglected ( $\Delta S_{ex} \cong 0$ ). Accordingly, the cation exchange energies ( $\Delta E_{ex}$ ) were close to the cation exchange free energies ( $\Delta G_{ex}$ ) and were used for calculating the cation exchange equilibrium constants ( $K_{ex}$ ). The cation exchange equilibrium constants ( $K_{ex}$ ) (Table 1) can be compared directly with the experimental results: Hanshaw (Hanshaw, 1963) and Crooks et al. (Crooks et al., 1993) determined that  $K_{ex}$  approximates 0.2 and 0.06~0.12 for  $Na^+/K^+$ , respectively, for montmorillonite, which is in good agreement with the present value of 0.13

and further demonstrated the cation exchange mechanism posed in Scheme 1. Table 1 showed the  $Na^+/K^+$  exchange equilibrium constant using the bare metal ions was calculated to be  $7.8 \times 10^{16}$  and deviated remarkably from the experimental data.

## 4 CONCLUDING REMARKS

We used density functional theory calculations to address some critical issues that are the adsorption of metal ions and cation exchange at clay surfaces. The interaction energies of metal ions at the clay surfaces were pronouncedly enhanced due to the increase of surface charges suggesting the reinforced adsorption strengths, while for given clay particles (with determined surface charges), the adsorption strengths declined greatly with the increased loading of metal ions. Accordingly, the latter adsorbed metal ions were more facile to be detached from clay surfaces.

Metal ions adsorbed at clay surfaces can be inter-exchanged, and the exchange difficulty significantly relied on the identity of metal ions and the type of clay minerals. The Hofmeister effects abided by the sequence of  $Cs^+ > K^+ > Na^+ > Li^+$  for montmorillonite that agreed finely with the experimental observations. The Hofmeister sequence remained for kaolinite while was altered substantially for beidellite where the sequence was presented as  $Na^+ > Li^+ > Cs^+ \geq K^+$ .

The mechanism of cation exchange at clay surfaces has been posed and got strong support from the present density functional theory and previous molecular dynamics results. The cation exchange equilibrium constants were calculated for the various alkali ions at the surfaces of montmorillonite, beidellite, and kaolinite that are in line with the experimental observations available.

## ACKNOWLEDGEMENTS

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