Kinetics of cation adsorption on charged soil mineral as strong electrostatic force presence or absence

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Abstract

Purpose The purposes of this research were to: (1) establish new analytical kinetic equation for describing the effect of strong electrostatic force on adsorption; (2) experimentally determine if it is a strong or weak electrostatic force adsorption process; and (3) evaluate the adsorption energies of the strong and weak force adsorptions based on the proposed new theory of cation adsorption kinetics.

Materials and methods The constantly charged material-montmorillonite was used in the experiment. The montmorillonite was saturated with two Cation species: K⁺ and Ca²⁺, respectively, using KNO₃ or Ca(NO₃)₂ before it was used for the experiment. The miscible displacement technique under a steady flow condition was adopted to the kinetic studies of Mg²⁺ (Mg(NO₃)₂) adsorption. In the experiment, 0.5000 g of K⁺- or Ca²⁺-saturated montmorillonite was layered on the exchange column, the thickness of sample layer was approximately 0.2–0.3 mm, the cross-sectional area of the column (sample area) was 15 cm². The concentration of Mg²⁺ in the flowing liquid was 10⁻⁴ mol L⁻¹. The flow velocity of the flowing liquid was 1.0 mL·min⁻¹. Effluent was collected at 10-min intervals.

Results and discussion Firstly, new and exact rate models for describing ion adsorption have been advanced. Secondly, based on the experiments of Mg²⁺/K⁺ and Mg²⁺/Ca²⁺ exchange in K⁺ and Ca²⁺-saturated montmorillonites, Mg²⁺ adsorption in K⁺-saturated sample appeared zero-order kinetic process in the initial stage of the strong force adsorption for t=0–405 min, and then the adsorption process converted to the first-order kinetics of the weak force adsorption, which agrees with the theoretical prediction. However, for the Ca²⁺-saturated sample, merely first-order kinetic process appeared for Mg²⁺ adsorption. Either for Mg²⁺/K⁺ exchange or Mg²⁺/Ca²⁺ exchange, the quantities of Mg²⁺ by weak force adsorption at equilibrium were almost the same. Thirdly, several important dynamic and thermodynamic parameters can be theoretically calculated based on the new theory in describing cation adsorption.

Conclusions For Mg²⁺/K⁺ exchange, both strong and weak electrostatic force adsorptions exist, but for Mg²⁺/Ca²⁺ exchange only the weak electrostatic force adsorption occurs. The strong and weak force adsorption processes can be quantitatively described by the new analytical kinetic equations of the zero- and the first-order kinetics, respectively. Because each parameter in the analytical kinetic equations has its definitive physical meaning, several important dynamic and thermodynamic parameters in cation exchange can be theoretically estimated.

Keywords Cation adsorption · Charged soil · Diffusion layer (DL) · Strong electrostatic force · Weak electrostatic force

1 Introduction

The negative charges on soil particle surface, together with counter-ions in diffuse layer (DL), form an electrostatic
field in the soil solution adjacent soil particle surface. Recently, Li and Wu (2007); Li et al. (2010); Li and Li (2010) found that, cation exchange is essentially a cation diffusion process in the electrostatic field of DL. Li et al. (2010); Li and Li (2010) also found that, the electrostatic field in the DL can substantially speed up the cation diffusion or adsorption process. Besides, experimental results revealed that, when the soil samples were Ca\(^{2+}\)-saturated, only the first-order kinetic process was observed for Mg\(^{2+}\) adsorption in the Mg\(^{2+}/\text{Ca}^{2+}\) exchange experiment (Li et al. 2010). In contrast, as soil samples were K\(^{+}\)-saturated, both zero- and first-order kinetic processes appeared for Mg\(^{2+}\) adsorption in Mg\(^{2+}/\text{K}^{+}\) exchange experiment (Li and Li 2010). The zero-order kinetic process was considered to be a strong electrostatic force adsorption for Mg\(^{2+}\) (Li and Li 2010). Why did the zero-order process for Mg\(^{2+}\) adsorption appeared in Mg\(^{2+}/\text{K}^{+}\) exchange but did not in Mg\(^{2+}/\text{Ca}^{2+}\) exchange experiment, and how could we experimentally distinguish these two states of cation adsorptions?

\[ f_i(x,t) = f_{i0}e^{-\frac{4p_i x \phi(x,t)}{\pi R T}} \left[ 1 - \sum_{n=0}^{\infty} \frac{4}{(2n + 1)\pi} e^{-\frac{x^2l^2(2n+1)^2t}{l^2}} \sin \left( \frac{(l - x)}{l} \frac{(2n + 1) \pi}{2} \right) \right] \]  

(1)

where \( f_i(x,t) \) is the concentration of \( i \)th ion species at the distance \( x \) away from particle surface and time \( t \); \( \phi(x,t) \) is the electric potential in the electric field of DL; \( Z_i \) is the charges of the ion species; \( F \) is the Faraday constant; \( R \) is the gas constant; \( T \) is the absolute temperature; \( D_{pi} \) is the apparent diffusion coefficient of ion \( i \)th species in soil, and for soil \( D_{pi} = \theta (l/l_e)^2 D_p r \) (Kemper and Van Schaik 1966), \( \theta \) is the volumetric water content, \( (l/l_e)^2 \) is the tortuosity factor, \( D_p \) is the diffusion coefficient of the ion; and \( r \) is a coefficient accounting for ionic interaction.

Because the series in Eq. 1 converges rapidly, at large \( t \) (often larger than several 10 min depending on the value of \( \pi^2\Delta l/4l^2 \)), only the term \( n=0 \) needs to be considered, Eq. 1 becomes:

\[ f_i(x,t) = f_{i0}e^{-\frac{4p_i x \phi(x,t)}{\pi R T}} \left[ 1 - \frac{4}{\pi} e^{-\frac{x^2l^2}{l^2}} \sin \left( \frac{l - x}{l} \frac{\pi}{2} \right) \right] \]  

(2)

For a period of time \( t=0\sim t \), the total quantity of \( i \)th cation species diffusion/adsorption through the plane of \( x=l \) into the space of \( x=0\sim l \) should be expressed as:

\[ N_i(t) = S \int_0^l f_i(x,t) \, dx \]  

(3)

where \( N_i(t) \) is the total adsorption quantity (mol/g) from \( t=0 \) to \( t \); \( S \) is the specific surface area of the sample with unit dm\(^2\)g\(^{-1}\).

This research is to develop new kinetic equations by considering the strength of the electrostatic force from the charged particle surface, to determine if the adsorption is caused by the strong or weak electrostatic force in one experiment, and to evaluate the adsorption energies of the strong and weak adsorptions based on the new theory of cation adsorption kinetics.

### 2 Theory

#### 2.1 The flux equations for ion adsorption by considering the electric field from surface charges

In the experiment of the miscible displacement, the adsorption process can be illustrated in Fig. 1. Under this experimental condition, Li et al. (2010) demonstrated that, in the domain of \( x=0\sim l \), the ionic dynamic distribution can be described by the following equation:

\[ j_i = \frac{dN_i(t)}{dt} \]

\[ = D_{pi} \left\{ \int_0^l \pi \frac{f_{i0} }{l} e^{-\frac{x^2l^2}{l^2}} e^{-\frac{4p_i x \phi(x,t)}{\pi R T}} \sin \left( \frac{(l - x)}{l} \frac{\pi}{2} \right) \, dx \right\} \]  

(4)

According to the definition of the apparent concentration or activity by Li et al. (Li and Wu 2004, 2007; Li et al. 2010), Eq. 2 is changed to:

\[ A_i(x,t) = f_i(x,t) e^{-\frac{4p_i x \phi(x,t)}{\pi R T}} \]

\[ = f_{i0} \left[ 1 - \frac{4}{\pi} e^{-\frac{x^2l^2}{l^2}} \sin \left( \frac{l - x}{l} \frac{\pi}{2} \right) \right] \]  

(5)

where \( A_i(x,t) \) is the apparent concentration or activity of \( i \)th ion species at distance \( x \) away from particle surface and time \( t \). Introducing Eq. 5 into Eq. 4, there is

\[ j_i = \frac{dN_i(t)}{dt} = \frac{\pi^2 D_{pi}}{4l} \left\{ \int_0^l e^{-\frac{4p_i x \phi(x,t)}{\pi R T}} f_{i0} - A_i(x,t) \, dx \right\} \]  

(6)

Equation 6 is the flux equation for describing ion diffusion/adsorption by considering the electric field from soil particle surface under the miscible displacement experiment. Equation 6 implies that, the electric field is...
through the average effect of the electric field from $x=0$ to $l$ to influence cation diffusion/adsorption rate or the flux.

2.2 The adsorption kinetics as strong electrostatic adsorption force presence

The presence of strong electrostatic adsorption force means a strong negative energy area or a deep potential well near the soil particle surface (as shown in Fig. 2). Once a cation falls into (adsorbed) the strong negative energy area or the potential well, the cation will be strongly adsorbed and thus it will be very difficult to escape from the potential well. Therefore, the strongly adsorbed cation can be treated as “disappeared” immediately from the solution adjacent particle surface. The “disappear” of the absorbed cation means that the activity of the cation in the solution near soil particle surface (in the potential well) is approximately zero. Obviously, this phenomenon will only appear in the initial stage of the cation exchange experiment. This process can be illustrated as in Fig. 2. Mathematically, it can be expressed as:

$$f(x) - A_t(x, t) \approx f_0$$

(7)

Introducing Eq. 7 into Eq. 6, we get the flux equation at the presence of strong adsorption force:

$$j_i = \frac{dN_i(t)}{Sdt} = \frac{\pi^2 D_{pi}}{4l^2} f_0 \int_0^l e^{-\frac{2\phi(x)}{RT}} dx$$

(8)

Thus, the rate equation for describing ion adsorption can be expressed as:

$$\frac{dN_i(t)}{Sdt} = k_1 = k_1[N_i(t)]^0$$

(9)

where $k_1$ is the rate coefficient, and (Li et al. 2010):

$$k_1 = \frac{D_{pi} l^2}{4l^2} f_0 \int_0^l e^{-\frac{2\phi(x)}{RT}} dx$$

(10)

Because Eq. 9 is proportional to the zero power of $N_i(t)$, it can be referred as the zero-order rate equation. Thus, the zero-order kinetic process in cation adsorption implies the presence of strong adsorption force.

Li and Xue (1996); Li et al. (2010) suggested an approximate equation for describing zero-order kinetic process, in which the rate coefficient is assumed as:

$$k_1 = \frac{D_{pi} l^2}{4l^2} f_0 \int_0^l e^{-\frac{2\phi(x)}{RT}} dx$$

(11)

which is slightly different from the exact expression of Eq. 10.

In order to conveniently using the experimental data directly, Eq. 9 can be written to the discrete form:

$$\frac{N_i(t_{m+1}) - N_i(t_m)}{S(t_{m+1} - t_m)} = k_1 [N_i(t_{k+1/2})]^0$$

(12)

where $m = 0, 1, 2, 3, \ldots, N_i(t_{m+1/2}) = N_i(t_m) + 0.5[N_i(t_{m+1}) - N_i(t_m)]$. Equation 12 implies that, using experimental data obtained in the presence of strong adsorption forces to plot a relationship curve of $[N_i(t_{m+1}) - N_i(t_m)]/S(t_{m+1} - t_m)$ vs. $N_i(t_{m+1/2})$, a straight line which is parallel to abscissa axis can be expected, and the intercept of the straight line will be the rate coefficient $k_1$ of ion adsorption for the strong force adsorption.

However, when the strong adsorption sites are saturated by the adsorbed cations (strong force adsorption ceased or completed), then the driving force for cation adsorption will shift to the weak electrostatic force, which can be illustrated as Fig. 3.

In the process of weak force adsorption, the distance of ion diffusion is shortened from $0-l$ to $0-l'$ as shown in
Nevertheless, we should note that in Eq. 15, the initial time moment of the weak force adsorption but not replaced by \( l \), where \( \text{Ni} \) is the weak force adsorbed quantity at equilibrium: 

\[
\text{Ni}_\infty = \text{Sf}_0 \int_0^{l'} e^{-\frac{2\pi^2 \sigma(x)}{\text{S}}} dx
\]  

(14)

\[
k_2' = \frac{\pi^2 D_p l_f}{4l^2} \text{Sf}_0 \int_0^{l'} e^{-\frac{2\pi^2 \sigma(x)}{\text{S}}} dx
\]  

(15)

Equation 13 shows that ion diffusion/adsorption kinetics in the process of weak force adsorption is a first-order kinetic process.

From the above analysis, the adsorption process can be conceptually described in two stages: zero- and first-order processes. However, in the second stage (the weak force adsorption), the experimentally determined \( N_i(t) \) values include the contribution of the adsorbed cation quantities in the first stage, and it is difficult to determine how many cations are strongly adsorbed in advance in the first stage. In order to directly use the experimental data of \( N_i(t) \) and \( N_{\infty} \) to analyze the kinetic characteristics, the two straight lines could be obtained. In the initial stage of adsorption, the straight line will be parallel to the absorbaxis axis, and the intercept of the straight line will be the rate coefficient \( k_1 \); then, at a given time moment, that relationship curve will transfer to another straight line, the intercept and the slope of the straight line will be \( k_2 \) and \( \pi^2 D_p l_f/4l^2 \text{S} \), respectively. The turning point of the two straight lines corresponds to the time when the strong force adsorption transfer to the weak force adsorption. Considering \( l'\leq l \), there must be \( k_2>k_1 \). Thus, if both strong and weak forces adsorption presence, the two straight lines could be illustrate in Fig. 4.

When the Eqs. 12 and 16 were directly used to fit to the experimental kinetic data, the value of \( N_{\infty} \) is not required in advance. In the past, it was common practice to use the

![Fig. 3](image-url)

**Fig. 3** A conceptual diagram of ion adsorption for the weak force adsorption.

![Fig. 4](image-url)

**Fig. 4** The adsorption rate curves containing both strong and weak force adsorptions: (① strong force adsorption, ② weak force adsorption.)
integral form to describe the experiment data, and a straight
line of \(\ln(1 - \frac{N(t)}{N_{\infty}})\) vs. \(t\) can be obtained when there
exists the first-order process (Sparks and Jardine 1984; Aharoni et al. 1991; Jardine and Sparks 1984; Li and Xue 1996). But if the integral form is used, the \(N_{\infty}\) value must be
known in advance. Unfortunately, direct and accurate
determination of the true \(N_{\infty}\) is usually not possible. From
theoretical analysis, the directly determined \(N_{\infty}\) within a
finite time will always be lower than the true value, because
the true value can only be obtained when \(t=\infty\).

When a lower than the true value of \(N_{\infty}\) is used for
describing the experimental data, the slope of the fitted
curve of \(\ln(1 - \frac{N(t)}{N_{\infty}})\) vs. \(t\) will approach to infinite as
time \(t\) increases, similar to the dashed line shown in Fig. 5.
Considering the slope is the rate coefficient, \(\frac{\pi^2 D_p}{4 l^2 S}\), if
the obtained slope is infinite, this result must be absurd.

3 Material and methods

3.1 Material and sample preparation

The constantly charged material-montmorillonite was used as
the experimental material. The montmorillonite was bought
from Chi-Feng WHTB mining Co., Ltd., China. The surface
properties of the montmorillonite determined by the method
recently developed by Li et al. (unpublished material) are
shown in Table 1. The montmorillonite was pre-H+-saturated
for the surface properties determination, and the method was
based on the exchange equilibrium of \(\text{Na}^+/\text{Ca}^{2+}\) at \(\text{pH}=7\) for
the montmorillonite.

Theoretically speaking, the monovalent cations such as \(\text{K}^+\),
\(\text{Na}^+\) have weaker effect on shielding the negative electrostatic
field from soil particle surface than that of the divalent
cations such as \(\text{Ca}^{2+}, \text{Mg}^{2+}\). Therefore, the electric field
strength of the samples saturated with monovalent cations is
much greater than that of the divalent cations saturated with
the same electrolyte concentration. This implies that, as the
negative charges on particle surface are saturated by \(\text{K}^+\), a

Stronger electrostatic field is potentially created, and thus a
stronger force adsorption may exist for \(\text{Mg}^{2+}\) adsorption in
the \(\text{Mg}^{2+}/\text{K}^+\) exchange experiment. On the other hand, as the
negative charges on the particle surface are saturated by \(\text{Ca}^{2+}\),
no strong electrostatic field will be created, and no strong
force adsorption will exist for \(\text{Mg}^{2+}\) adsorption in the \(\text{Mg}^{2+}/\text{Ca}^{2+}\) exchange experiment. Therefore, in the experiment the
samples were pre-saturated by \(\text{K}^+\) and \(\text{Ca}^{2+}\), respectively, and
the exchange cation was selected \(\text{Mg}^{2+}\).

3.2 Kinetic studies of adsorption

The kinetics of \(\text{Mg}^{2+}\) (\(\text{Mg(NO}_3\text{)}_2\)) adsorption in the \(\text{K}^+/\text{Ca}^{2+}\)-saturated
montmorillonites (\(\text{Mg}^{2+}/\text{K}^+\) and \(\text{Mg}^{2+}/\text{Ca}^{2+}\) exchange) were investigated by the miscible displacement
under a steady flow condition. The experiment was carried
out as follows: approximately 0.5 g of \(\text{K}^+\)- or \(\text{Ca}^{2+}\)-saturated
montmorillonite was layered on an exchange column (the
mass of the samples were determined at the end of each
experiment finished). The thickness of the sample layer was
very thin in the sample chamber for the purpose of reducing
the effect of longitudinal concentration gradient in the
experiment, since our theoretical analysis is based on the
one-dimensional case. In our experiments, the sample layers
were in the 0.2–0.3 mm range (Li et al. 2010). The sample
cross-sectional area was about 15 cm². The experimental
temperature was 298 K. The concentration of \(\text{Mg}^{2+}\) in the
flowing liquid was \(10^{-4} \text{ mol L}^{-1}\). The flow velocity of the
solutions was \(1.0 \text{ ml min}^{-1}\). Effluent was collected at 10-min
intervals. The quantity of the ion that flowed through the
interface \(x=l\) into the fixed liquid film at \(x=0\) for a period
of time \(t=0\) was calculated based on the difference of \(\text{Mg}^{2+}\)
concentration in the influent and the effluent.

4 Results and discussion

4.1 \(\text{Mg}^{2+}\) adsorption kinetic analyses for \(\text{Mg}^{2+}/\text{K}^+\)
and \(\text{Mg}^{2+}/\text{Ca}^{2+}\) exchange

The experimental results of \(\left[\frac{N(t_m+1)-N(t_m)}{S(t_m+1)-t_m}\right]\) vs.
\(N(t_{m/2})\) for \(\text{Mg}^{2+}\) adsorption in \(\text{Mg}^{2+}/\text{K}^+\) and \(\text{Mg}^{2+}/\text{Ca}^{2+}\) exchanges are shown in Figs. 6 and 7, respectively.

Figure 6 shows that: (1) The zero-order kinetic process
was present in the initial stage of adsorption for
\(t=0\)–405 min, which is an indication of strong force

\begin{table}[h]
\centering
\caption{Determined surface properties of the montmorillonite}
\begin{tabular}{llll}
\hline
Sample & Specific surface area \\
& \((S, \text{ m}^2\text{ g}^{-1})\) & Surface charge density \\
& \((\sigma_0, \text{ mmol} \text{ cm}^{-2})\) & Surface charge number \\
& \((\text{emol} \text{ kg}^{-1})\) & \\
\hline
Montmorillonite & 650.5 & 9.562×10^{-4} & 62.2 & \\
\hline
\end{tabular}
\end{table}
adsorption for Mg$^{2+}$ in the experiment of Mg$^{2+}$/K$^+$ exchange. Since there exists no strong chemical bond between Mg$^{2+}$ and the particle surface for the sample, the strong force adsorption can be attributed to the electrostatic force; and (2) The experimental results shown in Fig. 6 agree well with the theoretical prediction (see Fig. 4). After a period of time (about 405 min) in the experiment, the adsorption process shifted to the first-order kinetic process, and the turning point from the zero-order to the first-order was very distinct.

However, for the Mg$^{2+}$ adsorption in the Mg$^{2+}$/Ca$^{2+}$ exchange, the zero-order kinetic process did not appear with the theoretical prediction (see Fig. 7). Therefore, for Mg$^{2+}$ adsorption in Mg$^{2+}$/Ca$^{2+}$ exchange, only the weak force adsorption process was present.

It is well known that the electrostatic field strength around a particle in solution for Ca$^{2+}$-saturated sample will be much weaker than that for the K$^+$-saturated sample. Using the data shown in Table 1, the distribution of the potential energy $E(x)=ZF\rho(x)$ of Mg$^{2+}$ in the space adjacent particle surface was calculated (Li et al. 2004). Figure 8 shows the distributions of the potential energy of Mg$^{2+}$ in the space adjacent to the particle surface for Ca$^{2+}$- and K$^+$-saturated montmorillonites, respectively. In the calculation, we used the initial concentration in bulk solution of $10^{-5}$ molL$^{-1}$ for Ca$^{2+}$ and K$^+$ in the suspensions of Ca$^{2+}$- and K$^+$-saturated montmorillonites. We know that, in the preparation of a basic cation species saturated sample, the concentration of the basic cation species in bulk solution cannot much lower than $10^{-5}$ molL$^{-1}$. If the concentration is much lower than $10^{-5}$ mol/l, the adsorption quantity of H$^+$ on particle surface cannot be neglected because of H$^+$/K$^+$ or H$^+/Ca^{2+}$ exchange even at pH=7.

Figure 8 indicates that, at a given position in the space adjacent to particle surface, the potential energy of Mg$^{2+}$-saturated in the K$^+$-saturated sample is much lower than that in the Ca$^{2+}$-saturated sample. For example, at a distance of 1 nm away from particle surface, the potential energy of adsorbed Mg$^{2+}$ is $E_{Mg}$=-48,803 Jmol$^{-1}$ for the K$^+$-saturated sample; while it is $E_{Mg}$=-21,806 Jmol$^{-1}$ for the Ca$^{2+}$-saturated sample. Therefore, Mg$^{2+}$ can be adsorbed much stronger in the K$^+$-saturated montmorillonite than that in the Ca$^{2+}$-saturated montmorillonite. On the other hand, at a distance of 1 nm away from particle surface, the difference of potential energy between $E_{Mg}$ and $E_{Ca}$ is $\Delta E_{Mg/Ca}=E_{Mg}−E_{Ca}=-21,806+21,806=0$ Jmol$^{-1}$ for the Mg/Ca exchange; while the difference of potential energy between $E_{Mg}$ and $E_{K}$ was $\Delta E_{Mg/K}=E_{Mg}−E_{K}=-48,803+48,803/2=-24,401.5$ Jmol$^{-1}$ for the Mg/K exchange, which indicates that the Mg$^{2+}$ exchange for K$^+$ is much easier than Mg$^{2+}$ exchange for Ca$^{2+}$. Therefore, the Mg/K exchange exhibits the zero-order kinetic process, while the Mg/Ca exchange does not.

### 4.2 Estimation of dynamic and thermodynamic parameters in cation exchange

Because each parameter in the new kinetic equations has its definite physical meaning, some important dynamic and

![Image](image-url)
thermodynamic parameters in cation exchange can be calculated based on the new theory for describing the cation adsorption.

(1). Estimation of the adsorbed quantities of Mg$^{2+}$ by the strong and weak force adsorption at equilibrium

From Eq. 16, using the slope and the intercept of the straight line shown in Figs. 6 or 7, the total adsorbed quantities: $N_\infty$ can be calculated as:

$$N_\infty = \frac{k_2}{|\text{slop}|}$$  (19)

Since both strong and weak force adsorptions coexisted for the Mg$^{2+}$ adsorption in the Mg/K exchange, from Fig. 6 the calculated $k_2$=6.2811×10$^{-7}$ mmol min$^{-1}$ m$^{-2}$, and $|\text{slop}|=0.0148×10^{-7}$ kmn min$^{-1}$ m$^{-2}$. Using the two values, in Eq. 19, the calculated the total adsorbed quantities: $N_\infty$ = 424.4mmolkg$^{-1}$. The adsorption quantity of Mg$^{2+}$ at the turning point represents the maximum quantity of the strong force adsorption at equilibrium, while the difference between the total adsorption and the adsorption at the turning point is the weak force adsorption (see Fig. 6). According to the fitting equations shown in Fig. 6, at the turning point we had:

$$4.5476 = -0.0148x + 6.2811$$  (20)

where $x$ is the adsorption quantity of Mg$^{2+}$ at the turning point.

From Eq. 20 we can get the quantity of the strong force adsorption of Mg$^{2+}$ at equilibrium, it was 117.1 mmolkg$^{-1}$. We can further calculate the quantity of the weak force adsorption of Mg$^{2+}$ at equilibrium, it was 424.4−117.1=307.3 mmolkg$^{-1}$. Considering the electro-neutrality principle, for a constantly charged material-montmorillonite, the total surface charge or the surface charge at the origin of the strong force adsorption layer is 424.4×2 mmol$\text{cmol}_\text{L^{-1}}$ kg$^{-1}$=84.9 cmol$\text{cmol}_\text{L^{-1}}$ kg$^{-1}$. Correspondingly, the charge at the origin of the weak force layer is 307.3×2 mmol$\text{cmol}_\text{L^{-1}}$ kg$^{-1}$=61.5 cmol$\text{cmol}_\text{L^{-1}}$ kg$^{-1}$, which is very close to the determined surface charge number of 62.2 cmol$\text{cmol}_\text{L^{-1}}$ kg$^{-1}$, as shown in Table 1.

Considering H$^+$ has a stronger adsorption force in a given electrostatic field than Ca$^{2+}$, this results might imply that, if a H$^+$-saturated sample were used in the cation exchange experiment for surface properties determination, a portion of the strongly adsorbed H$^+$ could not be exchanged by a basic cation species, e.g., Ca$^{2+}$ and Na$^+$ there.

Since only the weak force adsorption exists for Mg$^{2+}$ adsorption in the Mg/Ca exchange, from Fig. 7 and Eq. 19, the calculated adsorption quantity of Mg$^{2+}$ at equilibrium is 4.4773/0.0152=294.6 mmolkg$^{-1}$, which means that the surface charges at the origin of the weak force adsorption layer is 58.92 cmol$\text{cmol}_\text{L^{-1}}$ kg$^{-1}$. This result also indicates that, because Ca$^{2+}$ has a stronger adsorption force in a given electrostatic field than Mg$^{2+}$, a portion of the strongly adsorbed Ca$^{2+}$ cannot be exchanged by Mg$^{2+}$.

The above discussions shows that, either from the experiment of Mg/K exchange, Mg/Ca exchange, or Ca/H and Na/H exchange, the obtained surface charge numbers at the origin of the weak force adsorption layer are almost the same, they are 61.5, 58.9 and 62.2 cmol$\text{cmol}_\text{L^{-1}}$ kg$^{-1}$, respectively. The results seemingly implied, only when the strong force adsorption exists for cation exchange, e.g., the Mg/K exchange, the total surface charge number at the origin of the strong force adsorption layer can be obtained.

(2). Estimation of the thicknesses of the strong and weak force adsorption layers

Based on the new theory, the average thicknesses of the strong and weak force adsorption layers can be calculated. From Eqs. 11 and 17, we obtain:

$$\frac{l'}{l} = \sqrt{\frac{k_1}{k_2}}$$  (21)

In this exchange experiment, the sample was almost water saturated, and the saturated water content in this experiment for the montmorillonite was 2.44 mlg$^{-1}$ approximately. Therefore the average thickness of the fixed liquid film was $l = 2.44 \times 10^{-6}$ (m$^3$ g$^{-1}$)/ 650.5 (m$^2$ g$^{-1}$) = 3.75nm.

From Fig. 6, we had $k_2$=4.5476×10$^{-7}$ mmol min$^{-1}$ m$^{-2}$, $k_2$=6.2811×10$^{-7}$ mmolmin$^{-1}$ m$^{-2}$, introducing them into Eq. 21, we get $l'/l=0.8509$. Therefore, the average thickness of the weak force adsorption layer was $l'=0.8509 l=3.192$ nm, and the average thickness of the strong force adsorption layer was 0.1491l=0.5591 nm in this experiment for the montmorillonite.

(3). Estimation of the apparent diffusion coefficient of cations

From Eqs. 17 and 18, we have:

$$D_{p} = \frac{4S{l'}^2 \pi}{N_\infty} \cdot \frac{k_2}{N_\infty}$$  (22)

Introducing the corresponding values into Eq. 22, we get the apparent diffusion coefficient of Mg$^{2+}$ in the montmorillonite: $D_{p} = 4 \times 650.5 \times (3.192 \times 10^{-9})^2 \times 6.2811 \times 10^{-7}/3.14^2 \times 0.4244 = 3.979 \times 10^{-2}$/m$^2$/min$^{-1}$.

(4). Estimation of the average activity coefficient of the adsorbed cations
Low (1981) defined an average activity coefficient of electrostatic adsorbed ions:

$$\bar{y}_i = \frac{1}{\phi} \int_0^l f_i e^{-\frac{f_i x}{\kappa}} dx$$  \hspace{1cm} (23)

where $\bar{y}_i$ is the average activity coefficient for all the electrostatic adsorbed Mg$^{2+}$. Combining Eqs. 18 and 23 gives:

$$\bar{y}_i = \frac{S\phi \rho_0}{N_\infty}$$ \hspace{1cm} (24)

Also, for the strong force adsorption ions, according to the definition of the average activity coefficient of adsorbed ions by Li and Wu (2007), there is:

$$\bar{y}_i(s) = \frac{f_i(s)}{\bar{f}_i(s)} = \frac{\phi_0}{S(l-f_i)f_\rho_0} N_i(s)$$ \hspace{1cm} (25)

for the weak force adsorption ions, there is:

$$\bar{y}_i(w) = \frac{f_i(w)}{\bar{f}_i(w)} = \frac{\phi_0}{S\rho_\infty} = \frac{S\phi \rho_0}{N_i(w)}$$ \hspace{1cm} (26)

where $\bar{y}_i(s), \bar{y}_i(w)$ is the average activity coefficient of the adsorbed Mg$^{2+}$ for the strong and weak force adsorptions, respectively; $f_i(s), f_i(w)$ is the average concentration of the adsorbed Mg$^{2+}$ at equilibrium for strong and weak force adsorptions, respectively; $N_i(s), N_i(w)$ are the quantities of the adsorbed Mg$^{2+}$ at equilibrium for strong and weak force adsorptions, respectively.

Based on the above obtained values of $N_\infty, N_i(s)$ and $N_i(w)$, the average activity coefficients of the total electrostatic adsorption Mg$^{2+}$, the strong electrostatic force adsorption Mg$^{2+}$, and the weak electrostatic force adsorption Mg$^{2+}$ can be calculated, the results are listed in Table 2. The data in Table 2 show that: (1) the average activity coefficient of Mg$^{2+}$ is far smaller than 1 due to the influence of the electrostatic field from surface charges of soil particles; (2) the average activity coefficient of Mg$^{2+}$ for the strong electrostatic force adsorption is much lower than that for the weak electrostatic force adsorption; (3) for the Mg/Ca exchange, all the adsorbed Mg$^{2+}$ have high activity because only weak force adsorption exists.

The Debye characteristic length, $1/\kappa$ was estimated to be 17.3 nm in this experiment, where $\kappa$ is the Debye-Huckel parameter. The above discussions showed that, the average thickness of liquid film in the montmorillonite was merely 3.75 nm in the experiment, thus $l<<1/\kappa$, which implies that the diffuse layer at the inner surface of the montmorillonite was not fully expanded.

Considering the electro-neutrality rule:

$$S\phi \int_0^l e^{-\frac{2f_i(x)}{\kappa}} dx = S\phi \int_0^l e^{-\frac{2f_i(x)}{\kappa}} dx$$ \hspace{1cm} (27)

thus as $l<<1/\kappa$, there will be:

$$\bar{y}_i(l) = \frac{1}{\phi} \int_0^l e^{-\frac{2f_i(x)}{\kappa}} dx < \bar{y}_i(1/\kappa)$$

$$= \frac{1}{\kappa} \int_0^l e^{-\frac{2f_i(x)}{\kappa}} dx$$ \hspace{1cm} (28)

Equation 28 shows that, as $l<<1/\kappa$, there must be $\bar{y}_i(l)\bar{y}_i(1/\kappa)$. Therefore, under the same temperature and electrolyte conditions for the same sample, the activity of the adsorbed ions in a not fully expanded diffuse layer is much lower than that in a fully expanded diffuse layer.

Table 2  The average activity coefficients of the adsorbed Mg$^{2+}$

| Treatments      | $N_\infty$ a (mmolkg$^{-1}$) | $N_i(s)$ b (mmolkg$^{-1}$) | $N_i(w)$ c (mmolkg$^{-1}$) | $\bar{y}(s) \times 10^{-4}$ d | $\bar{y}(w) \times 10^{-4}$ e | $\bar{y} \times 10^{-4}$ f |
|-----------------|--------------------------|--------------------------|--------------------------|------------------|------------------|------------------|
| Mg/K exchange   | 424.4                    | 117.1                    | 307.3                    | 3.106            | 6.756            | 5.755            |
| Mg/Ca exchange  | 294.6                    | 0                        | 294.6                    | ~                | ~                | ~                |

\(^a\) Totally adsorbed quantities of Mg$^{2+}$ at equilibrium  
\(^b\) Strong force adsorption quantities of Mg$^{2+}$ at equilibrium  
\(^c\) Weak force adsorption quantities of Mg$^{2+}$ at equilibrium  
\(^d\) Average activity coefficient of the strong force adsorption Mg$^{2+}$  
\(^e\) Average activity coefficient of the weak force adsorption Mg$^{2+}$  
\(^f\) Average activity coefficient for the whole adsorbed Mg$^{2+}$

5 Conclusions

By considering the electric field from particle surface, new exact kinetic equations for describing cation adsorption were developed. The new equations show that, when both strong force adsorption and weak force adsorption coexist in an exchange experiment, the initial stage of strong force...
adsorption can be described by the zero-order kinetics. The adsorption then shifts to the first-order kinetics of the weak force adsorption. In this study, $K^+$- and $Ca^{2+}$-saturated montmorillonites were used in the $Mg^{2+}/K^+$ and $Mg^{2+}/Ca^{2+}$ exchange to verify the theory. As predicted, because $K^+$-saturated montmorillonite can form a much stronger electrostatic field adjacent to the particle surface than the $Ca^{2+}$-saturated montmorillonite, $Mg^{2+}$ adsorption in $K^+$-saturated sample appeared to be a zero-order kinetic process in the initial stage ($t=0–405 \text{ min}$) of the strong force adsorption; the adsorption process then shifted to the first-order kinetics of the weak force adsorption. However, for the $Ca^{2+}$-saturated sample, only the first-order kinetic process was observed for $Mg^{2+}$ adsorption, because only weak electrostatic field presents in the system. Either for $Mg^{2+}/K^+$ exchange or $Mg^{2+}/Ca^{2+}$ exchange, the quantities of $Mg^{2+}$ weak force adsorption at equilibrium were approximately the same (307.3 and 294.6 mmolkg$^{-1}$, respectively).

The new kinetic equations are mathematically precise, and they were derived from the actual physical mechanism of cation adsorption. Thus, those new equations are fundamentally different from the classic apparent kinetic equations. All the parameters in the new equations have definite physical significance. Therefore, using the new equations, some important dynamic and thermodynamic parameters in cation exchange can be estimated from the experimental data. These parameters include the total adsorption quantity, the strong force adsorption quantity and the weak force adsorption quantity of cation at equilibrium; the thicknesses of the strong force adsorption layer and the weak force adsorption layer; the apparent diffusion coefficient of cation in clay; and the average activity coefficients of the adsorbed cations for the strong and weak force adsorptions.

The study also indicates that, only when the strong force adsorption exists for cation exchange, e.g., the Mg/K exchange, the total surface charge number at the origin of the strong force adsorption layer can be determined through the cation exchange method.

6 Recommendations and perspectives

The new theory unifies the diffusion process of cations in solution, the diffusion process of cations in diffuse layer, and the exchange process of cations on surface, which opens a new window for future research of investigating the chemical adsorption mechanisms of heavy metal ions on particle surface. Currently, for heavy metal ions adsorption, only an overall process containing all types of diffusion processes, physical adsorption process and chemical adsorption process, can be detected in experiment.

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