THE CHEMICAL MODELLING OF CLAY/ELECTROLYTE INTERACTIONS FOR MONTMORILLONITE

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ABSTRACT: A study of the ion-exchange properties of montmorillonite has been performed in order to facilitate computer predictions of the chemical properties of natural fluids and mineral assemblies. Clay/electrolyte interactions can be described using a technique based on the concept of hypothetical surface complex formation. This technique, which is compatible with ion-association models such as GEOCHEM, can be used to simulate simultaneous ion-exchange, hydrolysis of clay edges and anion adsorption on clay surfaces. Effects such as variable cation-exchange capacity and compositionally dependent exchange constants, normally indicating non-ideal behaviour, can be simulated using different combinations of ideal reactions involving charged surfaces and complexing groups representing clay edges. The modelling procedures are flexible and thermodynamically self-consistent. The techniques were applied to data on the ion-exchange characteristics of Wyoming bentonite to yield thermodynamic data for the reactivity of this clay with alkali metals, alkaline earths and a range of first-row transition metals at 25°C.

It is common in the application of the classical thermodynamic treatment of ion-exchange (Argersinger, 1950; Gaines & Thomas, 1953; Hogfeld, 1953) to assume that reactivity is dominated by a process of stoichiometric replacement of ions on the surfaces of a material of fixed charge. However, with clays this reaction may be accompanied by simultaneous anion uptake and hydrolysis, with the consequence that the effects of these additional reactions are embodied in the values of solid-phase activity coefficients. This feature may be undesirable, and it is the aim of this paper to offer a simple description of clay/electrolyte interactions which formally acknowledges the existence of multiple reactions.

The approach developed here is compatible with existing multi-component equilibrium models (Nordstrom et al., 1979) based on the principle of ion association. In essence, the methods herein involve transforming classical ion-exchange constants into sets of formation constants which can be used in the above speciation models. A preliminary attempt has been made to apply these techniques to the properties of Wyoming bentonite.

THE PROPERTIES OF MONTMORILLONITE

It is appropriate to first review the behaviour of montmorillonite with a view to defining a set of properties which form the basis of a numerical description of surface reactivity.

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Ideal ion-exchange behaviour

The stoichiometric replacement of ions on a surface of fixed charge can be described by the ion-exchange reaction (equation 8). Ideal ion-exchange is consistent with the compositional independence of the conditional equilibrium constant (equation 10). Sposito & Mattigod (1979) used data by Maes et al. (1976) to show this to be the case for a range of first-row transition metals exchanging with Na on Chambers montmorillonite. Measurements by Sposito et al. (1981) on Cu/Na exchange on Wyoming bentonite yielded an equilibrium constant of $1.32 \pm 0.08$, which is consistent with ideality. Similar measurements for Ca/Na, Mg/Na and Ca/Mg supported ideality with slightly less certainty (Sposito et al., 1983a,b,c).

Gast (1969) has shown that binary reactions between Na, K and Rb on Wyoming bentonite give conditional equilibrium constants which vary by less than 15% over the entire isotherm; only reactions involving Cs, and possibly Rb, show significant signs of non-ideal behaviour. Near ideal behaviour is also exhibited by binary reactions between Na, Li and NH$_4$ on Camp Berteau montmorillonite (Gast, 1969; Gast et al., 1969). Ideality on montmorillonite is supported generally by a range of data reviewed by Bolt (1982), although this review shows that other clay minerals are unlikely to conform to ideal behaviour.

Anion adsorption

There is much evidence to suggest that an increase in the occupancy of clay surfaces by divalent ions is accompanied by an increase in the total adsorbed metal charge and an apparent increase in the selectivity for the divalent ion. Data reviewed by Sposito et al. (1983a) support the argument that anions form complexes with divalent cations on the surfaces of clays to become part of the surface excess, resulting in an increase in the total quantity of charge-neutralizing cations. It appears that in dilute electrolyte solutions monovalent cations do not encourage this type of adsorption (Gast, 1969). Additionally, Sposito et al. (1983a,b) could not detect anion adsorption in perchlorate background ionic media, suggesting that larger monovalent cations are not easily accommodated on or near clay surfaces.

Acid/base behaviour

Clay surfaces have similar affinities for both Na and the proton (Gilbert & Laudelout, 1965). Consequently, protons should not displace significant quantities of charge-neutralizing cations at pH > 4. However, acid/base titration characteristics determined by Marshall & Krinbill (1942) and Marshall & Bergman (1942a; 1942b) and the pH-dependence of the cation-exchange capacity (CEC) (Maes et al., 1976) show selective removal of Na in the pH range 4–6. These data are consistent with a negatively charged group, comprising ~15% of the total clay charge, which can be neutralized by cations including the proton. This functional group probably results from hydrolysis of AlOH and SiOH groups on clay edges. The simplest description considers the group to be a negative species with cation-complexing properties. Reactions of this species take the form:

$$N^{2+} + Z_{e}E^{-} \rightleftharpoons NE_{Z_{e}}$$  \[1\]

where $E^{-}$ is the edge species and $N^{2+}$ is any cation of charge $K_{s+}$. This simple treatment assumes that activity coefficients for the edge species conform to the Debye–Hückel limit,
which may not be the case, and neglects the specific adsorption of anions to the edge sites at low pH (Bolt, 1978). These problems may be resolved in later refinements of the treatment.

THE SIMULATION OF CHEMICAL SPECIATION

The general aspects of chemical speciation models which can be modified to include the description of ion exchange are as follows.

Chemical equilibria

For a system containing $J$ primary components (elements or stable ligands such as $\text{SO}_4^{2-}$) and $I$ complexes, a general reaction equation can be written for the formation of the $i$th complex:

$$
\sum_{j=1}^{J} v_{i,j} c_j + n_i \text{H}_2\text{O} \rightleftharpoons p_i
$$

where $v_{i,j}$ is the number of moles of the uncomplexed species $c_j$ in the reaction to form one mole of complex $p_i$, and $n_i$ is the number of moles of water in the reaction. Both $n$ and $v$ are positive if the species are consumed and negative if produced in the reaction.

The thermodynamic equilibrium constant for this reaction is:

$$
K_i = \frac{m_{pl} \gamma_{pl}}{a_w^i \prod_{j=1}^{J} (m_{c_j} \gamma_{c_j})^{v_{i,j}}}
$$

where $m_{c_j}$ and $m_{pl}$ are the molal concentrations of the uncomplexed species and the complex respectively, $\gamma$ is the respective single-ion activity coefficient and $a_w$ is the activity of water.

Mass balance

Equation (4) can be combined with statement of mass balance to calculate speciation. The general mass balance equation for the $k$th primary component gives the summation of all species which contain the component and is:

$$
T_k = m_{ck} + \sum_{i=1}^{I} v_{i,k} m_{pl}
$$
where $T_k$ is the total quantity of any primary component in the system. The variable $m_{pi}$ can be eliminated from (6) using (4) to give:

$$T_k = m_{ck} + \sum_{i=1}^{I} v_{i(k)} K^w_{i} \prod_{j=1}^{J} m_{ij}^{\alpha_j}.$$  \hspace{1cm} (7)

This mass balance equation applies to all components except protons or hydroxides whose concentrations are described by an equation similar to (7) (Morel & Morgan, 1972).

Thus, equation (7) constitutes $J$ equations with $J$ uncomplexed species as the basis set. These equations can be solved using a linear multidimensional Newton-Raphson method. The solution of these equations gives the electrolyte composition including pH. However, the mass balance equations include mass action quotients which have a composition dependence through the activity coefficients; therefore the following sequence is followed.

1. Estimation of ionic strength, activity coefficients and the subsequent calculation of mass action quotients using equation (5).
2. Solution of equation (7) to yield values of $m_{ci}$ to $m_{cj}$.
3. Calculation of $m_{pi}$ with equation (4) using predicted values $m_{ci}$ to $m_{cj}$ leading to an improved estimate of ionic strength.

Items (1) to (3) are repeated until a constant value of ionic strength is achieved.

This framework can be used to describe ion-exchange components as if they were complexed species using a procedure suggested by Shaviv & Mattigod (1985).

**CLAY/ELECTROLYTE INTERACTIONS**

**Ion-exchange**

The reaction equation describing stoichiometric replacement of ions on the surface of a solid fixed charge is:

$$Z_A A_{(s)} + Z_B B X_{z_A} \rightleftharpoons Z_A B_{(s)} + Z_B A X_{z_A},$$  \hspace{1cm} (8)

where $Z_A$ and $Z_B$ are the valence charges on ions $A$ and $B$, $X$ is the solid exchanger and (s) denotes ions in the solution phase.

The thermodynamic equilibrium constant for this reaction is:

$$K_a = \frac{(x_A f_A)^{Z_A} (m_B g_B)^{Z_A}}{(x_B f_B)^{Z_A} (m_A g_A)^{Z_A}},$$  \hspace{1cm} (9)

where $x_A$ and $x_B$ are the mole fractions of ions on the exchanger phase, $f_A$ and $f_B$ are the respective activity coefficients, $m_A$ and $m_B$ are the molalities of ions in the aqueous phase and $g_A$ and $g_B$ the single-ion activity coefficients respectively.

A conditional equilibrium constant can be defined as:

$$K_v = \frac{x_A^2 (m_B g_B)^{Z_A}}{x_B^2 (m_A g_A)^{Z_A}},$$  \hspace{1cm} (10)

therefore,

$$K_a = K_v (f_A^2 / f_B^2).$$  \hspace{1cm} (11)
The equations to here are consistent with the classical thermodynamic treatment which yields the solid-phase activity coefficients using the Gibbs–Duhem equation (Argersinger et al., 1950). Our approach is to describe ion-exchange by implementing a convention based on the concept of surface complex formation. This is a quasi-thermodynamic approach designed to predict the macroscopic transfer of ions between phases; it is not a description of molecular configurations at clay surfaces.

Defining a reactive component $X^-$ as a hypothetical aqueous species representing one mole of charged surface with unit valency allows hypothetical complex reactions for this species to be written: i.e.

$$A_{(b)}^{Z_A} + Z_A X^- \rightleftharpoons AX_{Z_A}$$  \hspace{1cm} (12)

and

$$B_{(b)}^{Z_B} + Z_B X^- \rightleftharpoons BX_{Z_B}$$  \hspace{1cm} (13)

Such equations are identical with those describing the formation of aqueous complexes from hydrated aqueous ions and have similarly defined equilibrium constants: i.e.

$$K_1 = \frac{m_{AX}}{(m_{AX})^2}$$  \hspace{1cm} (14)

and

$$K_2 = \frac{m_{BX}}{(m_{AX})^2}$$  \hspace{1cm} (15)

Here, $m_{AX}$ and $m_{BX}$ are the molalities of the surface complexes (ion-exchange components). These reactions are hypothetical, therefore the single-ion activity coefficients for the complexes are defined as unity. Equilibrium constants such as these can be used in any conventional speciation model. However, since the reactions are hypothetical the value of $m_x$ is not directly measurable from the constants and must be evaluated using measured ion-exchange data in conjunction with some formal convention as follows.

The mole fraction terms in equation (10) can be evaluated from the molalities of the surface complexes, i.e.

$$x_A = \frac{m_{AX}}{m_{AX} + m_{BX}}$$  \hspace{1cm} (16)

and

$$x_B = \frac{m_{BX}}{m_{AX} + m_{BX}}$$  \hspace{1cm} (17)

Eliminating mole fractions from equation (11) and combining with equations (14) and (15) gives the relationship between an equilibrium constant for ion-exchange and the two conditional formation constants for the hypothetical surface reactions, i.e.

$$K_a = \left(\frac{K_1^{Z_A}}{K_2^{Z_B}}\right) \left(\frac{K_1^{Z_B}}{K_2^{Z_A}}\right) (m_{AX} + m_{BX})^{Z_A - Z_B}$$  \hspace{1cm} (18)

For the case of heterovalent exchange on a solid of fixed cation-exchange capacity, where $(Z_A \neq Z_B)$ and $(m_{AX} + m_{BX})$ is dependent on the level of exchange, the ratio of $(K_1^{Z_A}/K_2^{Z_B})$ must be dependent on both the level of exchange and the total quantity of exchanger in the system. This treatment differs from that of Shaviv & Mattigod (1985) who did not consider the
composition correction. The constants given by them will be compositionally dependent and cannot be used in any general application.

Both $K_1$ and $K_2$ are in principle unknown. However, if one constant is known ($K_2$ for example) then the value of $K_1$ required to maintain consistency with $K_2$ at any given level of exchange (i.e. a known value of $m_{AX} + m_{BX}$) is given by:

$$K_1 = \left[ K_a \frac{K_2^{f_a}}{f_a^{f_a}} (m_{AX} + m_{BX})^{(Z_a-Z_o)} \right]^{1/f_a}$$  \hspace{1cm} (19)

In this way reaction (13) may be used as a reference reaction, having a constant value of $K_2$, to evaluate the internally consistent value of $K_1$. This can be used with $K_2$ to simulate the process of ion-exchange in models such as GEOCHEM (Sposito & Mattigod, 1980). The only modification to such a model is the inclusion of the facility to continually modify $K_1$ for successive improvements in the predicted value of $m_{AX} + m_{BX}$ in accordance with equation (19). This is similar to the activity coefficient correction to the mass action quotient (equation 4) and may be performed simultaneously. The choice of reference reaction and constant is arbitrary but it is essential to use a constant which is large enough to ensure that the predicted value of $X^{-}$ is small enough to make a negligible contribution to mass balance. In order to generalize this approach for multi-component exchange the term $m_{AX} + m_{BX}$ in the mole fraction equations and equation (19) should be replaced with the sum of the molalities of all surface complexes including those containing adsorbed anions.

**Anion adsorption**

A reaction equation for the formation of one mole of surface complex from a cation $A^{2+}$, an anion $Y^{z-}$ and the hypothetical surface species $X^{-}$ is as follows.

$$v_A A^{2+} + v_Y Y^{z-} + v_X X^{-} \rightleftharpoons A_x Y_x X_x$$  \hspace{1cm} (20)

where the $v$s represent the number of moles of reactant and are chosen so that the resulting surface complex is neutral. The conditional equilibrium constant is:

$$K_{AIX} = \frac{m_{AXY}}{(m_A Y)^{v_A}(m_Y Y)^{v_Y}(m_X X)^{v_X}}.$$  \hspace{1cm} (21)

As with the case of simple ion-exchange, this constant must be evaluated using a measured ion-exchange constant and a complementary reference reaction. An important algebraic simplification can be obtained if the reference ion is monovalent. For the purpose of self-consistency the reference reaction should be the same as for the simultaneous ion-exchange reactions, i.e.

$$R^+ + X^{-} \rightleftharpoons RX.$$  \hspace{1cm} (22)

A complementary exchange reaction which includes the anion $Y^{z-}$ can be constructed, i.e.

$$v_A A_i + v_X RX + v_Y Y^{z-} \rightleftharpoons A_i X_x Y_x X_x + v_X R^+.$$  \hspace{1cm} (23)

This reaction has an experimentally measurable equilibrium constant $K_a$ of the form:

$$K_a = \frac{(x_{AYX} f_{AYX})^{v_Y}}{(m_A Y)^{v_A}(x_{RX} f_{RX})^{v_X}(m_X Y)^{v_X}}.$$  \hspace{1cm} (24)
The equilibrium constant for equation (23) can be evaluated from:

\[ K_{AXY} = \left[ K_a K_r \left( \frac{f_{AXY}}{f_{RX}} \right) \right] Q^{(1-\varepsilon_X)} \]  \hspace{1cm} (25)

\( Q \) is the sum of the molalities of all surface complexes evaluated from:

\[ Q = \left( m_{RX} + \sum_{j=1}^{J} m_{AjX} + \sum_{p=1}^{P} m_{AZX} \right), \]  \hspace{1cm} (26)

where \( J \) is the number of exchanging ions, \( P \) is the number of surface complexes containing anions and \( m_{AZX} \) is the molality of any surface complex containing anions; this includes the specified anion \( Y^{2-} \).

An example would be the uptake of chloride accompanying the ion-exchange of Ca on montmorillonite. The hypothetical surface complex reaction is:

\[ Ca^{2+} + X^- + Cl^- \rightleftharpoons CaClX, \]  \hspace{1cm} (27)

with the reference reaction being the reaction between Na and the hypothetical anion \( X^- \), i.e.

\[ Na^+ + X^- \rightleftharpoons NaX, \]  \hspace{1cm} (28)

The equilibrium constants for these reactions are:

\[ K_1 = \frac{m_{CaClX}}{(m_{Ca}y_{Ca})(m_{X}y_{X})(m_{Cl}y_{Cl})} \]  \hspace{1cm} (29)

and

\[ K_r = \frac{m_{NaX}}{(m_{Na}y_{Na})(m_{X}y_{X})} \]  \hspace{1cm} (30)

respectively.

The measurable quantity is the equilibrium constant for the reaction:

\[ Ca^{2+} + Cl^- + NaX \rightleftharpoons CaClX + Na^+, \]  \hspace{1cm} (31)

i.e.

\[ K_a = \frac{(x_{CaClX} f_{CaClX})(m_{Na}y_{Na})}{(m_{Ca}y_{Ca})(m_{Cl}y_{Cl})(x_{NaX} f_{NaX})}. \]  \hspace{1cm} (32)

Therefore, in accordance with equation (25):

\[ K_1 = \left[ K_a K_r \left( \frac{f_{CaClX}}{f_{NaX}} \right) \right] Q^{(1-\varepsilon_X)}. \]  \hspace{1cm} (33)

The equilibrium constant \( K_1 \), evaluated this way, can be used along with any number of additional surface complex reactions to describe simultaneous ion-exchange and anion adsorption. Reactions of this stoichiometry are particularly simple since the compositional correction reduces to unity.

**THERMODYNAMIC DATA FOR MONTMORILLONITE**

In view of the multiple reactivity of most clay/electrolyte interactions it is difficult to extract precise equilibrium constants for any one reaction in isolation. Consequently, elementary
methods of successive approximation were used, in conjunction with some simplifying approximations, to generate a preliminary database for montmorillonite.

First, a convention is adopted that the reference hypothetical surface reaction involves one mole of Na ions reacting with one mole of exchanger surface and has an equilibrium constant $K_R$ of $10^{10}$ (equations 31 and 33).

Reactions with monovalent cations

Ion-exchange measurements by Gast (1969) and data compiled by Bolt (1982) suggest that the affinity for clay surfaces is $\text{NH}_4 > K > H > \text{Na} \sim \text{Li}$. Average values for the ion-exchange constants for these reactions are presented in Table 1. Where inconsistencies arise in the published literature, data represent mean value taken from a range of sources (Gast, 1969, 1971; Gilbert & Laudelout, 1965; Gast et al., 1969; Martin & Laudelout, 1963). Equilibrium constants for reactions between these ions and the clay edges can be estimated using data by Maes et al. (1976) on the pH-dependence of CEC for Chambers montmorillonite. First it is assumed that the edge contribution to montmorillonite charge is 15% of the total charge of 1 mmol g$^{-1}$. The convention is adopted that the reaction between Na and the clay edge has an equilibrium constant of $10^{10}$. Then the value of the complementary reaction for the group with the proton is chosen as the one which on speciation of a 1% suspension of montmorillonite gives the same percentage drop in retained Na as that predicted by Maes et al. (1976). Constants for K and Li are estimated assuming that the same relative preference applies to the clay edges as to the surfaces, i.e. K is slightly preferred to Na or Li. Data are presented in Table 2.
TABLE 2. Complex-ion formation reactions with clay edges and conditional equilibrium constants.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$ + E$^-$ ⇌ NaE</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>H$_2$O + E$^-$ ⇌ HE + OH$^-$</td>
<td>1.02</td>
</tr>
<tr>
<td>NH$_4^+$ + E$^-$ ⇌ NH$_4$E</td>
<td>$2.90 	imes 10^{10}$</td>
</tr>
<tr>
<td>K$^+$ + E$^-$ ⇌ KE</td>
<td>$1.80 	imes 10^{10}$</td>
</tr>
<tr>
<td>Li$^+$ + E$^-$ ⇌ LiE</td>
<td>$0.95 	imes 10^{10}$</td>
</tr>
<tr>
<td>Ca$^{2+}$ + 2E$^-$ ⇌ CaE$_2$</td>
<td>$1.58 	imes 10^{24}$</td>
</tr>
<tr>
<td>Mg$^{2+}$ + 2E$^-$ ⇌ MgE$_2$</td>
<td>$1.58 	imes 10^{24}$</td>
</tr>
<tr>
<td>Sr$^{2+}$ + 2E$^-$ ⇌ SrE$_2$</td>
<td>$1.58 	imes 10^{24}$</td>
</tr>
<tr>
<td>Ba$^{2+}$ + 2E$^-$ ⇌ BaE$_2$</td>
<td>$1.58 	imes 10^{24}$</td>
</tr>
<tr>
<td>Cu$^{2+}$ + 2E$^-$ ⇌ CuE$_2$</td>
<td>$1.46 	imes 10^{24}$</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 2E$^-$ ⇌ ZnE$_2$</td>
<td>$1.46 	imes 10^{24}$</td>
</tr>
<tr>
<td>Cd$^{2+}$ + 2E$^-$ ⇌ CdE$_2$</td>
<td>$1.46 	imes 10^{24}$</td>
</tr>
<tr>
<td>Co$^{2+}$ + 2E$^-$ ⇌ CoE$_2$</td>
<td>$1.46 	imes 10^{24}$</td>
</tr>
<tr>
<td>Ni$^{2+}$ + 2E$^-$ ⇌ NiE$_2$</td>
<td>$3.98 	imes 10^{23}$</td>
</tr>
</tbody>
</table>

E$^-$ represents one mole of montmorillonite edge charge. Conditional equilibrium constants are defined in accordance with equation (14).

These reactions are true chemical reactions and not hypothetical in the same sense as those for ion-exchange. However the method of estimation gives relative preferences for the clay edge rather than true affinities.

Reactions with divalent cations

Binary ion-exchange isotherms for Na/Ca, Na/Mg, Ca/Mg and Na/Cu have been determined in perchlorate background ionic media (Sposito et al., 1983a). This precludes anion adsorption although these reactions must include contributions from clay edges. An interesting feature is that the Ca/Mg isotherm is congruent with the non-preference isotherm. Also, the binary reactions involving Na have a single value for $K_v$ of $1.48 \pm 0.3$. This is calculated neglecting data on the extremities which commonly have the greatest error. The value is typical for many divalent exchange reactions with Na on montmorillonite and is adopted as a convenient approximation for all univalent reactions in Table 1 including transition metal exchange determined by Maes et al. (1976).

Estimates of equilibrium constants for reactions between Ca, Mg or Cu and the clay edges can be extracted from these isotherms by a method of successive approximation. This involves performing a computer simulation of the exact experiments conducted by Sposito et al. (1983b) using the ion-exchange constants and the cation/edge constants estimated previously. The appropriate value of the divalent ion/edge constant is the one which best fits the isotherms. Ca edge constants were determined from the Ca/Mg isotherm rather than the Ca/Na isotherm in view of the greater uncertainty in the latter.

Separate experiments by Sposito et al. (1983b) for binary ion-exchange in the presence of chloride can be used to evaluate the chloride complexation constants (equations (21) and (24)) for Ca and Mg. These are again determined by successive computer simulation of the exact
TABLE 3. Complex-ion formation reactions, equilibrium constants and compositional dependencies.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Values of $K_a \times KQ_i$ and compositional dependency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$ + $X^-$ ⇌ NaX</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>$H_2O + X^- ⇌ HX + OH^-$</td>
<td>$1.26 \times 10^{-4} \times Q^0$</td>
</tr>
<tr>
<td>NH$_4^+$ + $X^- ⇌ NH_4X$</td>
<td>$2.90 \times 10^{10} \times Q^0$</td>
</tr>
<tr>
<td>K$^+$ + $X^- ⇌ KX$</td>
<td>$1.80 \times 10^{10} \times Q^0$</td>
</tr>
<tr>
<td>Li$^+$ + $X^- ⇌ LiX$</td>
<td>$0.95 \times 10^{10} \times Q^0$</td>
</tr>
<tr>
<td>Ca$^{2+}$ + $2X^- ⇌ CaX_2$</td>
<td>$1.48 \times 10^{10} \times Q^{-1}$</td>
</tr>
<tr>
<td>Mg$^{2+}$ + $2X^- ⇌ MgX_2$</td>
<td>$1.48 \times 10^{10} \times Q^{-1}$</td>
</tr>
<tr>
<td>Sr$^{2+}$ + $2X^- ⇌ SrX_2$</td>
<td>$1.48 \times 10^{10} \times Q^{-1}$</td>
</tr>
<tr>
<td>Ba$^{2+}$ + $2X^- ⇌ BaX_2$</td>
<td>$1.48 \times 10^{10} \times Q^{-1}$</td>
</tr>
<tr>
<td>Cu$^{2+}$ + $2X^- ⇌ CuX_2$</td>
<td>$1.35 \times 10^{10} \times Q^{-1}$</td>
</tr>
<tr>
<td>Zn$^{2+}$ + $2X^- ⇌ ZnX_2$</td>
<td>$1.48 \times 10^{10} \times Q^{-1}$</td>
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<td>Cd$^{2+}$ + $2X^- ⇌ CdX_2$</td>
<td>$1.48 \times 10^{10} \times Q^{-1}$</td>
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<tr>
<td>Co$^{2+}$ + $2X^- ⇌ CoX_2$</td>
<td>$1.48 \times 10^{10} \times Q^{-1}$</td>
</tr>
<tr>
<td>Ni$^{2+}$ + $2X^- ⇌ NiX_2$</td>
<td>$1.79 \times 10^{10} \times Q^{-1}$</td>
</tr>
<tr>
<td>Ca$^{2+}$ + $X^- + Cl^- ⇌ CaXCl$</td>
<td>$1.93 \times 10^{12} + Q^{-0}$</td>
</tr>
<tr>
<td>Mg$^{2+}$ + $X^- + Cl^- ⇌ MgXCl$</td>
<td>$1.81 \times 10^{12} \times Q^{-0}$</td>
</tr>
<tr>
<td>Sr$^{2+}$ + $X^- + Cl^- ⇌ SrXCl$</td>
<td>$1.90 \times 10^{12} \times Q^{-0}$</td>
</tr>
<tr>
<td>Ba$^{2+}$ + $X^- + Cl^- ⇌ BaXCl$</td>
<td>$1.90 \times 10^{12} \times Q^{-0}$</td>
</tr>
<tr>
<td>Cu$^{2+}$ + $X^- + Cl^- ⇌ CuXCl$</td>
<td>$2.49 \times 10^{12} \times Q^{-0}$</td>
</tr>
<tr>
<td>Zn$^{2+}$ + $X^- + NO_3^- ⇌ ZnXNO_3$</td>
<td>$4.98 \times 10^{12} \times Q^{-0}$</td>
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<tr>
<td>Cd$^{2+}$ + $X^- + NO_3^- ⇌ CdXNO_3$</td>
<td>$1.72 \times 10^{12} \times Q^{-0}$</td>
</tr>
<tr>
<td>Co$^{2+}$ + $X^- + Cl^- ⇌ CoXCl$</td>
<td>$1.85 \times 10^{12} \times Q^{-0}$</td>
</tr>
<tr>
<td>Ni$^{2+}$ + $X^- + Cl^- ⇌ NiXCl$</td>
<td>$1.03 \times 10^{11} \times Q^{-0}$</td>
</tr>
</tbody>
</table>

$X^-$ represents one mole of montmorillonite surface charge. Equilibrium constants are defined in accordance with equations (14) and (21). The term $Q$ is the compositional correction defined by equation (26).

Experiments using previously determined constants. The value of the unknown is the one which best fits the variation in CEC with level of exchange.

Similar methods of successive approximation were used to extract thermodynamic data for all reactions of first-row transition metals on Na-montmorillonite using ion-exchange isotherms and CEC values determined by Maes et al. (1976). Values of $K_a \times KQ_i$ for hypothetical surface reactions for the ith ion, along with their compositional dependencies, are given in Table 3.

**COMPUTER SIMULATIONS**

A range of observations resulting from montmorillonite/electrolyte interactions are simulated using data in Tables 2 and 3. Activity coefficient corrections were made to true solution components assuming ideal behaviour for the clay phase.

*Exchange between monovalent cations*

Fig. 1 shows simulated isotherms for Na/K exchange in chloride backgrounds at three different total chloride concentrations at a fixed pH of 7. Also shown are isotherms for this
reaction at total chloride concentration of 0.1 mol dm\(^{-3}\) over the pH range 6–4. All isotherms are congruent and consistent with a pH-independent selectivity, although apparent CECs, which exclude contributions from the proton, show a continual reduction with decreasing pH (Fig. 2). These features are consistent with data by Gast (1969, 1971) and Maes et al. (1976).
Fig. 3. Calcium/sodium exchange isotherms in different perchlorate backgrounds. Equivalent fraction of calcium in the clay ($E_{-Ca(c)}$) vs. equivalent fraction of calcium in solution ($E_{-Ca(s)}$).

Fig. 4. Calcium/sodium exchange in chloride and perchlorate solutions. Equivalent fraction of calcium in the clay ($E_{-Ca(c)}$) vs. equivalent fraction of calcium in solution ($E_{-Ca(s)}$).

**Exchange involving divalent cations**

Fig. 3 shows simulated isotherms for Na/Ca exchange at three different total concentrations of the non-complexing anion perchlorate. The isotherms are incongruent with an apparent increase in selectivity at lower perchlorate concentrations. The isotherms are consistent with ideal behaviour and constant apparent CEC and the concentration effect is a
natural consequence of heterovalent exchange (Barrer & Klinowski, 1974) which must be predicted if the numerical techniques are thermodynamically self-consistent.

The effect of anion adsorption is emphasized in Figs 4 and 5 which show Na/Ca and Na/Mg isotherms respectively at a total chloride concentration of 0.052 mol dm$^{-3}$. Comparisons with the equivalent perchlorate isotherm show the increased selectivity
observed for the divalent cation ion in the presence of chloride. These are simulations of the experiments performed by Sposito et al. (1983b), the data from which are included for comparison. Fig. 6 shows the increase in apparent CEC with increasing Na replacement to be over 20% at high divalent ion coverage. Generally experimental data in Figs 4 to 6 are predicted adequately; this is also true for Ca/Mg and Na/Cu isotherms measured by Sposito.
et al. (1981, 1983a) shown in Figs 7 and 8. Ion-exchange isotherms and CECs for transition metal exchange with Na determined by Maes et al. (1976) can be equally well predicted.

It is possible to define an apparent $K_v$ which is evaluated by including all cations of one type (regardless of actual surface speciation) into the mole fractions calculations. This apparent $K_v$ contains effects due multiple reactivity and is the constant determined most commonly. The effect of changing pH on the apparent $K_v$ for Zn/Na exchange is emphasized in Fig. 9. These simulations (of an isotherm constructed from a 1% suspension of clay at total nitrate concentration of 0.025 mol dm$^{-3}$) show the dependence of the apparent $K_v$ on the level of Na replacement at four different pHs. At the highest pH the compositional dependence of $K_v$ shows a minimum resulting from the combined effect of complex formation at clay edges, which progressively lowers selectivity in this case, and an increase in $K_v$ due to nitrate adsorption. As pH decreases, the clay edges become saturated with protons and the edge effect becomes less pronounced while the effect due to nitrate adsorption remains constant. These prediction are in general agreement with data by Maes et al. (1976).

Ternary ion exchange

Sposito et al. (1983c) constructed experiments on the ternary ion exchange between Ca, Mg and Na on a Wyoming bentonite in a 0.5 mol dm$^{-3}$ perchlorate background. Experiments involved constructing Ca/Mg isotherms using a 2-5% suspension of Na-montmorillonite in the presence of an additional concentration of Na. Isotherms were constructed at two different Na concentrations. Table 4 shows the simulation of the compositions of the clay phase after equilibration compared with measured compositions. In most cases predictions fall within the limits of experimental uncertainty given by Sposito et al. (1983c) although there is some tendency to underestimate the quantity of Mg adsorbed by a few percent at high Mg coverage.
TABLE 4. Predictions of the ionic compositions of montmorillonite under conditions of ternary exchange equilibria with calcium, magnesium and sodium.

<p>| Concentrations in mol kg^{-1} dry clay. |</p>
<table>
<thead>
<tr>
<th>Na^m</th>
<th>Na^p</th>
<th>Ca^m</th>
<th>Ca^p</th>
<th>Mg^m</th>
<th>Mg^p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 ± 0.08</td>
<td>0.36</td>
<td>0.00 ± 0.00</td>
<td>0.00</td>
<td>0.73 ± 0.01</td>
<td>0.64</td>
</tr>
<tr>
<td>0.4 ± 0.1</td>
<td>0.37</td>
<td>0.07 ± 0.003</td>
<td>0.067</td>
<td>0.43 ± 0.02</td>
<td>0.56</td>
</tr>
<tr>
<td>0.4 ± 0.1</td>
<td>0.36</td>
<td>0.143 ± 0.003</td>
<td>0.123</td>
<td>0.46 ± 0.02</td>
<td>0.52</td>
</tr>
<tr>
<td>0.3 ± 0.1</td>
<td>0.36</td>
<td>0.203 ± 0.01</td>
<td>0.192</td>
<td>0.40 ± 0.02</td>
<td>0.44</td>
</tr>
<tr>
<td>0.4 ± 0.2</td>
<td>0.36</td>
<td>0.270 ± 0.01</td>
<td>0.250</td>
<td>0.34 ± 0.01</td>
<td>0.39</td>
</tr>
<tr>
<td>0.3 ± 0.1</td>
<td>0.37</td>
<td>0.394 ± 0.08</td>
<td>0.32</td>
<td>0.33 ± 0.009</td>
<td>0.32</td>
</tr>
<tr>
<td>0.38 ± 0.07</td>
<td>0.36</td>
<td>0.410 ± 0.02</td>
<td>0.44</td>
<td>0.273 ± 0.005</td>
<td>0.23</td>
</tr>
<tr>
<td>0.3 ± 0.2</td>
<td>0.36</td>
<td>0.45 ± 0.01</td>
<td>0.45</td>
<td>0.200 ± 0.001</td>
<td>0.19</td>
</tr>
<tr>
<td>0.4 ± 0.1</td>
<td>0.38</td>
<td>0.53 ± 0.02</td>
<td>0.48</td>
<td>0.14 ± 0.01</td>
<td>0.14</td>
</tr>
<tr>
<td>0.29 ± 0.06</td>
<td>0.36</td>
<td>0.56 ± 0.02</td>
<td>0.57</td>
<td>0.06 ± 0.05</td>
<td>0.064</td>
</tr>
<tr>
<td>0.4 ± 0.2</td>
<td>0.38</td>
<td>0.61 ± 0.02</td>
<td>0.62</td>
<td>0.00 ± 0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.2 ± 0.06</td>
<td>0.23</td>
<td>0.00 ± 0.00</td>
<td>0.00</td>
<td>0.85 ± 0.06</td>
<td>0.78</td>
</tr>
<tr>
<td>0.14 ± 0.09</td>
<td>0.23</td>
<td>0.071 ± 0.005</td>
<td>0.078</td>
<td>0.79 ± 0.06</td>
<td>0.69</td>
</tr>
<tr>
<td>0.1 ± 0.03</td>
<td>0.23</td>
<td>0.145 ± 0.005</td>
<td>0.152</td>
<td>0.76 ± 0.07</td>
<td>0.62</td>
</tr>
<tr>
<td>0.1 ± 0.07</td>
<td>0.23</td>
<td>0.250 ± 0.02</td>
<td>0.26</td>
<td>0.62 ± 0.04</td>
<td>0.523</td>
</tr>
<tr>
<td>0.20 ± 0.06</td>
<td>0.23</td>
<td>0.370 ± 0.01</td>
<td>0.34</td>
<td>0.52 ± 0.02</td>
<td>0.47</td>
</tr>
<tr>
<td>0.15 ± 0.08</td>
<td>0.23</td>
<td>0.45 ± 0.01</td>
<td>0.39</td>
<td>0.42 ± 0.01</td>
<td>0.49</td>
</tr>
<tr>
<td>0.16 ± 0.07</td>
<td>0.22</td>
<td>0.60 ± 0.01</td>
<td>0.47</td>
<td>0.29 ± 0.02</td>
<td>0.31</td>
</tr>
<tr>
<td>0.17 ± 0.08</td>
<td>0.23</td>
<td>0.59 ± 0.04</td>
<td>0.53</td>
<td>0.25 ± 0.02</td>
<td>0.24</td>
</tr>
<tr>
<td>0.15 ± 0.09</td>
<td>0.23</td>
<td>0.64 ± 0.02</td>
<td>0.61</td>
<td>0.14 ± 0.02</td>
<td>0.16</td>
</tr>
<tr>
<td>0.23 ± 0.08</td>
<td>0.22</td>
<td>0.63 ± 0.03</td>
<td>0.64</td>
<td>0.076 ± 0.006</td>
<td>0.085</td>
</tr>
<tr>
<td>0.1 ± 0.09</td>
<td>0.23</td>
<td>0.93 ± 0.03</td>
<td>0.78</td>
<td>0.00 ± 0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Concentrations in mol kg^{-1} dry clay.

m = measured.

p = predicted.

CONCLUSIONS

A technique to model ion-exchange and related phenomena on clays has been developed using the concept of hypothetical surface complex formation. This method, which is compatible with ion-association models such as GEOCHEM (Sposito & Mattigod, 1980), can be used to simulate multiple reactivity including simultaneous ion-exchange, complex-ion formation and anion adsorption. Available literature data on the reactivity of montmorillonite have been reviewed and a preliminary thermodynamic dataset compiled. These data were used to simulate the essential features of the reactivity of Wyoming bentonite in dilute electrolytes to show that effects such as variable cation-exchange capacity and non-ideal behaviour can arise from combinations of ideal reactions of the clay surfaces and edges. For this particular clay all reactions are assumed to be ideal, with activity corrections made to true solution species only. This is consistent with experimental evidence although the techniques are flexible enough to accommodate exchanger-phase activity coefficients if required. Improved data will be obtained if future experiments are designed to examine specific effects while minimizing or removing the contributions from additional reactions.
REFERENCES


