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MODELING OF H^+ AND Cu^{2+} ADSORPTION ON CALCIUM-MONTMORILLONITE

MARKUS STADLER[1] AND PAUL W. SCHINDLER
Institute for Inorganic Chemistry, University of Berne,
Freiestrasse-3, CH-3012-Berne, Switzerland

Abstract—The interaction of H^+- and Cu^{2+}-ions with Ca-montmorillonite was investigated in 0.1 mol/dm^3 solutions of $Ca(ClO_4)_2$ at 298.2 K by potentiometric titrations using both glass electrodes (for H^+) and ion specific electrodes (for Cu^{2+}). The experimental data were interpreted on the basis of the surface complexation model. The calculations were performed with the least-squares program FITEQL (Westall, 1982) using the constant capacitance approximation. The best fit was obtained with a set of equilibria of the general form

$$\mathrm{p\,H^+ + q\,Cu^{2+} + {\equiv}SOH \Leftrightarrow (H^+)_p(Cu^{2+})_q({\equiv}SOH)^{(p+2q)+}}$$

$$\beta^{s}_{p,q(int)} = \frac{[\mathrm{H_pCu_q({\equiv}SOH)^{(p+2q)}}]}{[\mathrm{H^+}]^p[\mathrm{Cu^{2+}}]^q[\mathrm{{\equiv}SOH}]}$$

and the constants $\log \beta^{s}_{1,0(int)} = 8.16$ (± 0.04), $\log \beta^{s}_{-1,0(int)} = -8.71$ (± 0.08), $\log \beta^{s}_{0,1(int)} = 5.87$ (± 0.06), $\log \beta^{s}_{-1,1(int)} = -0.57$ (± 0.12), $\log \beta^{s}_{-2,1(int)} = -6.76$ (± 0.02). An appropriate modeling of the H^+ adsorption data requires the introduction of a second surface group ≡ TOH with the acidity constant

$$\mathrm{{\equiv}TOH - H^+ \Leftrightarrow {\equiv}TO^-} \quad \log \beta^{s}_{-1,0(int)} = -5.77\ (\pm\ 0.07).$$

In addition, the ion exchange equilibria $Ca^{2+} - Cu^{2+}$ and $Ca^{2+} - H^+$ had to be taken into account. Arguments are presented to identify the groups ≡SOH and ≡TOH as surface aluminol groups ≡Al(OH)(H_2O) and surface silanol groups ≡Si-OH, respectively.

Key Words—Adsorption, Copper, Modeling, Montmorillonite.

INTRODUCTION

Interaction with clay minerals is of primary importance in the chemical speciation and the fate of trace metals in soils and other environmental systems. This interaction can, for convenience, be separated into ion-exchange based on isomorphous substitution leading to unspecific adsorption or outer-sphere complexation (Sposito, 1984) and surface complexation based on interaction with surface hydroxyl groups and leading to specific adsorption, i.e., the formation of inner sphere complexes (Sposito, 1984; Schindler *et al.*, 1987). The thermodynamic treatment of ion-exchange has been summarised by Sposito (1981). Surface complexation modeling of oxides and hydroxides has recently been reviewed by Davis and Kent (1990) and Schindler and Sposito (1991). A comprehensive description of clay-metal interaction must include both ion-exchange and surface complexation.

Cu uptake by Ca-montmorillonite has been investigated by El-Sayed *et al.* (1970). This work is however restricted to ion-exchange in the pH range of 4.5–5.0. In the present work, an attempt is made to model the Cu uptake by Ca-montmorillonite from 0.1 mol/dm^3 solutions of $Ca(ClO_4)_2$ in the range of $3.5 \le pH \le 8.5$ including both ion-exchange and surface complexation. Since complex formation with surface hydroxyl groups results in release of H^+ ions, a separate investigation on the interaction of H^+ ions with Ca-montmorillonite had to be included. A similar approach to describe the uptake of Cu, Cd and Pb by kaolinite has already been reported by Schindler *et al.* (1987).

MATERIALS AND METHODS

Montmorillonite

SWy-1 Montmorillonite (Na-montmorillonite) from Crook County, Wyoming, was provided by the Clay Minerals Society. The < 2 μm fraction was collected by controlled sedimentation and treated with a 1 mol/dm^3 $CaCl_2$ solution to exchange Na^+ and K^+ by Ca^{2+}. After this procedure, the sample was lyophilised. Another sample was treated in the same way with a 1 mol/dm^3 $CuCl_2$ solution to prepare a Cu-montmorillonite.

X-ray diffraction revealed layer distances of 12.5 Å (Na-montmorillonite), 15.2 Å (Ca-montmorillonite) and 12.5 Å (Cu-montmorillonite), respectively. These results are in good accordance with El-Sayed *et al.* (1970): 14.97 Å for Ca-montmorillonite and 12.27 Å for Cu-montmorillonite. Total surface area (EGME method, Eltantawy and Arnold, 1973) and external surface area (BET method) were found to be 661.5 m^2/g and 21.4 m^2/g, respectively. The exchange capacity (CEC) of the Ca-montmorillonite was 0.93 meq/g.

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[1] Author to whom correspondence should be addressed.

Solutions

Solutions of $HClO_4$ (Merck suprapur) and $Ca(OH)_2$ (Merck p.a.) were standardised with Titrisol (Merck) solutions. A 2.5 mol/dm^3 stock solution of $Ca(ClO_4)_2$ was obtained from $CaCO_3$ (Merck p.a.) and $HClO_4$. The Ca^{2+} concentration was determined by complexometry. A 1.0 mol/dm^3 stock solution of $Cu(ClO_4)_2$ was prepared by reacting an excess of CuO (Merck p.a.) with standardised $HClO_4$. The Cu(II) concentration was measured by complexometry.

Double distilled water boiled under N_2 and passed through a 0.1 μm filter (Sartorius cellulose-nitrate filter) was used in all experiments. All solutions were filtered and stored under N_2.

Apparatus

All titrations were performed in a thermostatted vessel furnished with a combined glass electrode (Metrohm). Additionally, a Cu-electrode (Orion) with an Ag/AgCl reference electrode was used for most of the experiments in the presence of Cu(II). The suspensions were protected from atmospheric CO_2 by a stream of N_2 presaturated with 0.1 mol/dm^3 $Ca(ClO_4)_2$ and introduced into the system through a capillary. To prevent direct contact with air, the outflowing N_2 was bubbled through another vessel with 0.1 mol/dm^3 $Ca(ClO_4)_2$.

The potentiometric titrations were performed with an automatic system built in this laboratory. The electrodes were connected via amplifiers to two Keithley DMM196 multimeters. Addition of base was performed by a dosimat (Metrohm E655). Both the multimeters and the dosimat were connected to a PC with the aid of an IEEE interface. The progress of the titration was controlled by a computer program developed by the authors.

Titrations

For the study of the interaction of H^+-ions with montmorillonite, a weighed amount of clay, A [g], was added to a volume V_0 [dm^3] of a solution S1 of the general composition $[H^+] = H_0$ [mol/dm^3], $[Ca^{2+}] = (0.1 - H_0/2)$ [mol/dm^3], $[ClO_4^-] = 0.2$ [mol/dm^3].

The suspensions were stirred for one week in order to establish the equilibrium between the clay and the electrolyte solution. The concentration of Al(III) originating from a dissolution process was found to be less than $2.5 \cdot 10^{-6}$ mol/dm^3 at pH 3.5.

After the equilibration period, the suspension was titrated with a volume v [dm^3] (added in increments of $1 \cdot 10^{-4}$ dm^3) of a solution S2 of the composition $[OH^-] = B_0$ [mol/dm^3], $[Ca^{2+}] = (0.1 + B_0/2)$ [mol/dm^3], $[ClO_4^-] = 0.2$ mol/dm^3. The concentration of solid in the suspension, C_s, is given by

$$C_s = \frac{A}{V_0 + v} [\mathrm{g/dm^3}]. \qquad (1)$$

After each addition of base, the electromotive force (e.m.f.) of the glass electrode was monitored. E.m.f. readings were taken every 30 seconds. Establishment of the equilibrium was assumed if 1) two consecutive readings differed less than 0.01 mV and 2) a given reading did not differ more than 0.05 mV from the average of the six foregoing readings. For the electrode system used, the Nernst equation is given by

$$E_H = E_H^0 + k \cdot \log h \qquad (2)$$

where h is used to denote the free hydrogen ion concentration $[H^+]$. E_H^0 and k were obtained from titrations of S1 with S2. In addition, the total hydrogen concentration H was obtained from

$$H = \frac{V_0 \cdot H_0 - v \cdot B_0}{V_0 + v} [\mathrm{mol/dm^3}]. \qquad (3)$$

For the study of the Cu uptake by montmorillonite, a weighed amount of clay was placed in a solution S3 containing $[H^+] = H_0$ mol/dm^3, $[Cu^{2+}] = C_0$ mol/dm^3, $[Ca^{2+}] = (0.1 - H_0/2 - C_0)$ mol/dm^3. Preparation of the suspension, equilibration time, titration and the e.m.f. monitoring of the glass electrode were the same as described above. The total Cu concentration (C) is given by

$$C = \frac{C_0 \cdot V_0}{V_0 + v} [\mathrm{mol/dm^3}]. \qquad (4)$$

In most of the titrations, a Cu electrode was used. E.m.f. readings were taken every 30 seconds. The Nernst equation of this electrode is given by

$$E_{Cu} = E_{Cu}^0 + k_{Cu} \cdot \log c \qquad (5)$$

where c symbolises the free Cu concentration $[Cu^{2+}]$. E_{Cu}^0 and k_{Cu} were obtained from titrations of S1 with S3. Alternatively, aliquots of 0.004 dm^3 were taken from suspensions and analysed for Cu by AAS.

DATA AND MODELING

Data treatment

During the modeling procedure, it was found that two surface hydroxyl groups denoted by $\equiv$SOH and $\equiv$TOH having different total concentrations and different acidities were necessary for an appropriate description of the system. Interactions between the clay and the perchlorate-ions can be neglected (e.g. see Sposito *et al.*, 1983). The investigated system can thus be described with six components:

$$H^+, Cu^{2+}, Ca^{2+}, X^-, \equiv SOH \text{ and } \equiv TOH,$$

where X^- denotes the ion-exchanger sites.

In formulating the pertinent equilibria, the presence of a constant ionic medium permits the replacement of activities by concentrations for dissolved species. In addition, activity coefficients of surface species and species involved an ion exchange equilibria have been neglected.

H^+, Ca^{2+} and Cu^{2+} are involved in the solution equilibria (6)–(8):

$$H_2O \Leftrightarrow H^+ + OH^- \qquad K_w = [H^+]\cdot[OH^-] \tag{6}$$

$K_w = 10^{-13.78}$ (Martell and Smith, 1976)

$$Ca^{2+} (+ H_2O) \Leftrightarrow CaOH^+ + H^+$$

$$*K_1 = \frac{[CaOH^+]\cdot[H^+]}{[Ca^{2+}]} \tag{7}$$

$$m\,Cu^{2+} (+ n\,H_2O) \Leftrightarrow Cu_m(OH)_n^{(2m-n)+} + n\,H^+$$

$$*\beta_{m,n} = \frac{[Cu_m(OH)_n^{(2m-n)+}]\cdot[H^+]^n}{[Cu^{2+}]^m}. \tag{8}$$

It was found that the hydrolysis of Cu can be simplified to $*\beta_{1,1} = 10^{-8.29}$ and $*\beta_{2,2} = 10^{-10.70}$, neglecting the other Cu-hydroxo complexes. The equilibrium constants were taken from Baes and Mesmer (1976) and calculated for $I = 0.3$ with the aid of the Davis-equation (Davis, 1962).

For the subsequent data treatment with FITEQL, the ion-exchange equilibria were formulated according to Shaviv *et al.* (1985) and Fletcher *et al.* (1989). The treatment is based on the hypothetical equilibria (9–11):

$$2\,X^- + Ca^{2+} \Leftrightarrow CaX_2 \qquad K_0 = \frac{[CaX_2]}{[Ca^{2+}]\cdot[X^-]^2} \tag{9}$$

$$X^- + H^+ \Leftrightarrow HX \qquad K_1 = \frac{[HX]}{[X^-]\cdot[H^+]} \tag{10}$$

$$2\,X^- + Cu^{2+} \Leftrightarrow CuX_2 \qquad K_2 = \frac{[CuX_2]}{[Cu^{2+}]\cdot[X^-]^2}. \tag{11}$$

The ion-exchange

$$CaX_2 + 2\,H^+ \Leftrightarrow 2\,HX + Ca^{2+}$$

is thus given by

$$K_{Ca,H} = \frac{[HX]^2\cdot[Ca^{2+}]}{[CaX_2]\cdot[H^+]^2} = \frac{K_1^2}{K_0}. \tag{12}$$

Similarly, the Ca-Cu exchange

$$CaX_2 + Cu^{2+} \Leftrightarrow CuX_2 + Ca^{2+}$$

is described by

$$K_{Ca,Cu} = \frac{[CuX_2]\cdot[Ca^{2+}]}{[CaX_2]\cdot[Cu^{2+}]} = \frac{K_2}{K_0}. \tag{13}$$

The value of K_0 was set arbitrarily as 10^{+20}. Such a high value is necessary to make the value of $[X^-]$ a negligible contribution to the mass balance. It was found that within the range of $10^{10} < K_0 < 10^{20}$ the obtained values of $K_{Ca,H}$ and $K_{Ca,Cu}$ were independent from the actual choice of K_0.

Equilibria involving acid/base reactions of surface hydroxyl groups can be described by the general Eq. 14 and 15:

$$p\,H^+ + q\,Cu^{2+} + {\equiv}SOH \Leftrightarrow (H^+)_p(Cu^{2+})_q({\equiv}SOH)^{(p+2q)+}$$

$$\beta^s_{SOH,p,q} = \frac{[H_pCu_q({\equiv}SOH)^{(p+2q)}]}{[H^+]^p\cdot[Cu^{2+}]^q\cdot[{\equiv}SOH]} \tag{14}$$

$$u\,H^+ + v\,Cu^{2+} + {\equiv}TOH \Leftrightarrow (H^+)_u(Cu^{2+})_v({\equiv}TOH)^{(u+2v)+}$$

$$\beta^s_{TOH,u,v} = \frac{[H_uCu_v({\equiv}TOH)^{(u+2v)+}]}{[H^+]^u\cdot[Cu^{2+}]^v\cdot[{\equiv}TOH]}. \tag{15}$$

Considering the electrostatic properties of a charged surface, a correction for the coulombic energy must be introduced in Eqs. 14 and 15 to obtain the intrinsic constants:

$$\beta^s_{SOH,p,q,(int)} = \beta^s_{SOH,p,q}\cdot e^{\frac{(p+2q)\cdot F\cdot\psi}{R\cdot T}} \tag{14a}$$

$$\beta^s_{TOH,u,v,(int)} = \beta^s_{TOH,u,v}\cdot e^{\frac{(u+2v)\cdot F\cdot\psi}{R\cdot T}}. \tag{15a}$$

For every component, a mass balance equation can be formulated (Eqs. 16–21):

$$\begin{aligned} H = {} & h - K_w\cdot h^{-1} - *K_1\cdot[Ca^{2+}]\cdot h^{-1} \\ & - \sum n\cdot *\beta_{m,n}\cdot c^m\cdot h^{-n} + K_1\cdot[X^-]\cdot h \\ & + \sum p\cdot\beta^s_{SOH,p,q(int)}\cdot h^p\cdot c^q\cdot[{\equiv}SOH] \\ & \cdot e^{-((p+2q)F\psi/RT)} \\ & + \sum u\cdot\beta^s_{TOH,u,v(int)}\cdot h^u\cdot c^v \\ & \cdot[{\equiv}TOH]\cdot e^{-((u+2v)F\psi/RT)} \end{aligned} \tag{16}$$

$$\begin{aligned} C = {} & c + \sum m\cdot *\beta_{m,n}\cdot c^m\cdot h^{-n} \\ & + K_2\cdot[X^-]^2\cdot c + \sum q\cdot\beta^s_{SOH,p,q(int)} \\ & \cdot h^p\cdot c^q\cdot[{\equiv}SOH]\cdot e^{-((p+2q)F\psi/RT)} \\ & + \sum v\cdot\beta^s_{TOH,u,v(int)}\cdot h^u\cdot c^v\cdot[{\equiv}TOH] \\ & \cdot e^{-((u+2v)F\psi/RT)} \end{aligned} \tag{17}$$

$$\begin{aligned} [Ca^{2+}]_{tot} = {} & [Ca^{2+}] + *K_1\cdot[Ca^{2+}]\cdot h^{-1} \\ & + K_0\cdot[X^-]^2\cdot[Ca^{2+}] \end{aligned} \tag{18}$$

$$\begin{aligned} [X]_{tot} = {} & [X^-] + K_0\cdot[X^-]^2\cdot[Ca^{2+}] \\ & + K_1\cdot[X^-]\cdot h + K_2\cdot[X^-]^2\cdot c \end{aligned} \tag{19}$$

$$\begin{aligned} [{\equiv}SOH]_{tot} = {} & [{\equiv}SOH] + \sum \beta^s_{SOH,p,q(int)}\cdot h^p \\ & \cdot c^q\cdot[{\equiv}SOH]\cdot e^{-((p+2q)F\psi/RT)} \end{aligned} \tag{20}$$

$$\begin{aligned} [{\equiv}TOH]_{tot} = {} & [{\equiv}TOH] + \sum \beta^s_{TOH,uv(int)}\cdot h^u \\ & \cdot c^v\cdot[{\equiv}TOH]\cdot e^{-((u+2v)F\psi/RT)}. \end{aligned} \tag{21}$$

The surface charge T_σ is given by Eq. 22 (in units of mol/dm^3):

$$\begin{aligned} T_\sigma = {} & \sum (p + 2q)\cdot\beta^s_{SOH,p,q(int)}\cdot h^p\cdot c^q \\ & \cdot[\equiv SOH]\cdot e^{-((p+2q)F\psi/RT)} \\ & + \sum (u + 2v)\cdot\beta^s_{TOH,u,v(int)}\cdot h^u\cdot c^v \\ & \cdot[\equiv TOH]\cdot e^{-((u+2v)F\psi/RT)}. \end{aligned} \tag{22}$$

Eq. 23 relates the surface charge T_σ with s (specific surface area [m^2/g]) and C_s (concentration of solid [g/dm^3]) and gives the charge in [C/m^2]:

$$\sigma = \frac{T_s\cdot F}{s\cdot C_s}. \tag{23}$$

The constant capacitance model (Schindler and Gamsjäger, 1972) offers a simple relationship between ψ and σ:

$$\sigma = \kappa\cdot\psi \tag{24}$$

or

$$\psi = \frac{T_\sigma\cdot F}{s\cdot C_s\cdot\kappa} \tag{25}$$

where κ denotes the double-layer capacitance [C/m^2]. It should be emphasised that κ and s are not experimentally accessible quantities. Physically reasonable κ values for oxides lie between 0.2 and 2.0 C/Vm^2·s can be estimated from BET measurement by N_2 adsorption. The resulting value is, strictly speaking, only valid for N_2 adsorption onto water-free montmorillonite as pointed out by James and Parks (1982). It is possible, that the surface exposed to the solution is somewhat different. Therefore, it is reasonable to use κ and s as flexible parameters to minimise the given error. The starting values were s = 100 m^2/g and κ = 1.0 C/Vm^2.

The mathematical evaluation of $\beta^s_{SOH,p,q(int)}$, $\beta^s_{TOH,u,v(int)}$, $^*K_1$, K_1, K_2, $[\equiv SOH]_{tot}$ and $[\equiv TOH]_{tot}$ was performed by the computer program FITEQL (Westall, 1982). The optimisation procedure of this program starts by calculating H and C based on estimated values of the adjustable parameters using Eq. 16 and 17 respectively. Comparison with experimental data of the total hydrogen concentration and the total Cu concentration, H_{exp} and C_{exp}, respectively, yields:

$$Y_H = H - H_{exp} \tag{26}$$

$$Y_C = C - C_{exp} \tag{27}$$

where Y_H and Y_C denote the errors in the mass balances of H$^+$ and Cu(II), respectively. After this evaluation, the program calculates the weighed sum of the error squares over all data points:

$$\sum\left(\frac{Y}{\sigma Y}\right)^2.$$

The computer program minimises this quantity by varying the parameters that are to be optimised. The goodness of the fit is given by a value for the overall variance in Y, denoted by SOS/DF. For reasonably good fits, a value of 0.1 < SOS/DF < 20 is common (Westall, 1982).

Experimental data

For all titrations, A was 1 g, V_0 was 0.100 dm^3 and B_0 was 0.025 mol/dm^3. $V_0 + v$ never exceeded 0.110 dm^3; therefore, the concentration of solid in the suspension, C_s, could kept close to 10 g/dm^3.

Two titrations with H_0 = 0.002 mol/dm^3 (231 data points, 3.5 < −log h < 8.9) and one titration with H_0 = 0.001 mol/dm^3 (61 data points, 3.5 < −log h < 9.7) were performed to model the interactions of H$^+$ and clay.

Titrations with H_0 = 0.002 mol/dm^3 and C_0 = 0.0001 mol/dm^3 (two titrations, 58 data points), C_0 = 0.0002 mol/dm^3 (two titrations, 104 data points) and C_0 = 0.0005 mol/dm^3 (two titrations, 145 data points) were used to study the adsorption of Cu in the range of 3.5 < −log h < 8.5. During the titrations, the system always was undersaturated with respect to $Cu(OH)_s$.

Furthermore, about 20 other experiments with 0.03 ≤ I ≤ 0.3 and 0 ≤ H_0 ≤ 0.005 mol/dm^3 were used to determine the p.n.z.p.c. (point of net zero proton charge) of Ca-montmorillonite.

RESULTS AND DISCUSSION

H$^+$-sorption

General. To illustrate the experimental data, the quantity:

$$\Delta H = H - h + K_w\cdot h^{-1}[\text{mol/dm}^3]$$

i.e., the concentration of protons bound by the system, is plotted as a function of log h (Figure 1). The figure reveals the presence of three buffer regions: The region −log h < 4 is possibly dominated by the ion-exchange equilibrium (Eq. 12). On the other hand, the region −log h > 9 reflects the hydrolysis of the medium cations (Eq. 7). The intermediate region displays the acid-base equilibria of surface hydroxyl groups. They can be modeled assuming the equilibria

$$\equiv SOH + H^+ \Leftrightarrow \equiv SOH_{2^+} \qquad \beta^s_{SOH,1,0}$$

$$\equiv SOH - H^+ \Leftrightarrow \equiv SO^- \qquad \beta^s_{SOH,-1,0}$$

$$\equiv TOH - H^+ \Leftrightarrow \equiv TO^- \qquad \beta^s_{TOH,-1,0}.$$

In view of the strong overlap of the buffer regions, it is not possible to directly evaluate the maximum amount of protons bound or released by these surface hydroxyl groups. Hence, the total concentrations $[\equiv SOH]_{tot}$ and $[\equiv TOH]_{tot}$ had to be optimised together with the pertinent equilibrium constants. The obtained parameters are listed in Table 1. As can be seen in Figure 1, the point of zero net proton charge (p.z.n.p.c.), where ΔH = 0, is located at −log h = 7.7.

Table 1. Parameters obtained from FITEQL runs.

log β^sSOH,1,0	+8.16 (± 0.04*)
log β^sSOH,−1,0	−8.71 (± 0.08*)
log β^sTOH,−1,0	−5.77 (± 0.07*)
log $K_{a(Ca,H)}$	+2.44 (± 0.01*)
log $^*K_1$	−11.58 (± 0.03*)
log β^sSOH,0,1	+5.87 (± 0.06*)
log β^sSOH,−1,1	−0.57 (± 0.12*)
log β^sSOH,−2,1	−6.76 (± 0.02*)
log $K_{ex(Ca,Cu)}$	0.30 (± 0.37*)
$[SOH]_{tot}$[mol/l]	0.000598 (± 5.E−6)
$[TOH]_{tot}$[mol/l]	0.000355 (± 4.E−6)
$\kappa \cdot s$ $[C \cdot g^{-1} \cdot V^{-1}]$	91

* = 3 σ.

With the methods used in this study, it is not possible to precisely distinguish between protons which are bound to montmorillonite by (reversible) acid-base and ion-exchange reactions and protons that are consumed by irreversible dissolution processes. Nevertheless, there is evidence that the fraction of protons used up in irreversible dissolution processes is negligible small as compared to the reversibly bound fraction of protons: On one hand, at log h = −3.5, only a small amount of dissolved Al^{3+} was detected in the suspension after an equilibration time of seven days. On the other hand, the p.z.n.p.c. of Ca-montmorillonite always was found to be constant for initial log h values ranging from 3.0 ≤ −log h ≤ 8.0. This indicates that the acid-base properties of Ca-montmorillonite do not markedly change in measured log h range. This behaviour is unlikely for dissolution processes with subsequent re-adsorption because it can be suggested that re-adsorption of dissolved Al^{3+} and Si^{4+} on the solid will result in a changed surface with modified acidic properties.

The H^+-Ca^{2+}-exchange. The reaction equation describing the exchange reaction of Ca^{2+} by 2 H^+ in the montmorillonite interlayer is:

$$CaX_2 + 2\,H^+ \leftrightarrow 2\,HX + Ca^{2+} \tag{28}$$

According to Fletcher and Sposito (1989), the thermodynamic equilibrium constant of reaction (28) may be expressed with

$$K_{a(Ca,H)} = \frac{m_{Ca^{2+}} \cdot \gamma_{Ca^{2+}}}{m^2_{H^+} \cdot \gamma^2_{H^+}} \cdot \frac{x^2_{H^+} \cdot f^2_{H^+}}{x_{Ca^{2+}} \cdot f_{Ca^{2+}}} \tag{29}$$

where $m_{Ca^{2+}}$, m_{H+} are the mole fractions of soluted Ca^{2+}, H^+ and $x_{Ca^{2+}}$, x_{H+} are the corresponding mole fractions in the ion-exchanger phase. $\gamma_{Ca^{2+}}$ and γ_{H+} denote the activity coefficients of soluted Ca^{2+} and H^+ respectively, related to the infinite dilution scale. f_{Ca} and f_H are the rational activity coefficients of the respective ion-exchanger species. The description of ion-exchange reactions by Eq. 29 is often used (Banin, 1969; Fletcher and Sposito, 1989). Replacing the mole fractions by concentrations, one obtains

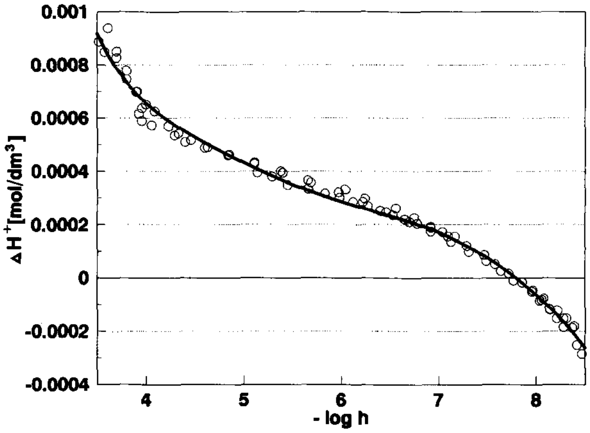


Figure 1. Titration curve of Ca-montmorillonite in 0.1 mol/dm³ $Ca(ClO_4)_2$ at 298.2 K. The quantity ΔH defined by $\Delta H = H - h + K_w \cdot h^{-1}$ corresponding to the hydrogen ions bound by the system is plotted as a function of −log h. Approximately every tenth data point is presented. The solid line was calculated using the parameters given in Table 1.

$$K_{a(Ca,H)} = \frac{[Ca^{2+}] \cdot \gamma_{Ca^{2+}}}{[H^+]^2 \cdot \gamma^2_{H^+}} \cdot \frac{[HX]^2 \cdot f^2_{H^+}}{[CaX_2] \cdot f_{Ca^{2+}}} \cdot \frac{[Ca^{2+}] + [H^+]}{[CaX_2] + [HX]}. \tag{30}$$

Combining Eq. 30 with Eq. 12 yields

$$K_{a(Ca,H)} = K_{(Ca,H)} \cdot \frac{\gamma_{Ca^{2+}}}{\gamma^2_{H^+}} \cdot \frac{f^2_{H^+}}{f_{Ca^{2+}}} \cdot \frac{[Ca^{2+}] + [H^+]}{[CaX_2] + [HX]}. \tag{31}$$

Eq. 31 is simplified by assuming the rational activity coefficients f_H and f_{Ca} to be unity. This assumption can be justified by the fact that soil components normally show an ion-exchange behaviour which is close to ideality (Sposito, 1984), i.e., the ion-exchange equilibria at finite ionic strengths do not markedly differ from the ion-exchange equilibrium at the reference state (homoionic material at I = 0) as defined by Gaines and Thomas (1953).

The ratio $\gamma_{Ca^{2+}}/\gamma^2_{H+}$ (as obtained from the Davis, 1962, equation) is 0.537. In solution at −log h > 3.5, $[H^+]$ is negligible as compared to $[Ca^{2+}]$, thus $[Ca^{2+}] + [H^+] \approx [Ca^{2+}] = 0.1$ mol/dm³.

Eq. 32 relates $[CaX_2]$ and [HX] with the cation exchange capacity (CEC) and the concentration of suspended clay, C_s:

$$\begin{aligned} 2 \cdot [CaX_2] + [HX] &= CEC \cdot C_s \\ &= 9.3 \cdot 10^{-3} \text{mol/dm}^3 \end{aligned} \tag{32}$$

As can be seen in Figure 2, the amount of [HX] at −log h > 3.5 can be neglected. One thus obtains $[CaX_2] + [HX] \approx 4.65 \cdot 10^{-3}$ mol/dm³.

With these simplifications, Eq. 31 can be rewritten:

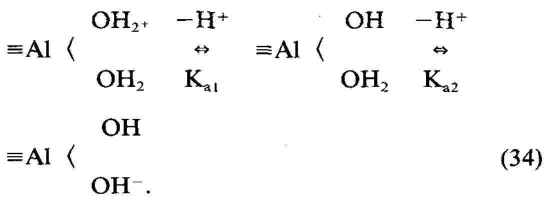
$$K_{a(Ca,H)} = K_{Ca,H} \cdot 11.45 \tag{33}$$

Published values of log $K_{a(Ca,H)}$ are 0.017 (Fletcher *et al.*, 1989), −0.344 (Benson, 1982) and 1.78 (Banin, 1969). Attempts to fit the data including a log $K_{a(Ca,H)}$ value of 0.017 lead to a poor agreement between experimental values and calculated data in the region of $3.5 < -\log h < 4.5$. The best fit was obtained with a value of log $K_{a(Ca,H)} = 2.44$. We consider this value as doubtful, because the amount of H^+ bound by the solid that cannot be attributed to protonation of ≡SOH-groups is comparatively small. It also reflects the problems of separating ion-exchange and surface protonation. The speciation diagram (Figure 2) shows a clear predominance of CaX_2 over the entire data range when a log $K_{a(Ca,H)}$ value of 2.44 is assumed. In additional runs (not presented), the model was tested in the region of $4.5 < -\log h < 10$ without consideration of the ion-exchange. As could be expected, the resulting parameters did not significantly differ from the presented ones, indicating the weak dependence of the model on $Ca^{2+} - H^+$ exchange. Because of the obviously minor importance of the ion-exchange, no further attempts to improve the accuracy of $K_{a(Ca,H)}$ were made.

On the nature of the ≡SOH and ≡TOH groups. From the composition of montmorillonite, one expects the presence of surface silanol- and aluminol groups:

The ≡TOH group acts exclusively as a proton donor, it can thus be identified as a surface silanol group. This identification is further supported by the comparison of log $\beta^s_{TOH,-1,0}$ with published values of the acidity constant of surface silanol groups (Schindler and Stumm, 1987) ranging from log $\beta^s_{-1,0} = -5.71$ to -6.8.

On the other hand, the amphoteric behaviour of the ≡SOH group is also found for surface aluminol groups. Reported values for log $\beta^s_{1,0}$ lie between +7,4 and +7.2 (Schindler and Stumm, 1987). Log $\beta^s_{-1,0}$ values in the range −9.5 to −10.0 were cited by the same authors. The observation that log $\beta^s_{SOH,1,0}$ is very close to $-\log \beta^s_{SOH,-1,0}$ suggests however, that the acting group is ≡Al(OH)OH_2. The pertinent equilibria can be visualised by the scheme



$$\equiv Al \langle {OH_{2^+} \atop OH_2} \underset{K_{a1}}{\overset{-H^+}{\Leftrightarrow}} \equiv Al \langle {OH \atop OH_2} \underset{K_{a2}}{\overset{-H^+}{\Leftrightarrow}} \equiv Al \langle {OH \atop OH^-}. \qquad (34)$$

This corresponds to the protonation scheme of a diprotic acid. For identical and independent groups, the macroscopic acidity constants differ by a factor of 4: $K_{a1} = 4 \cdot K_{a2}$ (King, 1965). This agrees very well with the experimental observation $((\beta^s_{SOH,1,0})^{-1} = 3.56\ (\pm\ 0.35) \cdot \beta^s_{SOH,-1,0})$. The scheme (34) has already been suggested by Pulfer (1984), Westall (1987) and Hiemstra et al. (1989). However, the figures reported for surface groups at γ-Al$(OH)_3$ (log $\beta^s_{1,0} = 5.24$, log $\beta^s_{-1,0} = -8.08$ (Pulfer, 1984)) differ considerably from the values found in this study. This difference may at least in part be attributed to the fact that the γ-Al$(OH)_3$ used in the study by Pulfer (1984) had been pre-treated with diluted acid (Pulfer, 1981).

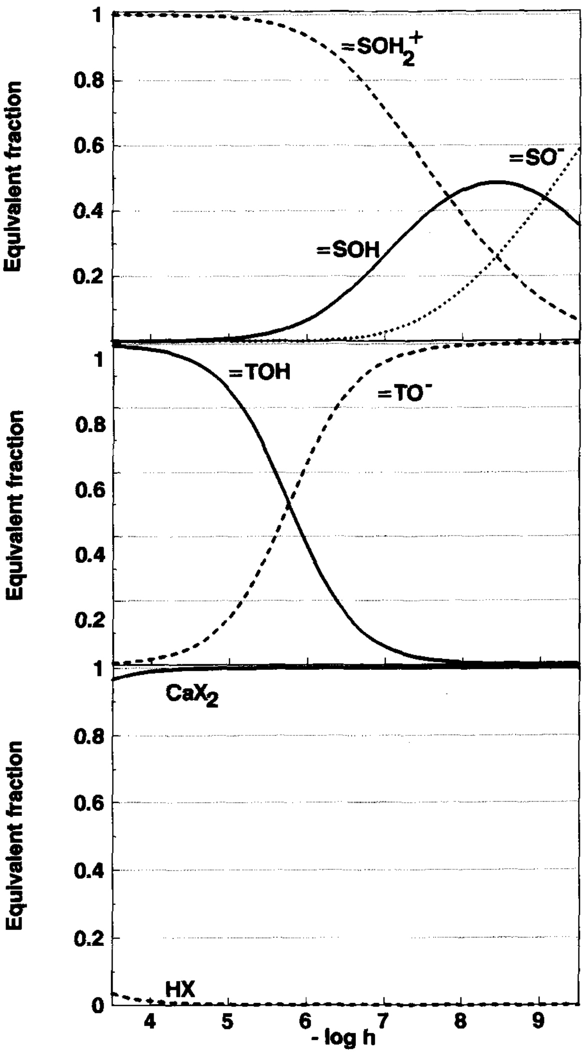


Figure 2. Speciation diagram of the system Ca-montmorillonite − H+. The amounts of aluminol-, silanol- and ion-exchange species relative to the corresponding total concentrations are plotted against −log h. The speciation was calculated using the parameters given in Table 1.

Cu(II)-sorption

In Figure 3, the sorption of Cu is plotted as

$$\Delta C = \frac{C - c}{C} \cdot 100\ [\%]$$

against −log h. In the range of $3.5 < -\log h < 4.5$, a nearly constant value for $\Delta C = 10\%$ can be noted that is mainly attributed to Ca-Cu ion-exchange (Eq. 13). In the region of $4.5 < -\log h \leq 6.5$ a steep increase of ΔC up to 100% is observed. At log $h > 6.5$, Cu is

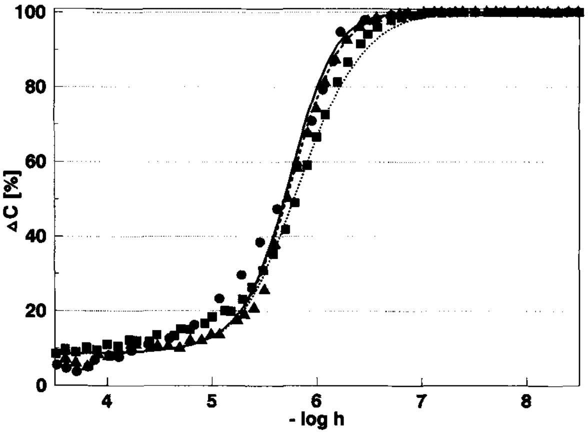


Figure 3. Cu sorption by Ca-montmorillonite at 298.2 K. ΔC, defined by ΔC = (C − c)/C·100 [%], i.e., the Cu ions sorbed by the solid, is plotted as a function of −log h. Filled symbols denote data measured by the Cu-electrode: C = 0.0001 mol/dm³ (●), C = 0.0002 mol/dm³ (▲) and C = 0.0005 mol/dm³ (■). The lines were computed using the data given in Table 1: C = 0.0001 mol/dm³ (Solid line (——)), C = 0.0002 mol/dm³ (Dashed line (− − −)) and C = 0.0005 mol/dm³ (Dotted line (. . .)).

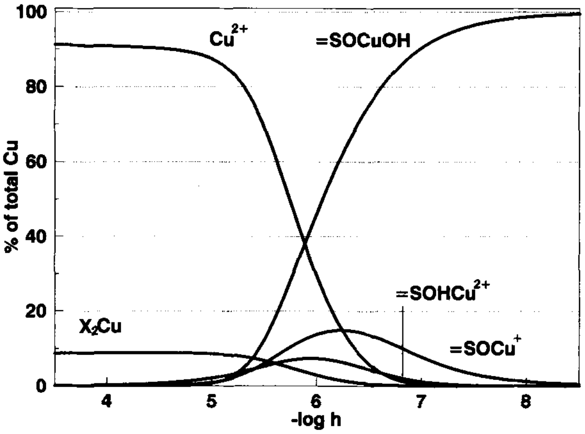


Figure 4. Speciation diagram of the system Ca-montmorillonite – Cu^{2+} – H^+. The amount of Cu-clay species relative to C is plotted as a function of −log h. Total Cu concentration C = 0.0005 mol/dm³. The lines represent a calculation based on the data given in Table 1.

entirely bound to the clay. The increase in ΔC is caused by the interaction of Cu and the surface hydroxyl groups.

Ca-Cu exchange. The thermodynamic exchange constant is given by (Sposito, 1984):

$$K_{ex(Ca,Cu)} = \frac{[CuX_2]\cdot[Ca^{2+}]}{[CaX_2]\cdot[Cu^{2+}]}\cdot\frac{f_{Cu}}{f_{Ca}}\cdot\frac{\gamma_{Ca}}{\gamma_{Cu}}$$

$$= K_{Ca,Cu}\cdot\frac{f_{Cu}}{f_{Ca}}\cdot\frac{\gamma_{Ca}}{\gamma_{Cu}}. \qquad (35)$$

Assuming ideal behaviour of montmorillonite (i.e., $f_{Cu} = f_{Ca} = 1$) and using the Davis equation (i.e., $\gamma_{Ca}/\gamma_{Cu} = 1$), Eq. 35 is simplified to

$$K_{ex(Ca,Cu)} = K_{Ca,Cu} \qquad (36)$$

The value for $K_{Ca,Cu}$ was calculated from 50 aliquots taken from suspensions in the range of $2.8 < -\log h < 4$. Additionally, 200 data points from titrations monitored by a Cu electrode in the same log h range were collected to obtain another data set to calculate $K_{Ca,Cu}$. An average value of $\log K_{Ca,Cu} = 0.30$ was obtained and included in the subsequent models without further optimisation. Reported values for $\log K_{ex(Ca,Cu)}$ are −0.009 (El Sayed *et al.*, 1970), 0.232 (Benson, 1982) and −0.13 (Fletcher and Sposito, 1989).

Cu^{2+} adsorption in the range of $-\log h > 5$. In the range of $5 < -\log h < 7$, a steep increase in ΔC is observed (Figure 3). This increase can be ascribed either to a further sorption of positively charged Cu species by the ion exchanger or to an adsorption of Cu by surface hydroxyl groups. Possible Cu species that could undergo ion-exchange are $Cu(OH)^+$ and $Cu_2(OH)_2^{2+}$. Two test runs with FITEQL optimising the hypothetical equilibrium

$$X^- + Cu^{2+} + OH^- \Leftrightarrow XCu(OH) \quad \log K_{37} = +5.02 \qquad (37)$$

and alternatively

$$2\,X^- + 2\,Cu^{2+} + 2\,OH^- \Leftrightarrow X_2Cu_2(OH)_2 \quad \log K_{38} = +13.26 \qquad (38)$$

combined with K_0 (Eq. 9) and the stability constants $^*\beta_{1,1}$ and $^*\beta_{2,2}$ (as defined in Eq. 8), respectively, resulted in unreasonably high ion-exchange constants for the exchange reactions:

$$X_2Ca + 2\,Cu(OH)^+ \Leftrightarrow 2\,XCu(OH) + Ca^{2+} \quad K_{ex,Ca,Cu(OH)}$$

$$= \frac{K_{37}^2}{K_0} = 10^{+6.76} \qquad (39)$$

and

$$X_2Ca + Cu_2(OH)_2^{2+} \Leftrightarrow X_2Cu_2(OH)_2 + Ca^{2+} \quad K_{ex,Ca,Cu_2(OH)_2}$$

$$= \frac{K_{38}}{K_0} = 10^{+3.96}. \qquad (40)$$

Furthermore, the calculated mass balance of H^+, as given by Eq. 16, was in both cases found to inadequately represent experimental data as obtained from glass electrode measurements, leading to a very high error estimate, SOS/DF, of 386.3 and 406.0, respectively. Ion-exchange reactions thus seem to be inappropriate to explain the Cu sorption at $-\log h > 5$.

The similarity of Figure 3 to the adsorption curve of Cu by kaolinite as presented by Schindler *et al.* (1987) leads to another interpretation of the Cu adsorption at $-\log h > 5$: Schindler *et al.* (1987) suggest the adsorption of Cu by kaolinite to take place mainly at ampholytic surface aluminol groups for $I \geq 0.1$ and $-\log h > 5$. Based on this suggestion, several complexes containing surface hydroxyl groups and Cu were tested. Again in the present study, the evaluation of the data indicated a strong interaction of aluminol ($\equiv$SOH) sites with Cu. Silanol sites ($\equiv$TOH) were found not to adsorb Cu. An acceptable fit could be obtained by assuming the formation of $\equiv$SOCuOH only. Improvement could be achieved by introducing $\equiv SOCu^+$ or $\equiv SOHCu^{2+}$. Finally, the best fit (SOS/DF = 15.63) involved three simultaneous equilibria:

$$\equiv SOH + Cu^{2+} \Leftrightarrow \equiv SOHCu^{2+} \qquad \beta^{s}_{SOH,0,1}$$

$$\equiv SOH + Cu^{2+} \Leftrightarrow \equiv SOHCu^{+} + H^{+} \qquad \beta^{s}_{SOH,-1,1}$$

$$\equiv SOH + Cu^{2+} \Leftrightarrow \equiv SOHCuOH + 2\,H^{+} \qquad \beta^{s}_{SOH,-2,1}.$$

The resulting parameters are presented in Table 1. The data can not directly be compared to the values given by Schindler *et al.* (1987) since these authors assumed a different set of surface complexes.

The speciation of the system is presented in Figure 4. At $-\log h < 5.5$, Cu is mainly sorbed by ion-exchange (CuX_2). The log h-dependent adsorption begins at $-\log h = 4.5$ and becomes important at $-\log h > 5.5$ with the predominating species $\equiv$SOCuOH. The intermediate species $\equiv SOCu^+$ and $\equiv SOHCu^{2+}$ always play a minor role.

The structure of the clay-Cu complexes is not accessible with the experimental methods used in this study. However, it is reasonable to interpret the three equilibria given above as a stepwise deprotonation process of one single clay-Cu complex.

In accordance with Schindler *et al.* (1987), the results of this study suggest that a combination of Cu uptake by ion-exchange and Cu adsorption by surface aluminol groups better explains the interactions of Cu and Ca-montmorillonite in the range of $3 < -\log h < 8.5$ than Cu uptake by ion-exchange alone. At $-\log h > 7$ and $C = 0.0005$ mol/dm^3, up to $4 \cdot 10^{-6}$ mol Cu per g of clay is adsorbed on aluminol surface sites, this means that Cu occupies up to 66% of the totally available aluminol surface sites.

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