

## THE EFFECT OF DISSOLVED LIGANDS UPON THE SORPTION OF Cu(II) BY Ca-MONTMORILLONITE

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**Abstract**—The effect of three organic ligands on the adsorption of Cu on Ca-montmorillonite was studied. The results indicate that these effects include three different processes:

- 1) Enhanced uptake of positively charged Cu-ligand complexes by ion-exchange.
- 2) Formation of ternary surface complexes involving surface aluminol groups.
- 3) Inhibited uptake due to competition between the surface ligands and the dissolved ligands for dissolved copper.

Ethylenediamine promotes Cu uptake by ion-exchange at low pH but tends to suppress adsorption at aluminol groups by ligand competition at high pH. The same mechanisms are operative for  $\beta$ -alanine; however, the uptake of  $\text{Cu}(\beta\text{-ala})^+$  by ion-exchange is not promoted by the attached ligand. The influence of malonate includes both ligand competition and formation of ternary complexes. A quantitative interpretation based on the surface complexation model using the least-square programs FITEQL (Westall, 1982) and GRFIT (Ludwig, 1992) is presented. The obtained equilibrium constants are listed in Tables 2b and 3.

**Key Words**—Adsorption,  $\beta$ -alanine, Copper, Ethylenediamine, Malonic acid, Modeling, Montmorillonite.

### INTRODUCTION

In a previous paper (Stadler and Schindler, 1993), a model of Cu adsorption on Ca-montmorillonite was presented. It was found that Cu interaction with montmorillonite can be described with a model that contains adsorption of Cu by ion-exchange in the interlayers of montmorillonite in the range of  $3 < \text{pH} < 4.5$  and by the formation of surface complexes with aluminol groups in the region  $\text{pH} > 4$ .

The uptake of metal ions by clay minerals (and oxides) is strongly influenced by the presence of ligands with complexing characteristics. Metal ions in natural systems are in part present as dissolved metal-ligand complexes because of the vast abundance of such ligands. The study of metal uptake by clay minerals in the presence of complexing ligands is, therefore, necessary to understand the fate of metals in soils.

The electrolyte concentration used in this study was significantly higher than normally found in natural soils. The authors are aware that this choice reduces the relevance of the study to the fate of heavy metals in natural soils. On the other hand, such a high electrolyte concentration offers some important advantages: Activity coefficients of almost all involved components, including surface species and dissolved species, can be neglected, which simplifies the modeling of the investigated systems. Moreover, numerous equilibrium constants in the range of  $1.0 > I > 0.1$  ( $I$  = ionic strength) for important reactions in this study are present in the

literature, which offers a broad and reliable control of the results of this work. Finally, the aim of this study is to give an overview over possible interactions of metals and surface components in the presence of organic ligands and to show the possibilities and limits of least-square programs in modeling and interpreting complex systems.

The influence of ligands on metal uptake is manifested in different ways. In the simplest case, dissolved ligands compete with the solid phase for the metal cation causing a decreased adsorption of the metal. Ligand competition for metal ions is always occurring, but this decreased adsorption can be compensated by other forms of ligand-metal-solid interactions: The formation of ternary complexes promotes metal adsorption at oxide minerals (Schindler and Stumm, 1987; Schindler, 1990). For clay minerals, an enhanced uptake of cationic metal-ligand complexes by ion-exchange as compared with the free metal ion has been reported (Bodenheimer *et al.*, 1962, 1963, and 1966; Cloos *et al.*, 1972; Maes *et al.*, 1978). This effect was interpreted as a stabilization of the metal-ligand complex by the interlayer phase as compared to the aqueous solution (Maes *et al.*, 1978). The possible formation of ternary surface complexes at clay-water interfaces has, so far, not been investigated.

In this paper, the clay mineral montmorillonite was chosen because of its variety of adsorption sites. Cu was selected because of its ability to form very stable complexes with different ligands. The ligands used in this study were ethylenediamine (en),  $\beta$ -alanine, and malonic acid.  $\beta$ -alanine and malonic acid form six

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Table 1. Layer distances of montmorillonite.

	d [Å]	Ref.
Ca-montmorillonite	14.5	Stadler and Schindler, 1993
Ca-en-montmorillonite	15.2	This work
Cu-montmorillonite	12	Stadler and Schindler, 1993
Cu-en-montmorillonite	15.5	This work

membered chelate rings with Cu, which are thought to stabilize Cu complexes, whereas en forms a five-membered chelate ring.

This work consists of two parts. In the first part, the interactions of montmorillonite with the chosen ligands were investigated. In the second part, the three ternary systems Cu-en-montmorillonite, Cu- $\beta$ -alanine-montmorillonite and Cu-malonate-montmorillonite were studied. Experimental data were used to establish a model for the investigated systems with the aid of the least-square fit programs FITEQL (Westall, 1982) and GRFIT (Ludwig, 1992).

## MATERIALS AND METHODS

### Survey

1.00 g Ca-montmorillonite was suspended in  $V_0 = 0.1 \text{ dm}^3$  of a solution S of the general composition  $[\text{H}^+] = H_0 \text{ mol/dm}^3$ ,  $[\text{Cu}_T] = C_0 \text{ mol/dm}^3$ ,  $[\text{L}] = L_0 \text{ mol/dm}^3$ ,  $[\text{Ca}_T] = (0.1 - C_0) \text{ mol/dm}^3$ ,  $[\text{ClO}_4^-] = 0.2 \text{ mol/dm}^3$  and pre-equilibrated for one week. Afterwards, the suspension was titrated at 298.2 K with  $v \text{ dm}^3$  of a solution S1 of the general composition  $[\text{Ca}^{2+}] = 0.1 \text{ mol/dm}^3$ ,  $[\text{OH}^-] = B \text{ mol/dm}^3$ ,  $[\text{ClO}_4^-] = (0.2 - B) \text{ mol/dm}^3$ .  $H_0$  was set close to  $0.002 \text{ mol/dm}^3$ ,  $L_0$  was varied in the range of  $0.0001 \leq L_0 \leq 0.0040 \text{ mol/dm}^3$ , and  $B$  was set at  $0.01 \text{ mol/dm}^3$ . In most of the titrations,  $C_0$  was  $0.0005 \text{ mol/dm}^3$ .

Separate titrations with  $C_0 = 0 \text{ mol/dm}^3$  were carried out to investigate ligand uptake by Ca-montmorillonite. After each addition of S1, the free concentration of hydrogen ions was measured every 30 s with the aid of a combined glass electrode. Equilibrium was assumed when 1) two consecutive readings of the emf  $E_H$  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. When the equilibrium was established, a small aliquot was collected and analyzed after centrifugation for both dissolved Cu ( $C_s$ ) and ligand ( $L_s$ ).

The following parameters are thus accessible: Total hydrogen ion concentration,  $H$ , is given by

$$H = \frac{H_0 \cdot V_0 - B \cdot v}{V_0 + v} \quad (1)$$

Free hydrogen ion concentration,  $h$ , is obtained from the Nernst equation:

$$h = 10^{\frac{E_H - E_H^0}{k}} \quad (2)$$

$E_H^0$  and  $k$  were obtained from calibrations using a series of solutions with known  $\text{H}^+$ -concentration. Total Cu concentration,  $C$ , and total ligand concentration,  $L$ , are calculated with Eqs. (3) and (4), respectively:

$$C = \frac{C_0 \cdot V_0}{V_0 + v} \quad (3)$$

$$L = \frac{L_0 \cdot V_0}{V_0 + v} \quad (4)$$

The amount of adsorbed Cu and ligand, respectively, is given by

$$C_{\text{ads}} = C - C_s \quad (5)$$

$$L_{\text{ads}} = L - L_s \quad (6)$$

Experimental and calculated data are presented in the figures as

$$\Delta C = \frac{C_{\text{ads}}}{C} \cdot 100 \quad [\%] \quad (5a)$$

$$\Delta L = \frac{L_{\text{ads}}}{L} \cdot 100 \quad [\%] \quad (6a)$$

### Chemicals

SWy-1 montmorillonite (Na-montmorillonite) from Crook County, Wyoming, was provided by the Clay Minerals Society. Ca-montmorillonite was prepared as described in Stadler and Schindler (1993).  $d_{001}$  spacings of Ca-montmorillonite as well as of other forms of montmorillonite were obtained from X-ray diffraction (Cu  $k\alpha$  radiation) and are given in Table 1.

Solutions of  $\text{HClO}_4$ ,  $\text{Ca}(\text{ClO}_4)_2$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{Cu}(\text{ClO}_4)_2$  were prepared and analyzed as described by Stadler and Schindler (1993).

$^{14}\text{C}$ -labelled ethylenediamine (purity  $\geq 97.1\%$ ) and  $^{14}\text{C}$ -labelled malonate (sodium salt, purity 98.9%) were provided by Amersham International.  $^{14}\text{C}$ -labelled  $\beta$ -alanine (purity  $> 98\%$ ) was obtained from Sigma. Diluted solutions with an activity close to 10 kBq per mmol of ligand ( $L$ ) were prepared by mixing labelled  $L$  with  $0.1 \text{ mol/dm}^3$  solutions of unlabelled ethylenediamine (Merck p.a.),  $\beta$ -alanine (Merck p.a.) and malonic acid (Merck p.a.), respectively. The activities of these solutions were regularly checked. Opti-Fluor (Packard Instrument Company) was used as liquid scintillation cocktail.

### Apparatus

The titration equipment used in this work and the procedure for calibrating the glass electrode have been described by Stadler and Schindler (1993). Centrifugation was carried out for 5 min at 2500 rpm.  $C_s$  was obtained from flame-AAS (Beckmann AAS 1248).  $L_s$

Table 2a. Stability constants used in this work.

Equilibrium	log K
$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	-13.76 <sup>1</sup>
$\text{Ca}^{2+} (+ \text{H}_2\text{O}) \leftrightarrow \text{CaOH}^+ + \text{H}^+$	-11.58 <sup>2</sup>
$\text{en} + \text{H}^+ \leftrightarrow (\text{en})\text{H}^+$	+9.96 <sup>3</sup>
$\text{en} + 2 \text{H}^+ \leftrightarrow (\text{en})\text{H}_2^{2+}$	+17.16 <sup>3</sup>
$\beta\text{-ala}^- + \text{H}^+ \leftrightarrow (\beta\text{-ala})\text{H}$	+10.07 <sup>4</sup>
$\beta\text{-ala}^- + 2 \text{H}^+ \leftrightarrow (\beta\text{-ala})\text{H}_2^+$	+13.58 <sup>4</sup>
$\text{mal}^{2-} + \text{H}^+ \leftrightarrow (\text{mal})\text{H}^-$	+5.23 <sup>4</sup>
$\text{mal}^{2-} + 2 \text{H}^+ \leftrightarrow (\text{mal})\text{H}_2$	+7.85 <sup>4</sup>
$\text{mal}^{2-} + \text{Ca}^{2+} \leftrightarrow \text{Ca}(\text{mal})$	+1.40 <sup>4</sup>
$2 \text{X}^- + \text{Ca}^{2+} \leftrightarrow \text{CaX}_2$	+20.00 <sup>2</sup>
$2 \text{X}^- + \text{Cu}^{2+} \leftrightarrow \text{CuX}_2$	+20.30 <sup>2</sup>
$\equiv\text{SOH} + \text{H}^+ \leftrightarrow \equiv\text{SOH}_2^+$	+8.16 <sup>2</sup>
$\equiv\text{SOH} - \text{H}^+ \leftrightarrow \equiv\text{SO}^-$	-8.71 <sup>2</sup>
$\equiv\text{TOH} - \text{H}^+ \leftrightarrow \equiv\text{TO}^-$	-5.77 <sup>2</sup>
$\equiv\text{SOH} + \text{Cu}^{2+} \leftrightarrow \equiv\text{SOHCu}^{2+}$	+5.87 <sup>2</sup>
$\equiv\text{SOH} - \text{H}^+ + \text{Cu}^{2+} \leftrightarrow \equiv\text{SOCu}^+$	-0.57 <sup>2</sup>
$\equiv\text{SOH} - 2 \text{H}^+ + \text{Cu}^{2+} \leftrightarrow \equiv\text{SOCuOH}$	-6.76 <sup>2</sup>

Equilibria with fixed stability constants, where I (ionic strength) = 0.3, 298.2 K.

<sup>1</sup> Sillén and Martell (1964).

<sup>2</sup> Stadler and Schindler (1993).

<sup>3</sup> Martell and Smith (1976). The value was obtained by interpolating the stability constants given for I = 0.1 and I = 0.5 (T = 298.2 K).

<sup>4</sup> Martell and Smith (1976), calculated from the value given for I = 0.1 (T = 298.2 K) with the aid of the Davies equation.

was determined with the aid of a scintillation counter (Kontron Betamatic Isc).

## DATA TREATMENT

The model of the  $\text{H}^+$ - and  $\text{Cu}^{2+}$  sorption on Ca-montmorillonite as presented in Stadler and Schindler (1993) was extended to the ligands studied in this work. The complete system, therefore, can be described with seven components:  $\text{H}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{X}^-$  (ion-exchanger species),  $\equiv\text{SOH}$  (aluminol groups),  $\equiv\text{TOH}$  (silanol groups) and L [ethylenediamine (en), and  $\beta$ -alanine ( $\beta$ -ala) and malonate (mal)].

A reduced system without Cu was chosen to study the interactions of the ligands with montmorillonite.

In speciation calculations, it was found that copper hydrolysis for  $C \leq 0.0005 \text{ mol/dm}^3$  is negligible in the presence of the strongly complexing ligands en,  $\beta$ -ala and mal. Furthermore, it was found in various test runs, that the inclusion of silanol groups ( $\equiv\text{TOH}$ ) was not critical to the fit of the different models presented in this study. The same fact was found for the Cu adsorption on montmorillonite (Stadler and Schindler, 1993).

The studied systems, therefore, include known equilibria (Tables 2a and 2b) and the interactions of en,  $\beta$ -ala and mal, respectively, with clay components. The stability constants of most of the equilibria used in this investigation could be derived from published values (Table 2a); however, some solution equilibria for which the pertinent equilibrium constants for the ionic me-

Table 2b. Stability constants used in this work.

Equilibrium	log K
$\text{en} + \text{Cu}^{2+} \leftrightarrow \text{Cu}(\text{en})^{2+}$	+11.20
$2 \text{en} + \text{Cu}^{2+} \leftrightarrow \text{Cu}(\text{en})_2^{2+}$	+20.59
$\beta\text{-ala}^- + \text{Cu}^{2+} \leftrightarrow \text{Cu}(\beta\text{-ala})^+$	+8.32
$2 \beta\text{-ala}^- + \text{Cu}^{2+} \leftrightarrow \text{Cu}(\beta\text{-ala})_2$	+13.86
$\text{mal}^{2-} + \text{Cu}^{2+} \leftrightarrow \text{Cu}(\text{mal})$	+4.94
$2 \text{mal}^{2-} + \text{Cu}^{2+} \leftrightarrow \text{Cu}(\text{mal})_2^{2-}$	+9.06

Equilibria with optimized stability constants where I = 0.3, T = 298.2 K.

dium used in this study could not be derived from published values were included in the optimization procedure described below. The obtained values are given in Table 2b. With regards to the very different properties of the individual ligands, it is not possible to summarize the different equilibria encountered in the course of this study by one general equation. Therefore, the equilibria considered in modeling the experimental data are defined separately for every ligand in the respective section.

Modeling was performed with the least-square programs FITEQL (Westall, 1982) and GRFIT (Ludwig, 1992), respectively. The latter program permits a graphical comparison of experimental and calculated data.

## RESULTS AND DISCUSSION

### The binary system Ca-montmorillonite-en (ethylenediamine)

The choice of ethylenediamine instead of 1,3 diani-nopropane, which forms a six membered chelate ring (as  $\beta$ -alanine and malonic acid do), was imposed by the problems encountered in estimating the concentration of dissolved ligand in the montmorillonite suspensions. Since the envisaged ligands do not possess chromophores that permit their determination by UV/VIS spectrometry, we were limited to ligands where <sup>14</sup>C labelled samples were commercially available and labelled 1,3 diani-nopropane was not available.

In the measured range of  $3 \leq -\log h \leq 8$ , en forms protonated and thus positively charged species that can undergo ion-exchange. In Figure 1a, the percentage of bound en is plotted against  $-\log h$ . The figure includes data with  $0.0001 \leq L_0 \leq 0.001 \text{ mol/dm}^3$ . With regard to the high Ca:en ratio, a maximum of about 3% of the ion-exchange capacity has been occupied by protonated en. The formal treatment of the pertinent ion-exchange reactions as required by FITEQL is described by the hypothetical equilibria (7-9), where the value for  $\log K_0$  (Eq. 7) was arbitrarily chosen according to the data treatment of the ion-exchange as presented by Stadler and Schindler (1993), which is based on the treatment of ion-exchange reactions presented by Shaviv *et al.* (1985) and Fletcher *et al.* (1989).

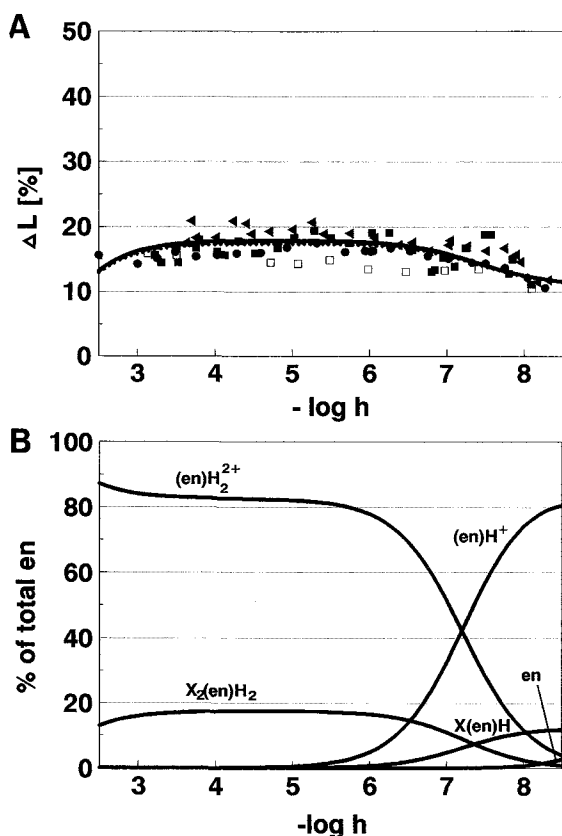
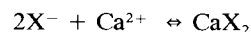
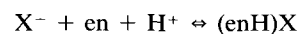


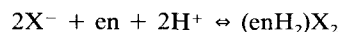
Figure 1. A) Adsorption of en on Ca-montmorillonite. The percentage of adsorbed en,  $\Delta L$ , is plotted as a function of  $-\log h$  ( $I = 0.3$ ,  $T = 298.2$  K). Symbols indicate experimental values for  $L_0 = 0.0001$  mol/dm<sup>3</sup> (●),  $L_0 = 0.0002$  mol/dm<sup>3</sup> (▲),  $L_0 = 0.0005$  mol/dm<sup>3</sup> (■),  $L_0 = 0.0010$  mol/dm<sup>3</sup> (□). Lines indicate calculated curves for  $L_0 = 0.0001$  mol/dm<sup>3</sup> (—),  $L_0 = 0.0002$  mol/dm<sup>3</sup> (----),  $L_0 = 0.0005$  mol/dm<sup>3</sup> (····) and  $L_0 = 0.0010$  mol/dm<sup>3</sup> (-·-·-). The curves were calculated with the stability constants given in Tables 2a and 3. B) Speciation of en in the system  $H^+$ , Ca-montmorillonite, en. The species are plotted in % of  $L_0$  (total en) against  $-\log h$  for  $L_0 = 0.0001$  mol/dm<sup>3</sup>. Calculations were performed with GRFIT based on the values given in Tables 2a and 3.



$$K_0 = \frac{[CaX_2]}{[Ca^{2+}] \cdot [X^-]^2} = 10^{+20} \quad (7)$$

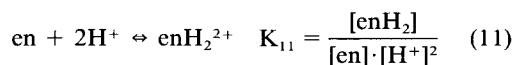
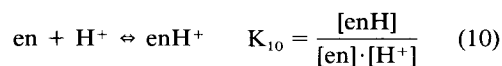


$$K_8 = \frac{[(enH)X]}{[en] \cdot [H^+] \cdot [X^-]} \quad (8)$$



$$K_9 = \frac{[(enH_2)X_2]}{[en] \cdot [H^+]^2 \cdot [X^-]^2} \quad (9)$$

Resulting constants are collected in Table 3. Combining Eqs. (7)–(9) with



one obtains the two ion-exchange constants  $K_{ex,Ca,enH}$  and  $K_{ex,Ca,enH_2}$ :

$$\begin{aligned} K_{ex,Ca,enH} &= \frac{[(enH)X] \cdot [Ca^{2+}]}{[CaX_2] \cdot [enH^+]^2} \\ &= \frac{K_8^2}{K_{10}^2 \cdot K_0} = 10^{-0.36} \quad (12) \end{aligned}$$

$$\begin{aligned} K_{ex,Ca,enH_2} &= \frac{[(enH_2)X_2] \cdot [Ca^{2+}]}{[CaX_2] \cdot [enH_2^{2+}]} \\ &= \frac{K_9}{K_{11} \cdot K_0} = 10^{+0.63} \quad (13) \end{aligned}$$

We note that the calculated value of  $\log K_{ex,Ca,enH}$  is close to reported values for divalent-monovalent ion-exchange. For the exchange reaction  $Ca^{2+} \rightleftharpoons Na^+$  an exchange constant of  $\log K_{ex} = -0.198$  is published (Benson, 1982). The constant of the exchange of  $Ca^{2+}$  by  $enH_2^{2+}$  is comparatively high and indicates signif-

Table 3. Equilibria of clay – ligand (–Cu) complexes obtained in this study.

Equilibrium	Stability constant
$X^- + en + H^+ \rightleftharpoons (enH)X$	$\log K_8 = +19.78 (\pm 0.06)^*$
$2 X^- + en + 2 H^+ \rightleftharpoons (enH_2)X_2$	$\log K_9 = +37.79 (\pm 0.21)^*$
$2 X^- + en + Cu^{2+} \rightleftharpoons Cu(en)X_2$	$\log K_{17} = +32.28^{**}$
$2 X^- + 2 en + Cu^{2+} \rightleftharpoons Cu(en)_2X_2$	$\log K_{18} = +42.41^{**}$
$2 X^- + 3 en + Cu^{2+} \rightleftharpoons Cu(en)_3X_2$	$\log K_{19} = +49.42^{**}$
$\equiv SOH + en + Cu^{2+} \rightleftharpoons \equiv SOHCu(en)^{2+}$	$\log K_{22} = +16.06^{**}$
$\equiv Y + \beta\text{-ala}^- + H^+ \rightleftharpoons \equiv Y(\beta\text{-ala})H$	$\log K_{14} = +14.60 (\pm 0.10)^*$
$X^- + Cu^{2+} + \beta\text{-ala}^- \rightleftharpoons Cu(\beta\text{-ala})X$	$\log K_{30} = +18.27^{**}$
$\equiv SOH + mal^{2-} + 2 H^+ \rightleftharpoons \equiv SOH_2(mal)H$	$\log K_{15} = +15.63 (\pm 0.03)^*$
$\equiv SOH + mal^{2-} + H^+ \rightleftharpoons \equiv SOH_2(mal)^-$	$\log K_{16} = +10.86 (\pm 0.03)^*$
$\equiv SOH + Cu^{2+} + mal^{2-} \rightleftharpoons \equiv SOCu(mal)^- + H^+$	$\log K_{32} = +3.12^{**}$
$\equiv SOH + Cu^{2+} + mal^{2-} \rightleftharpoons \equiv SOHCu(mal)$	$\log K_{33} = +9.34^{**}$

$I = 0.3$ ,  $T = 298.2$  K.

\* =  $3\sigma$ .

\*\* = Constants obtained from GRFIT; the present version gives no estimation of the standard deviation.

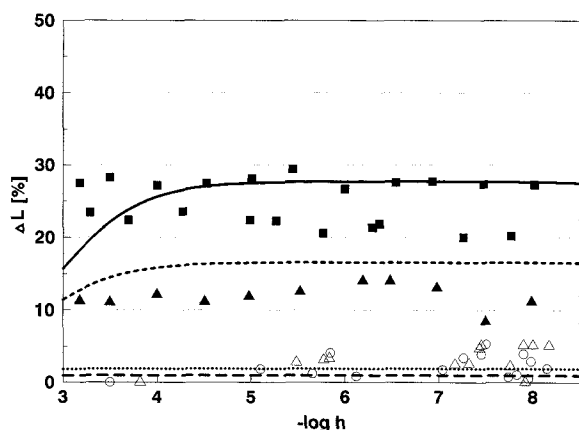


Figure 2. Sorption of  $\beta$ -alanine on Ca-montmorillonite ( $I = 0.3$ ,  $T = 298.2$  K).  $\Delta L$ , the percentage of  $\beta$ -ala sorbed, is plotted against  $-\log h$ . Symbols and lines as in Figure 1. Curves were calculated with the stability constants given in Tables 2a and 3.

icant preference of the ion-exchanger for  $\text{enH}_2^{2+}$  as compared with  $\text{Ca}^{2+}$ . As seen from the diagram (Figure 1b), the modeled speciation in the ion-exchanger phase closely reflects the speciation in solution. Uptake of  $\text{enH}^+$  and  $\text{enH}_2^{2+}$  to form interlayer complexes has already been investigated in an IR study by Cloos *et al.* (1972). These authors report a  $d_{001}$  spacing of 12.2 Å for the pure en form. In this work, only a partial exchange of  $\text{Ca}^{2+}$  by  $\text{enH}_2^{2+}$  of  $\leq 3\%$  of the total exchange capacity was investigated. The  $d_{001}$  spacing of Ca-montmorillonite was, thus, not significantly changed by the uptake of the small amount of  $\text{enH}_x^{x+}$ .

#### The system Ca-montmorillonite- $\beta$ -alanine

Experimental data of  $\beta$ -alanine sorption by Ca-montmorillonite are shown in Figure 2. The total amount of  $\beta$ -ala sorbed on the surface ( $\sim 2.5 \cdot 10^{-5}$  mol/dm<sup>3</sup>) does neither change with  $\log h$  (in the range of  $3 < -\log h < 8$ ) nor with increasing  $L_0$  concentrations varying from 0.0001 mol/dm<sup>3</sup> to 0.004 mol/dm<sup>3</sup>. This behavior could not be explained within the existing set of components. Therefore, an additional component  $\equiv Y$  ( $[\equiv Y]_{\text{tot}} = 4.0 \cdot 10^{-5}$  mol/dm<sup>3</sup>) was introduced. It must be emphasized that the presence of  $\equiv Y$  in the model is purely empirical and cannot be taken as evidence for the existence of such hydrophobic sites. The equilibrium

$$K_{14} = \frac{[\equiv Y(\beta\text{-ala})\text{H}]}{[\equiv Y] \cdot [\beta\text{-ala}^-] \cdot [\text{H}^+]} \quad (14)$$

serves merely to formally account for the observed unspecific, perhaps zero-order sorption within the scope of the FITEQL concept. This unsatisfactory handling of the experimental data in case of  $\beta$ -alanine shows clearly the limits of the available least-squares programs in fitting systems with complex and probably

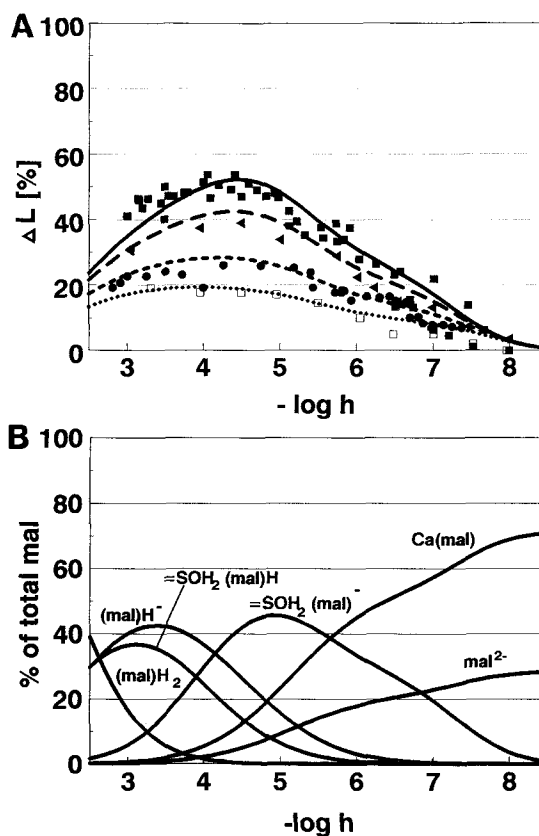


Figure 3. A) Sorption of mal on Ca-montmorillonite ( $I = 0.3$ ,  $T = 298.2$  K). The percentage of adsorbed ligand,  $\Delta L$ , is plotted against  $-\log h$ . Symbols and lines as in Figure 1. The curves were calculated with the stability constants given in Tables 2a and 3. B) Speciation of mal in the system  $\text{H}^+$ , Ca-montmorillonite, mal. The species are plotted in % of  $L_0$  (total mal) vs.  $-\log h$ . Calculations were performed with the aid of GRFIT (Ludwig, 1992) for  $L_0 = 0.0001$  mol/dm<sup>3</sup>.

not exclusively chemical interactions. However, with respect to the ternary system copper- $\beta$ -alanine-montmorillonite, this doubtful model fitting treatment was not excluded from this study.

The parameters obtained by the optimization procedure are listed in Table 3, the modeled curve is plotted in Figure 2. According to Tsunashima (1984), the protonated  $\beta$ -alanine undergoes ion-exchange with Ca-montmorillonite at  $-\log h < 4$ . In the present study, this ion-exchange was obviously suppressed by the prevailing high concentration of  $\text{Ca}^{2+}$  ions.

#### Adsorption of malonate and hydrogen-malonate on Ca-montmorillonite

The uptake of malonate by Ca-montmorillonite is shown in Figure 3a. Adsorption occurs preferentially under moderate acidic conditions with a maximum at  $-\log h = 4.5$  and becomes negligible at  $-\log h > 8$ . Similar behavior is widely observed with anionic species that undergo electrostatic interactions with a pos-

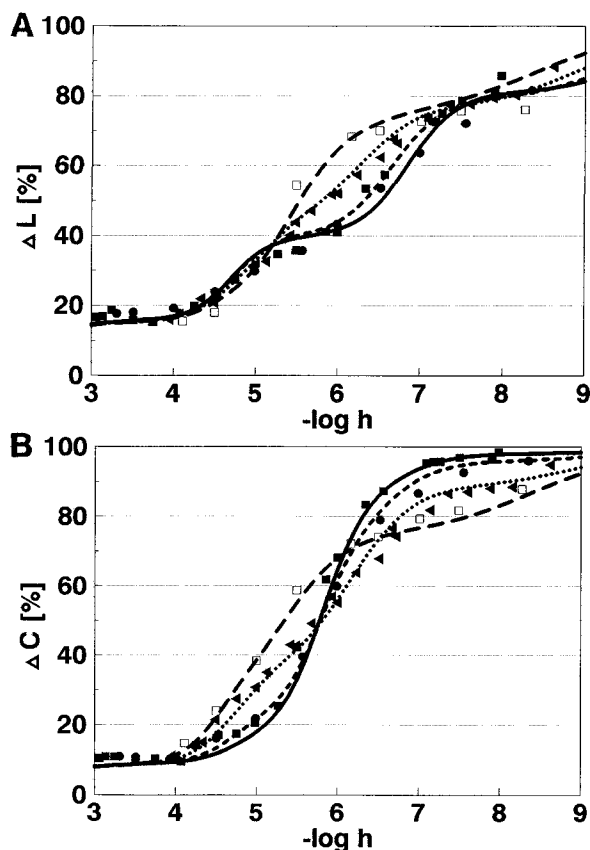
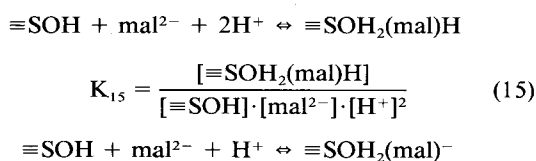


Figure 4. A) Adsorption of en on Ca-montmorillonite in the presence of Cu(II) ( $C_0 = 0.0005 \text{ mol/dm}^3$ ,  $I = 0.3$ ,  $T = 298.2 \text{ K}$ ). The percentage of adsorbed en,  $\Delta L$ , is plotted as a function of  $-\log h$ . B) Adsorption of Cu(II) on Ca-montmorillonite in the presence of en. ( $C_0 = 0.0005 \text{ mol/dm}^3$ ,  $I = 0.3$ ,  $T = 298.2 \text{ K}$ ). The percentage of adsorbed Cu(II),  $\Delta C$  is plotted against  $-\log h$ . Symbols and lines as in Figure 1. The curves were calculated with the stability constants given in Tables 2a, 2b, and 3.

itively charged surface. The speciation of L in the measured  $\log h$  range ( $3 < -\log h < 8$ ) is governed by the anions  $\text{mal}^{2-}$  and  $(\text{mal})\text{H}^-$ . For electrostatical reasons, the interaction of the ligand with montmorillonite is likely to take place at positively charged aluminol surface sites (Siffert *et al.*, 1980). Therefore, all models tested in this study included complexes of  $(\text{mal})\text{H}^-$  and  $\text{mal}^{2-}$  with protonated aluminol-groups.

The best fit was obtained with a combination of the two surface complexes  $\equiv\text{SOH}_2(\text{mal})\text{H}$  and  $\equiv\text{SOH}_2(\text{mal})^-$ :

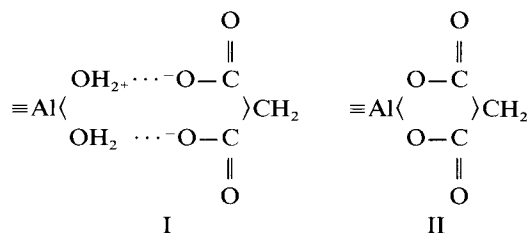


$$K_{16} = \frac{[\equiv\text{SOH}_2(\text{mal})^-]}{[\equiv\text{SOH}] \cdot [\text{mal}^{2-}] \cdot [\text{H}^+]} \quad (16)$$

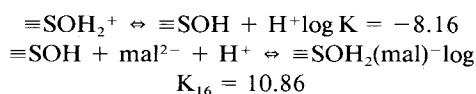
The obtained equilibrium constants are presented in Table 3.

The model is able to explain the adsorption properties of malonic acid in the whole  $\log h$  range measured in this study: As seen from Figure 3b, the speciation of L at  $-\log h \leq 3.0$  is dominated by malonic acid ( $\text{H}_2(\text{mal})$ ) that is not able to interact with the positively charged aluminol sites. In the range of  $3 < -\log h < 4$ , L is predominantly present as  $(\text{mal})\text{H}^-$  and  $\equiv\text{SOH}_2(\text{mal})\text{H}$ , respectively. In the subsequent  $\log h$  range ( $4 < -\log h < 5.5$ ) a slight decrease of  $\Delta L$  is observed in the same region as  $(\text{mal})\text{H}^-$  is transformed into  $\text{mal}^{2-}$ . The decrease in  $\Delta L$  becomes steeper at values of  $-\log h > 5.5$  due to the beginning deprotonation of surface aluminol groups. At  $-\log h > 8$ , L is completely desorbed.

The structure of the aluminol-malonate complex is not directly accessible with the methods used in this study. The obtained stability constants are, however, more in accordance with an outer sphere complex (I) than with an inner sphere complex based on ligand exchange (II)



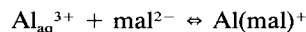
Combining



one obtains the equilibrium



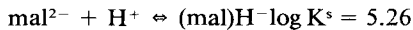
that is markedly smaller than what one would expect for the formation constant of Al(III)-malonate complex in solution,



on the basis of published values for  $\text{Sc}(\text{mal})^+$  ( $\log K = 5.87$ ,  $298.2 \text{ K}$ ,  $I = 1$  [Martell and Smith, 1976]) and  $\text{Fe}(\text{mal})^+$  ( $\log K = 7.5$ ,  $298.2 \text{ K}$ ,  $I = 1$  [Martell and Smith, 1976]). On the other hand, the observation that the protonation constant as obtained from Eqs. (15) and (16)

$\equiv\text{SOH}_2(\text{mal})^- + \text{H}^+ \leftrightarrow \equiv\text{SOH}_2(\text{mal})\text{H} \log K^s = 4.77$  is smaller than the protonation constant of malonate in solution





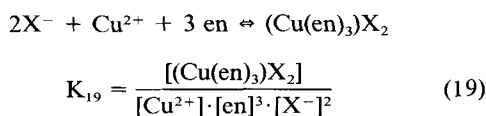
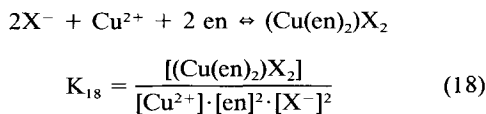
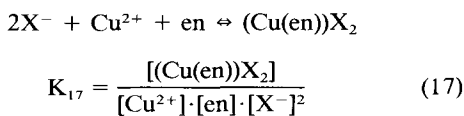
is in accordance with the formation of an outer sphere complex (I) and reflects the presence of the neighboring positive surface charge.

#### The ternary system ethylenediamine-copper-Ca-montmorillonite

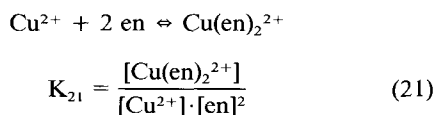
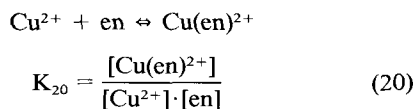
Collected data for en and copper adsorption are plotted in Figures 4a and 4b, respectively.

The system is clearly dominated by two processes. 1) The formation of very stable Cu-en complexes in solution: The formation of  $\text{Cu}(\text{en})^{2+}$  and  $\text{Cu}(\text{en})_2^{2+}$  is well documented, while the formation of a  $\text{Cu}(\text{en})_3^{2+}$ -complex is uncertain. 2) Uptake of Cu-en complexes by the interlayers of montmorillonite. The adsorption of  $\text{Cu}(\text{en})_2^{2+}$  by ion-exchange has already been described by Bodenheimer *et al.* (1963). Velghe *et al.* (1977) report the formation of  $\text{Cu}(\text{en})^{2+}$ ,  $\text{Cu}(\text{en})_2^{2+}$  and  $\text{Cu}(\text{en})_3^{2+}$  in the interlayer space. Maes *et al.* (1978) found a markedly enhanced stability of  $\text{Cu}(\text{en})^{2+}$  and  $\text{Cu}(\text{en})_2^{2+}$  in the interlayer as compared to the stability in solution.

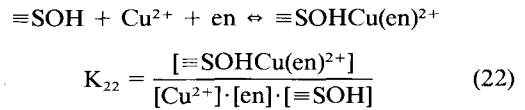
Therefore, the combined Cu-en uptake by montmorillonite can be described by the equilibria



In addition, the subsequent equilibria were included in the optimization procedure

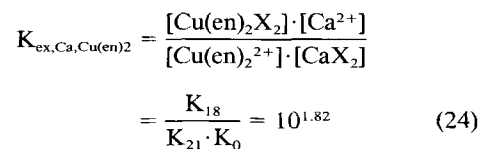
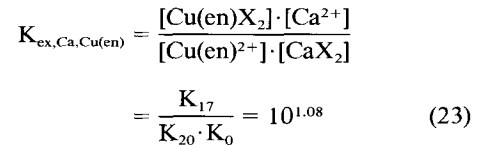


The model curves calculated from the above constants are already in good agreement with the experimental data. A slight improvement was achieved introducing the ternary surface complex  $\equiv\text{SOHCu}(\text{en})^{2+}$  as defined by Eq. (22).

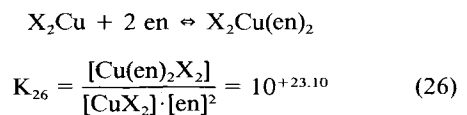
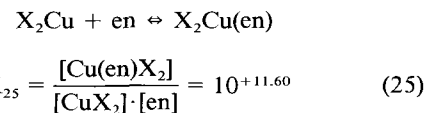


Resulting adsorption curves for en and  $\text{Cu}^{2+}$  are shown in Figures 4A and Figure 4B respectively; the constants are presented in Tables 2b and 3.

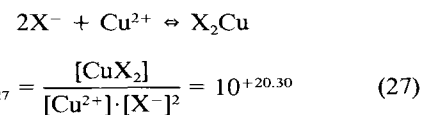
Combining Eqs. (17)–(18) and Eqs. (20)–(21) with Eq. (7) yields the equilibrium constants for the ion-exchange reactions with  $\text{Ca}^{2+}$ :



Maes *et al.* (1978) published log K values for the reactions



In order to facilitate the comparison of the results of this study with the data published by Maes *et al.* (1978), the equilibria 17 and 18 are combined with the uptake of Cu by the ion-exchanger as defined by Stadler and Schindler (1993):



Dividing Eq. (17) and Eq. (18), respectively, by Eq. (27) yields the equilibrium constants for Reaction 25 and 26. As can be seen, the resulting value of  $10^{+11.98}$  for  $K_{25}$  is higher than the one published by Maes *et al.* (1978) by a factor of 2.4, whereas the obtained value of  $10^{+22.11}$  for  $K_{26}$  is markedly lower than the one published by Maes *et al.* (1978).

When the difference  $\log K_{25} - \log K_{20}$  and  $\log K_{26} - \log K_{21}$  is calculated, a stabilization factor of 6.0 for the 1:1 Cu-en complex and 32.36 for the 1:2 Cu-en complex, respectively, is obtained. Maes *et al.* (1978) found a stabilization factor for the 1:2 complex in the range of 850–1250.

As already mentioned, the formation of  $\text{Cu}(\text{en})_3^{2+}$

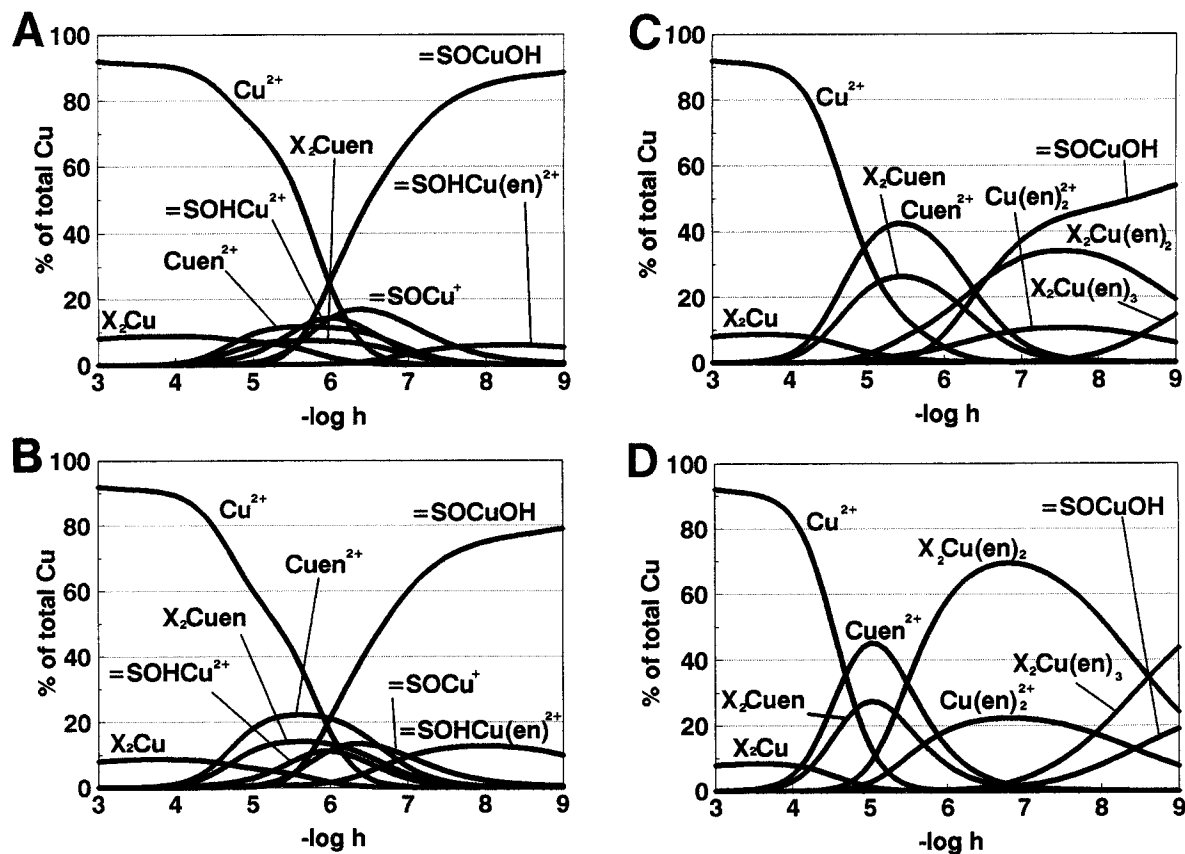
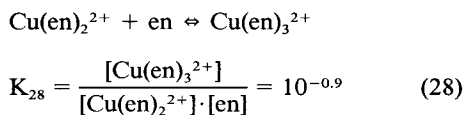


Figure 5. Speciation of Cu(II) in the system  $H^+$ , Ca-montmorillonite, en, Cu(II). The species are plotted in % of  $C_0$  (total Cu(II)) vs.  $-\log h$ . Calculations were performed with the aid of GRFIT for A)  $L_0 = 0.0001 \text{ mol/dm}^3$ , B)  $L_0 = 0.0002 \text{ mol/dm}^3$ , C)  $L_0 = 0.0005 \text{ mol/dm}^3$  and D)  $L_0 = 0.0010 \text{ mol/dm}^3$ .  $C_0$  was held constant at  $0.0005 \text{ mol/dm}^3$ .

in solution is not well established, and the species was, thus, not included in the model. The only published value for this complex (Bjerrum, 1948) seems to indicate that the tendency to attach a third ligand according to



is very low. On the other hand, the stability constant that characterizes the uptake of a third ligand molecule by  $X_2\text{Cu(en)}_2$  as obtained from Eqs. (18) and (19)

$$K_{29} = \frac{[\text{Cu(en)}_3X_2]}{[\text{Cu(en)}_2X_2] \cdot [\text{en}]} = \frac{K_{19}}{K_{18}} = 10^{+7.01} \quad (29)$$

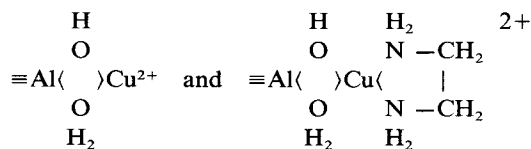
is amazingly high. The reliability of this value is questionable since the sensitivity of the model to the introduction of  $\text{Cu(en)}_3X_2$  into the calculations is comparatively modest.

The stability constant of the ternary complex  $\equiv\text{SOHCu(en)}^{2+}$  as defined by Eq. (22) was found to be very near a value expected from statistical considera-

tions (Schindler, 1990). These considerations predict for the quotient

$$Q_1 = \frac{K_{\equiv\text{SOHCu}^{2+}}}{K_{\equiv\text{SOHCu(en)}^{2+}}}$$

a value of 12 for the case that the structure of the complex can be visualized by



Using Eq. (20), Eq. (22), and the stability constant  $K_{\equiv\text{SOHCu}^{2+}}$  as defined in Table 2a, a value of  $Q_1 = 10.2$  is obtained.

As seen in Figure 4B, addition of en promotes Cu adsorption in the region  $4 < -\log h < 6$  and results in a partial desorption of Cu in the range  $7 < -\log h < 9$ . The reason for this ambivalent behavior can be seen from the speciation diagrams for Cu in Figure 5: In the range of  $4 < -\log h < 6$  the onset of formation of  $\text{Cu(en)}^{2+}$  species and their preference by the inter-layer leads to an enhanced uptake of Cu. In the region



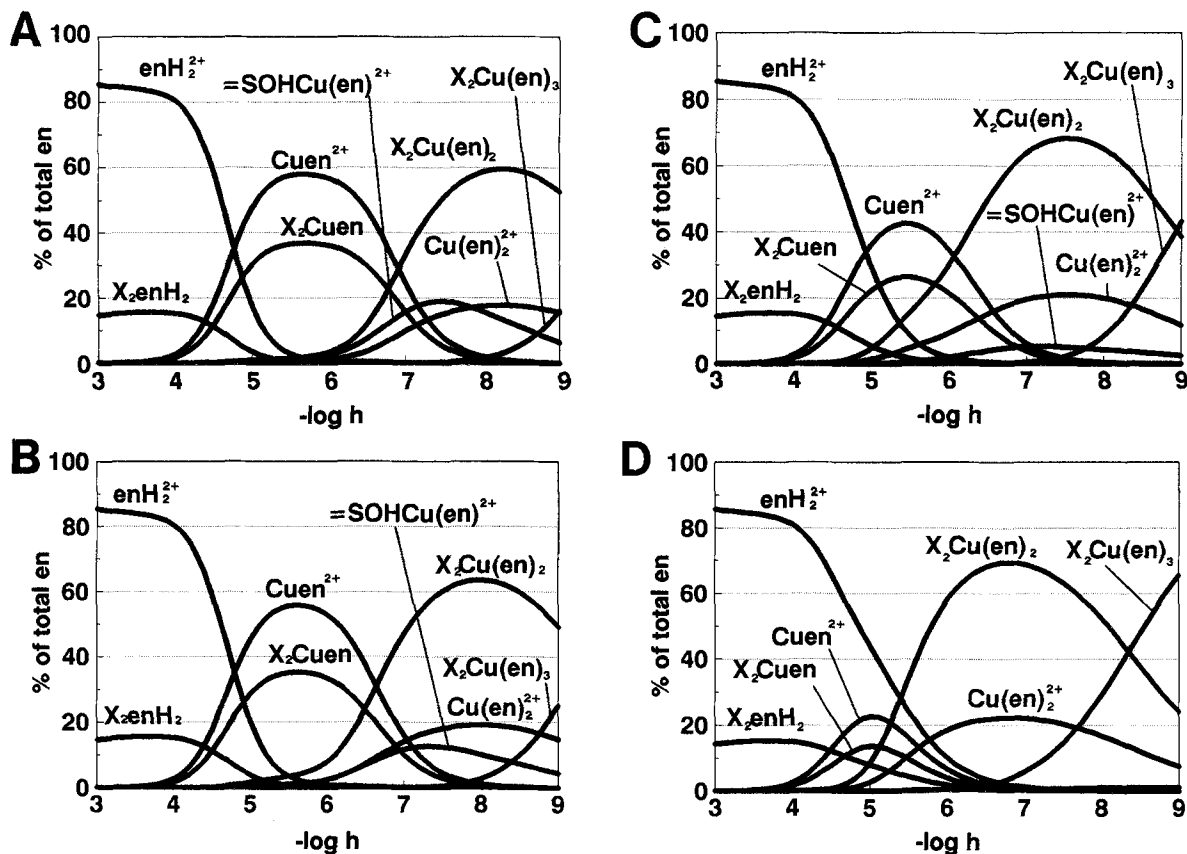


Figure 6. Speciation of en in the system  $H^+$ , Ca-montmorillonite, en, Cu(II). The species are plotted in % of  $L_0$  (total en) vs.  $-\log h$ . Calculations were performed with the aid of GRFIT for A)  $L_0 = 0.0001 \text{ mol/dm}^3$ , B)  $L_0 = 0.0002 \text{ mol/dm}^3$ , C)  $L_0 = 0.0005 \text{ mol/dm}^3$ , and D)  $L_0 = 0.0010 \text{ mol/dm}^3$ .  $C_0$  was held constant at  $0.0005 \text{ mol/dm}^3$ .

of  $7 < -\log h < 9$ , the formation of dissolved Cu-en complexes prevents Cu adsorption by surface hydroxyl groups. In this  $-\log h$  range, the complete uptake of  $\text{Cu(en)}_2$  by ion-exchange is impeded by the high  $\text{Ca}^{2+}$  concentration.

The obviously complicated effect of the increasing  $e_0$  concentration upon the en uptake (Figure 4A) is clarified by the speciation diagram of en (Figure 6): For the ratio en:Cu = 0.2,  $\text{Cu(en)}^{2+}$  is formed and partially bound as  $\text{X}_2\text{Cu(en)}$ . At  $-\log h > 6.5$ , Cu becomes increasingly bound as  $\equiv\text{SOCuOH}$  (Figure 5). This leads to an increase of the en:Cu ratio in solution and consequently to the formation of  $\text{Cu(en)}_2^{2+}$ , which in turn results in a formation of  $\text{X}_2\text{Cu(en)}_2$ . At higher en:Cu ratios, the species  $\text{X}_2\text{Cu(en)}_2$  and  $\text{X}_2\text{Cu(en)}_3$  are chiefly responsible for the en uptake above  $-\log h = 5$ .

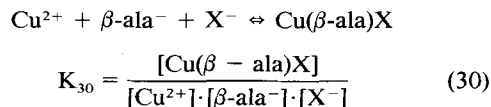
Ternary surface complexes were found, in both the en and the Cu speciation, to be of minor importance, influencing markedly the en adsorption only at low en:Cu ratios and in the range of  $-\log h < 6.5$ .

#### The system $\beta$ -alanine-copper-Ca-montmorillonite

The complexes of  $\beta$ -alanine and Cu in solution are  $\text{Cu}(\beta\text{-ala})^+$  and  $\text{Cu}(\beta\text{-ala})_2$  existing in the range of 3.0

$< -\log h < 8.5$  and  $-\log h > 4$ , respectively. The experimental data of Cu adsorption as presented in Figure 7B reflect clearly the influence of  $\beta$ -alanine competition in solution: The amount of Cu bound by Ca-montmorillonite is decreasing with increasing ligand concentration. Cu adsorption at very low Cu: $\beta$ -ala ratios (1:8) in the range of  $4.5 < -\log h < 7$  is found to be underestimated by a model including only ligand competition in solution, a fact which can be taken as an indication for a weak ternary complex.

Several assumptions were made and tested in model runs. Finally, the ion-exchange reaction



was found to improve the model. In addition, the stability constants of Cu(II)-( $\beta$ -ala) complexes in solution were included into the optimization procedure. The obtained stability constants are listed in Tables 2b and 3. Calculated model curves are shown in Figures 7A and 7B.

Reaction 30 takes place in the range of  $3.5 < -\log h$

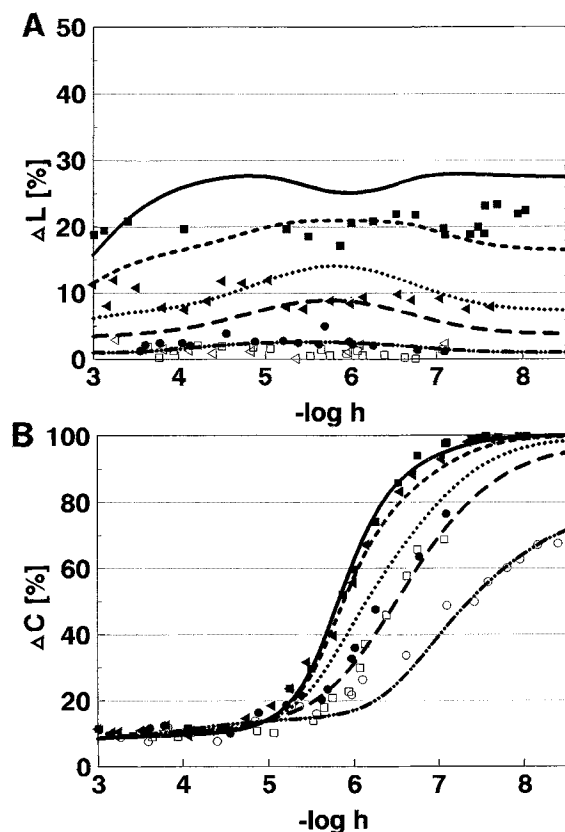


Figure 7. A) Sorption of  $\beta$ -ala on Ca-montmorillonite in the presence of Cu(II) ( $C_0 = 0.0005 \text{ mol/dm}^3$ ,  $I = 0.3$ ,  $T = 298.2 \text{ K}$ ). The percentage of sorbed ligand,  $\Delta L$ , is plotted against  $-\log h$ . B) Sorption of Cu on Ca-montmorillonite in the presence of  $\beta$ -ala. ( $C_0 = 0.0005 \text{ mol/dm}^3$ ,  $I = 0.3$ ,  $T = 298.2 \text{ K}$ ). The percentage of adsorbed Cu(II),  $\Delta C$ , is plotted against  $-\log h$ . Symbols and lines as in Figure 1. The curves were calculated with the stability constants given in Tables 2a, 2b, and 3.

$< 8.5$  and can, therefore, be used as an explanation for the observed enhanced copper adsorption in this  $-\log h$  region (Figure 7B). On the other hand, the presence of copper has a weak effect on the adsorption of  $\beta$ -alanine (Figure 7A): Due to complexation in solution, the amount of  $\beta$ -alanine being sorbed on the surface is reduced without changing the general behavior of this ligand towards Ca-montmorillonite. The uptake of the 1:1 copper- $\beta$ -alanine complex by ion-exchange is reported by Tsunashima (1984). As can be seen from both, the  $\beta$ -alanine- and the Cu speciation (Figures 8 and 9, respectively),  $\text{Cu}(\beta\text{-ala})\text{X}$  plays a very minor role for all investigated Cu:( $\beta$ -ala) ratios.

#### The ternary system malonate-copper-Ca-montmorillonite

In solution,  $\text{Cu}^{2+}$  and malonate form the complexes  $\text{Cu}(\text{mal})$  and  $\text{Cu}(\text{mal})_2^{2-}$ . Under the experimental conditions chosen in this study, the formation of these

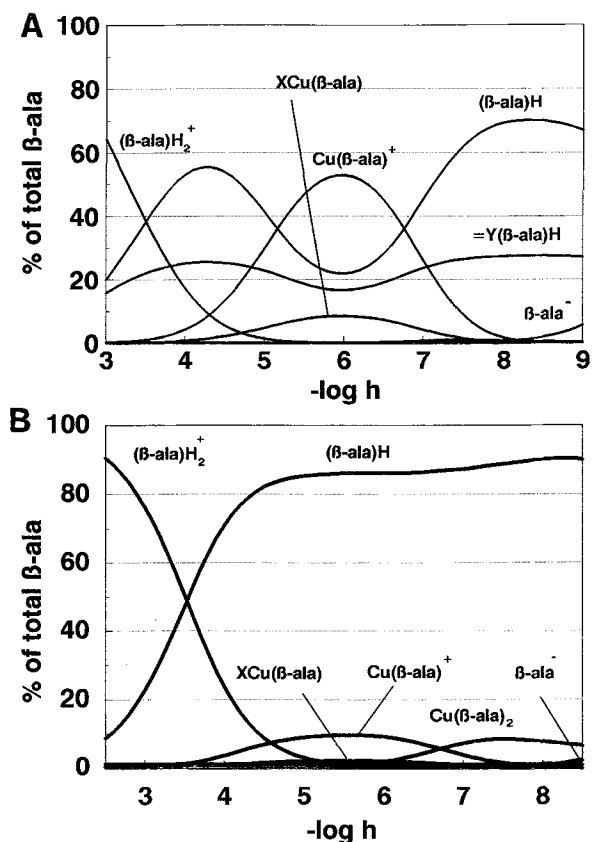
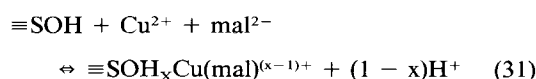


Figure 8. Speciation of  $\beta$ -ala in the system  $\text{H}^+$ , Ca-montmorillonite,  $\beta$ -ala, Cu(II). The species are plotted in % of  $L_0$  (total  $\beta$ -ala) vs.  $-\log h$ . Calculations were performed with the aid of GRFIT for A)  $L_0 = 0.0001 \text{ mol/dm}^3$  and B)  $L_0 = 0.0040 \text{ mol/dm}^3$ .  $C_0$  was held constant at  $0.0005 \text{ mol/dm}^3$ .

dissolved species is already important at  $-\log h = 3$ . As visualized by Figure 10B, addition of malonate leads to a parallel shift of Cu adsorption (involving  $\equiv\text{SOH}$  groups) to higher  $-\log h$  values; the extent of this shift increases with increasing ligand concentration. This shift reflects competition between surface ligand ( $\equiv\text{SOH}$  sites) and dissolved ligand. On the other hand, the formation of Cu-malonate complexes in solution decreases the concentration of adsorbable malonate ions. Comparison of Figures 3A and 10A shows that the percentage of adsorbed ligand decreases with increasing Cu concentration. An interesting feature of Figure 10A is the occurrence of a second adsorption maximum in the region of  $5.5 < -\log h < 6.5$ , i.e., in the range where Cu complexing by surface hydroxyl groups takes place. This suggests formation of ternary complexes according to the general equation



From various test runs it was seen that the principal species forms according to

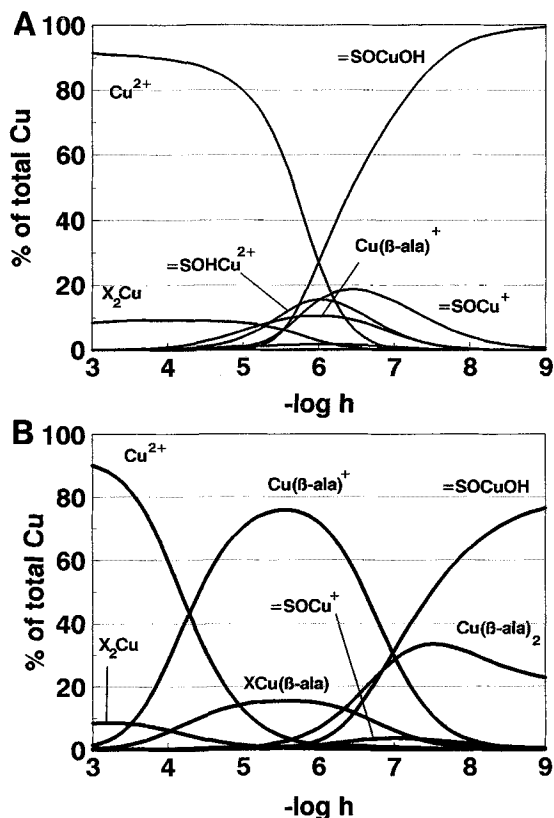
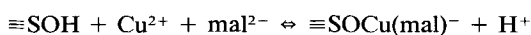
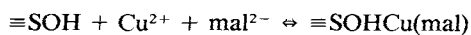


Figure 9. Speciation of Cu(II) in the system  $H^+$ , Ca-montmorillonite,  $\beta$ -ala, Cu(II). The species are plotted in % of  $C_0$  (total Cu(II)) vs.  $-\log h$ . Calculations were performed with the aid of GRFIT for A)  $L_0 = 0.0001 \text{ mol/dm}^3$  and B)  $L_0 = 0.0040 \text{ mol/dm}^3$ .  $C_0$  was held constant at  $0.0005 \text{ mol/dm}^3$ .



$$K_{32} = \frac{[\equiv\text{SOCu}(\text{mal})^-] \cdot [\text{H}^+]}{[\equiv\text{SOH}] \cdot [\text{Cu}^{2+}] \cdot [\text{mal}^{2-}]} \quad (32)$$

In addition, some evidence was found for the existence of one minor species



$$K_{33} = \frac{[\equiv\text{SOHCu}(\text{mal})]}{[\equiv\text{SOH}] \cdot [\text{Cu}^{2+}] \cdot [\text{mal}^{2-}]} \quad (33)$$

Including  $\equiv\text{SOHCu}(\text{mal})$  in the model resulted in a weak but significant improvement of the fit.

The proposed model is in fair agreement with the experimental data, as can be seen in Figure 10A (mal adsorption) and Figure 10B (Cu adsorption). As already pointed out in the discussion of the Cu-en system, statistical effects (Schindler, 1990) predict a decrease of the stability constant by a factor of 12. The quotients  $Q_2$  and  $Q_3$  can be formed according to

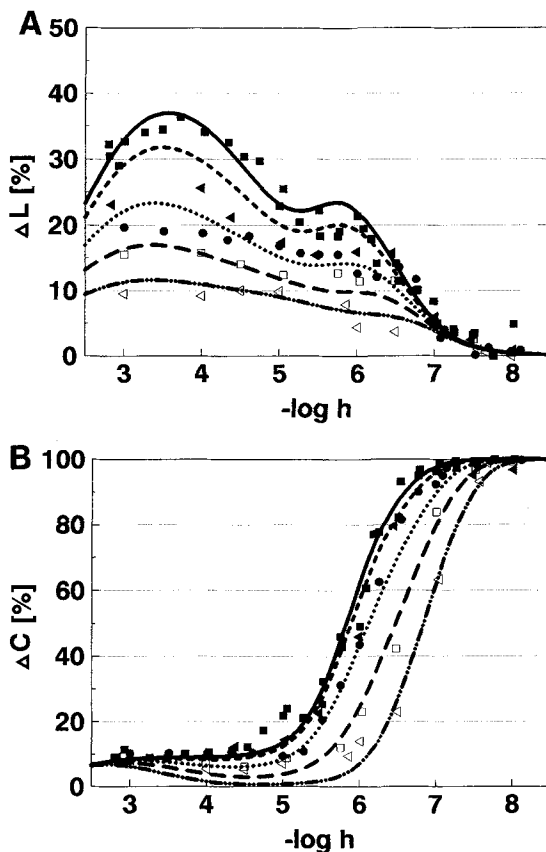


Figure 10. A) Sorption of mal on Ca-montmorillonite in the presence of Cu(II) ( $C_0 = 0.0005 \text{ mol/dm}^3$ ,  $I = 0.3$ ,  $T = 298.2 \text{ K}$ ). The % of adsorbed ligand,  $\Delta L$ , is plotted against  $-\log h$ . B) Sorption of Cu(II) on Ca-montmorillonite in the presence of mal ( $C_0 = 0.0005 \text{ mol/dm}^3$ ,  $I = 0.3$ ,  $T = 298.2 \text{ K}$ ). The percentage of adsorbed Cu(II),  $\Delta C$ , is plotted against  $-\log h$ . Symbols and lines as in Figure 1. The curves were calculated with the stability constants given in Tables 2a, 2b, and 3.

$$Q_2 = \frac{K_{\equiv\text{SOCu}^+}}{K_{\equiv\text{SOCu}(\text{mal})^-}} = \frac{K_{\equiv\text{SOCu}^+} \cdot K_{\text{Cu}(\text{mal})}}{K_{32}} = 17.8$$

$$Q_3 = \frac{K_{\equiv\text{SOHCu}^{2+}}}{K_{\equiv\text{SOHCu}(\text{mal})}} = \frac{K_{\equiv\text{SOHCu}^{2+}} \cdot K_{\text{Cu}(\text{mal})}}{K_{33}} = 29.5$$

where  $K_{\text{Cu}(\text{mal})}$  denotes the formation constant of the Cu-malonate 1:1 complex in solution and  $K_{\equiv\text{SOHCu}^{2+}}$  and  $K_{\equiv\text{SOCu}^+}$  are taken from Table 2a. It can be seen that the stability of the principal ternary surface complex  $\equiv\text{SOCu}(\text{mal})^-$  is in fairly good agreement with statistical predictions, whereas the less important species  $\equiv\text{SOHCu}(\text{mal})$  is somewhat weaker.

In Figure 11, the speciation of mal is plotted for two Cu:mal ratios. It can be seen that for a Cu:mal ratio of 5:1, the proposed ternary surface complex  $\equiv\text{SOCu}(\text{mal})^-$  would be the most important surface species at  $-\log h > 5.5$ . For a Cu:mal ratio of 1:4,  $\equiv\text{SOCu}(\text{mal})^-$  would already dominate at  $-\log h \geq 5$ . The second ternary complex ( $\equiv\text{SOCu}(\text{mal})\text{H}$ ) is predicted to be never present

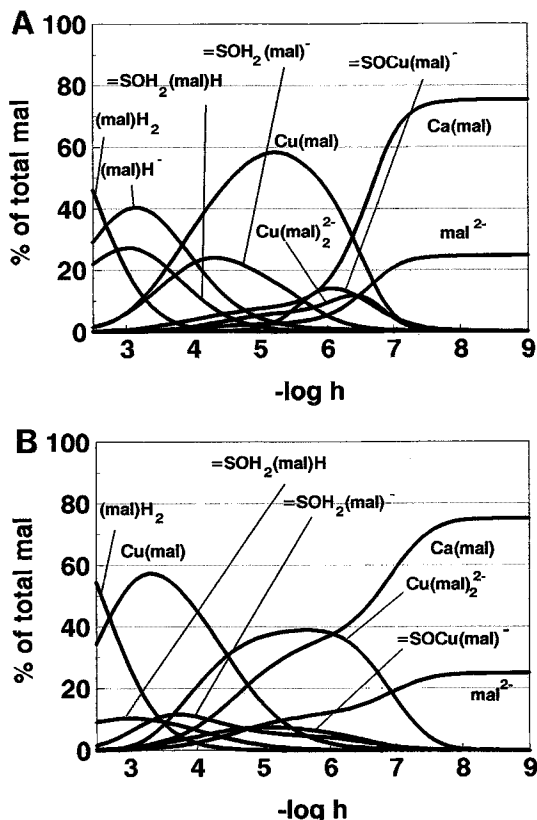


Figure 11. Speciation of mal in the system  $\text{H}^+$ , Ca-montmorillonite, mal, Cu(II). The species are plotted in % of  $L_0$  (total mal) vs.  $-\log h$ . Calculations were performed with the aid of GRFIT for A)  $L_0 = 0.0001 \text{ mol/dm}^3$  and B)  $L_0 = 0.0020 \text{ mol/dm}^3$ .  $C_0$  was held constant at  $0.0005 \text{ mol/dm}^3$ .

in noticeable amounts. Figure 12 shows the speciation of Cu. At high Cu:mal ratios (5:1), the copper speciation is clearly dominated by  $\text{Cu}^{2+}$  and the surface complex  $\equiv\text{SOCuOH}$ . Lowering the Cu:mal ratio down to 1:4 results in a predominance of dissolved  $\text{Cu}(\text{mal})$  and  $\text{Cu}(\text{mal})_2^{2-}$  complexes in the range of  $3.5 < -\log h < 7$ . The model anticipates the ternary surface complex  $\equiv\text{SOCu}(\text{mal})^-$  to exist in noteworthy amounts in the region of  $6 < -\log h < 8$ .

### CONCLUSION

The uptake of Cu ions by Ca-montmorillonite is markedly influenced by the presence of chelate forming organic ligands. The three ligands investigated in this paper exemplify all possible modes of interaction that were described in the Introduction. The presence of  $\beta$ -alanine tends to inhibit the adsorption of Cu by ligand competition. A small contribution from ion-exchange by  $\text{XCu}(\beta\text{-ala})$  was, however, noticed. The presence of malonate shifts the range of Cu uptake by surface hydroxyl groups towards alkaline regions. The effect is based on both ligand competition combined with the formation of ternary surface complexes. The addition

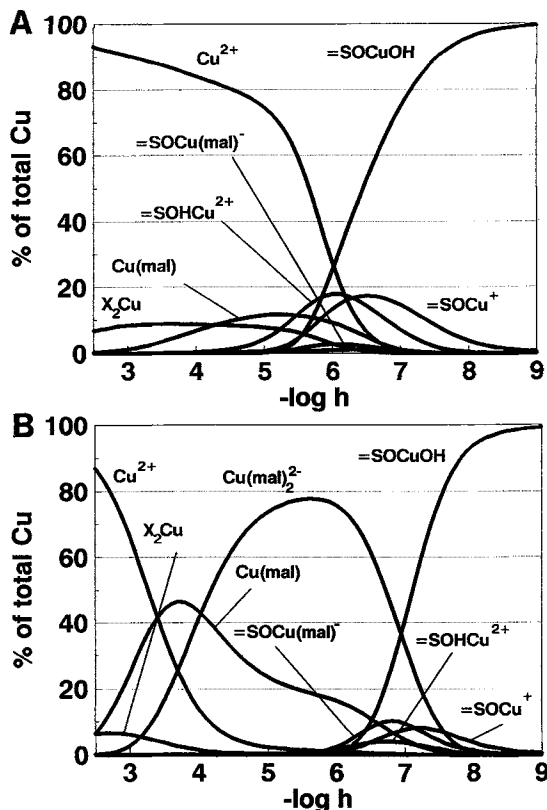


Figure 12. Speciation of Cu(II) in the system  $\text{H}^+$ , Ca-montmorillonite, mal, Cu(II). The species are plotted in % of  $C_0$  (total Cu(II)) vs.  $-\log h$ . Calculations were performed with the aid of GRFIT for A)  $L_0 = 0.0001 \text{ mol/dm}^3$  and B)  $L_0 = 0.0020 \text{ mol/dm}^3$ .  $C_0$  was held constant at  $0.0005 \text{ mol/dm}^3$ .

of en promotes Cu uptake in the acidic region by stabilizing the cationic species  $\text{Cu}(\text{en})_x^{2+}$  in the ion-exchanger. In the alkaline region, ligand competition clearly reduces the percentage of adsorbed Cu. The three above-mentioned mechanisms control in turn the influence of Cu upon the extent of ligand uptake by Ca-montmorillonite. Ligand competition ( $\beta$ -alanine, Figure 7) tends to reduce the ligand uptake, whereas the formation of ternary surface complexes (malonic acid, Figure 10A, in the range of  $5 < -\log h < 7$ ) enhances ligand adsorption. Enhanced ligand adsorption is finally also induced in cases where the metal-ligand complex is stabilized in the interlayer region of the clay mineral (en, Figure 4A). The different behavior of the three ligands is based on both the nature of the ligand atoms (N or O) and the charge of the ligand. The two factors are indeed coupled with each other. Cu(II) clearly prefers N-ligands as compared with O-ligands (Table 2b). Hence, ligand competition is more important for N-ligands than for O-ligands. This effect is, however, cancelled in part by the fact that proton affinity towards the ligand atoms shows the same trend. The main effect can be ascribed merely to the charge

of the ligand: Ligands that form cationic complexes may assist ion-exchange. Ligands that form uncharged or negatively charged complexes are expected to participate in the formation of ternary surface complexes since the corresponding binary Cu-clay surface complexes are formed in a  $-\log h$  range where the charge of the binary Cu-clay complex is positive. This effect can be recognized for the case of malonate.

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