

Interactions of calcium and fulvic acid at the goethite-water interface

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Abstract—Interactions of calcium and fulvic acid (Strichen) with the surface of goethite were studied with batch and titration experiments. The mutual influence of the interactions on the adsorption of fulvic acid, calcium ions and protons were examined. Adsorption of the fulvic acid to goethite decreased with increase in pH (pH range 3–11). Addition of Ca (1.0 mM) at intermediate and high pH significantly enhanced the adsorption of fulvic acid. Compared to the adsorption to pure goethite, the presence of fulvic acid enhanced the adsorption of Ca significantly. In comparison to the simple linear sum of Ca bound to fulvic acid and goethite, the interactions between goethite and fulvic acid led to a reduced adsorption of Ca at low pH and an enhanced adsorption at high pH. With the adsorption of fulvic acid, protons were released at low pH and coadsorbed at high pH. When Ca was added, fewer protons were released at low pH and fewer coadsorbed at high pH. The experimental results can be adequately described using a surface complexation model, the Ligand and Charge Distribution (LCD) model, in which the CD-MUSIC model for ion adsorption to mineral oxides and the NICA model for ion binding to humics are integrated. In the model calculations, adequate descriptions of the ternary system data (Ca-fulvic acid-goethite) were obtained with parameters derived from three binary systems (fulvic acid-goethite, Ca-goethite and Ca-fulvic acid) without further adjustment. The model calculations suggest that the interactions between Ca and fulvic acid at the surface of goethite are mainly due to the electrostatic effects. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

Humic substances (humic acid, fulvic acid) and metal (hydr)oxides are omnipresent in nature. They are recognized to be important geocolloids because of their high affinity for nutrients and pollutants. The interactions with colloidal particles may largely control the availability and transport of metal ions. Surface complexation models have been developed to describe the adsorption of ions on metal (hydr)oxides, for example, the simple two-site double layer model (Dzombak and Morel, 1990) and the more advanced Charge Distribution Multisite Complexation (CD-MUSIC) model (Hiemstra et al., 1989a,b; Hiemstra and Van Riemsdijk, 1996). More recently, ion-binding models for humics have also been developed. Ion binding to humic substances is a complicated process due to the chemical heterogeneity, electrostatic interaction, competition effects and variable stoichiometry of the binding. The NICA-Donnan model (NICA: Nonideal consistent Competitive Adsorption) (De Wit et al., 1993; Koopal et al., 1994, 2001; Benedetti et al., 1995; Kinniburgh et al., 1996, 1999; Milne et al., 2001, 2003) and Model VI (Tipping, 1998) are two examples of the advanced models for the description of proton and metal ion binding to humics that can handle this complexity.

In the natural environment, however, both humic substances and metal (hydr)oxides are simultaneously present. Humic substances adsorb readily onto oxide minerals (Tipping, 1981; Davis, 1982; Murphy et al., 1992; Gu et al., 1994; Spark et al., 1997a; Vermeer et al., 1998). Moreover, the presence of metal ions affects the adsorption of humic substances (Tipping, 1981;

Vermeer et al., 1998; Liu and Gonzalez, 1999; Weng et al., 2002) and vice versa (Robertson and Leckie, 1994; Zachara et al., 1994; Murphy and Zachara, 1995; Vermeer et al., 1999; Christl and Kretzschmar, 2001). The final outcome with respect to both the humics adsorption to the oxides and the metal ion binding to the complex is the net result of various interactions, and depends on the nature of the surface and the humics, the type of metal ion and factors such as pH and ionic strength. Due to the complication that the humics interact strongly with the metal oxide surface, direct application of either the CD-MUSIC model or the NICA model to describe the adsorption of metal ions is no longer possible.

Various approaches can be found in literature regarding the description of the adsorption of humics on mineral surfaces. Several attempts do not account explicitly for the electrostatic interactions (Tipping, 1981; Gu et al., 1994; Van De Weerd et al., 1999), although most authors agree that such interactions should ideally be an explicit part of the model. Some authors make a priori assumptions with respect to a limited number of hypothetical organic surface species (Ali and Dzombak, 1996a; Filius et al., 1997, 2000; Karlton, 1998), while electrostatic interactions are taken explicitly into account. In these models, the distribution of the adsorbed organic matter over the various surface species will vary with pH and loading of the surface sites with adsorbed organics, and follows from the model once it has been fitted to some adsorption data.

Another approach is to apply models that have been developed for adsorption of polyelectrolytes on surfaces to describe the adsorption of humics (Vermeer et al., 1997, 1998; Vermeer and Koopal, 1998). The advantage of such an approach is that a variation of the conformation of the adsorbed molecules with pH and loading is inherently present, without the need to make

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a priori assumptions about the presence of certain types of surface species. The model used by Vermeer et al. (Vermeer et al., 1997, 1998; Vermeer and Koopal, 1998) is based on statistical theory and the distribution in space (perpendicular to the surface) of the adsorbed molecules is calculated in a self-consistent way by the model. The presence of the variably charged organic molecules in the entire electrostatic layer is automatically taken into account. Although the model has good potential, to be able to apply such a theory one has to make some simplifying assumptions. Vermeer et al. (Vermeer et al., 1997, 1998; Vermeer and Koopal, 1998) assumed that humics can be represented as flexible polyelectrolytes with one type of carboxylic and one type of phenolic group. However, the chemical heterogeneity of ion binding to humics is in reality much larger than Vermeer et al. assumed (Milne et al., 2001). The distribution of the adsorbed molecules in space is especially important for large molecules with a high molecular weight. Fulvic acids with a molecular weight in the range of 700–1200 Da are in comparison to high molecular mass polyelectrolytes extremely small molecules. Most likely their adsorption takes place in a monolayer adjacent to the surface (the Stern layer) and their adsorption to mineral oxides may be treated similar to simple inorganic polyvalent ions like phosphate, if the chemical heterogeneity is accounted for.

The recently developed LCD (Ligand and Charge Distribution) model (Filius et al., 2001, 2003) combines the CD-MUSIC and the NICA concepts to describe the adsorption of fulvic acids to mineral oxides. The model derives its name from the fact that the statistical distribution of the functional groups, and the charge of the bound organic molecules over the interface are part of the model output. The advantage of the LCD model is that it allows taking into account all the details already present in both the CD-MUSIC and the NICA model. Once the LCD model has been calibrated for binary systems, it has the capability to make predictions on the mutual interactions between metal ions, fulvic acids and mineral oxides. It is also possible to extend the LCD model for the formation of the ternary complexes in which the metal ions form bridges between the surface sites of the mineral oxides and the ligands of the organic molecules. This type of ternary complexes has been suggested in literature (Liu and Gonzalez, 1999; Alcacio et al., 2001). So far, the LCD model has only been tested for the pH and salt concentration dependency of the adsorption of simple organic acids and fulvic acid to iron (hydr)oxides (Filius et al., 2001, 2003). No tests have been made on fulvic acid-goethite system in the presence of multivalent cations.

The general objective of this paper is to study the effects of calcium on the adsorption of Strichen fulvic acid (SFA) to the surface of goethite and vice versa (ternary system). Calcium is an important major cation present in the environment, which competes with trace metal ions for the binding sites in soil and water. Calcium is chosen in this study due to the reason that it represents cations that bind relatively weakly to the mineral oxides and to the humic substances. The results obtained in this work will be compared in a forthcoming paper to those obtained using copper, which represents cations that bind much stronger to the mineral surfaces and to the humics. In this paper the LCD model will be used to quantitatively describe the interactions on the basis of parameters that are derived from studies of the binary systems SFA-goethite, Ca-goethite and

Ca-SFA. We will also investigate whether it is necessary to incorporate the “bridging” type ternary complexes to describe the data adequately. This test will further validate the LCD model. The model results can also provide more insight to the relative importance of the various interaction mechanisms in the ternary system of metal ion-fulvic acid-mineral oxides.

2. MODEL DESCRIPTION

The Ligand and Charge Distribution (LCD) model (Filius et al., 2001, 2003) has been developed to describe the adsorption of relatively small organic molecules with multiple ligands on metal (hydr)oxides. The model can calculate in a self-consistent way simultaneously the distribution of the organic molecules over the solution phase and the adsorbed phase in conjunction with the speciation of other small ions that can interact with the surface. Figure 1 shows the basic structure of the LCD model approach. The LCD model is composed of three parts: NICA-Donnan, CD-MUSIC and Ligand Distribution (LD) model. Below a brief description of the most important features of the LCD model will be given.

2.1. Part I. NICA-Donnan Model

The first part of the LCD model is the NICA-Donnan model for ion binding to humics in the solution phase (I in Fig. 1) (Koopal et al., 1994; Kinniburgh et al., 1996; Kinniburgh et al., 1999; Koopal et al., 2001). Three important aspects of the model are described below.

2.1.1. NICA approach

The humics are heterogeneous substances with two important types of functional groups, i.e., carboxylic and phenolic groups. The NICA model accounts for the interactions of both the carboxylic and the phenolic groups with protons and metal ions. In the NICA approach, it is assumed that the affinity of the sites in each group is continuously distributed following the Sips distribution. The width of the distribution of each group of sites, indexed as p ($0 < p \leq 1$) in the NICA equation, represents the intrinsic heterogeneity of the sites. For a bimodal NICA model, the total amount $Q_{i,tot}$ (mol/kg) of component i (proton or metal ion) bound is given by:

$$Q_{i,tot} = \frac{n_{i,j}}{n_{Hj,j=1}} \sum_{j=1}^2 Q_{j,max} \left[\frac{(\bar{K}_{i,j} K_i^{el} c_i)^{n_{i,j}}}{\sum_i (\bar{K}_{i,j} K_i^{el} c_i)^{n_{i,j}}} \right] \times \left[\frac{\left\{ \sum_i (\bar{K}_{i,j} K_i^{el} c_i)^{n_{i,j}} \right\}^{p_j}}{1 + \left\{ \sum_i (\bar{K}_{i,j} K_i^{el} c_i)^{n_{i,j}} \right\}^{p_j}} \right] \quad (1)$$

In Eqn. 1, the adsorbing component (protons or metal ions) is indexed with i and the type of reactive ligand (carboxylic and phenolic) is indexed with j . The maximum number of ligands (site density) of type j is given as $Q_{j,max}$ (mol/kg). The concentration c_i refers to the concentration of i in solution (mol/L). $\bar{K}_{i,j}$ is the median specific affinity constant of the binding reaction of ion i to reactive ligand j . K_i^{el} is the electrostatic contribution to the affinity of ion i for the ligand and is calculated with the Donnan model (see 2.1.2). The parameter

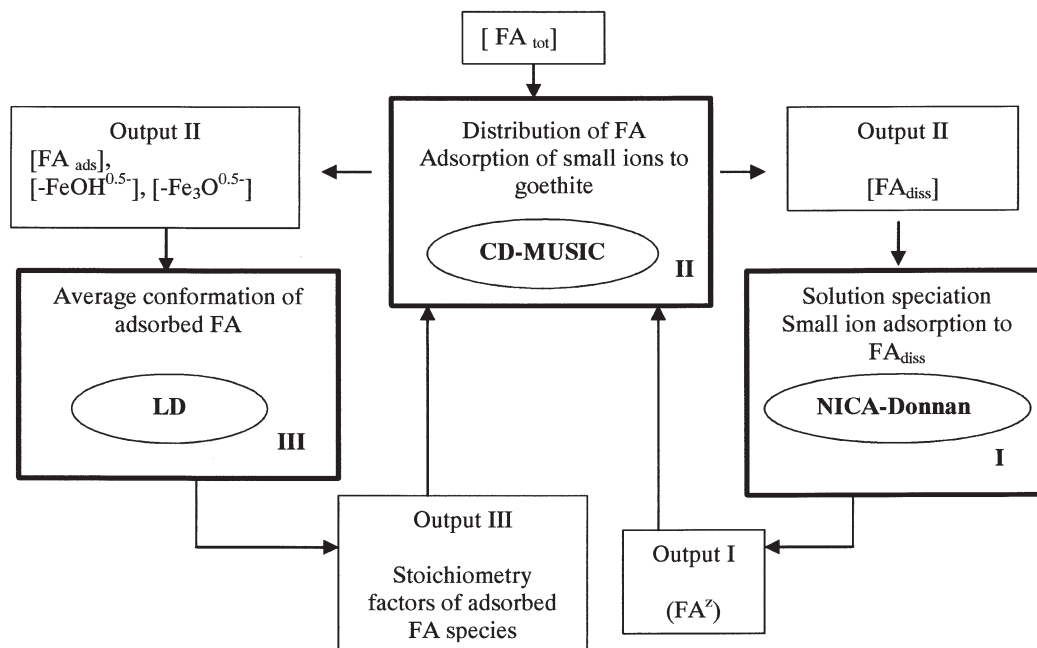


Fig. 1. Calculation scheme of the LCD model approach.

$n_{i,j}$ ($0 < n_{i,j} \leq 1$) expresses the degree of correlation between the affinity distribution of the proton and the metal ion i and the stoichiometry of the binding reaction of ion i . (Rusch et al., 1997). The ratio of $n_{i,j}$ and n_{Hj} in the NICA equation represents the stoichiometry. If this ratio is close to one the binding can be interpreted as being the result of a mono dentate binding (1:1 stoichiometry), whereas a ratio close to 0.5 represents a 2:1 stoichiometry.

2.1.2. Donnan approach

In solution, the electrostatic interaction between the dissolved organic matter and the small ions is described using the Donnan approach (Benedetti et al., 1996; Kinniburgh et al., 1996). In the Donnan model, it is assumed that the organic molecules are gel-like particles. The overall electro-neutrality in the gel phase is preserved by the accumulation or exclusion of salt ions in the gel to compensate the charge carried by the organic molecules. The volume of the gel phase (v_D , l/kg) is assumed to be only dependent on the ionic strength, I (mol/L). Although this is a simplified assumption, its advantage is that the Donnan volume can be calculated using an empiric relation (Kinniburgh et al., 1996):

$$\log v_D = b(1 - \log I) - 1 \quad (2)$$

where b is an adjustable parameter.

2.1.3. Reference-state of organic matter in solution

The calculation of the LCD model was carried out using the computer program ORCHESTRA (Meeussen, 2003). In ORCHESTRA calculations for the NICA model, Eqn. 1 was rearranged as:

$$Q_{i,\text{tot}} = \frac{n_{i,j}}{n_{Hj}} \sum_{j=1}^2 Q_{j,\text{max}} [(\bar{K}_{i,j} K_i^{\text{el}} c_i)^{n_{i,j}}] T_j \quad (3)$$

$$T_j = \left[\frac{1}{\sum_i (\bar{K}_{i,j} K_i^{\text{el}} c_i)^{n_{i,j}}} \right] \left[\frac{\left\{ \sum_i (\bar{K}_{i,j} K_i^{\text{el}} c_i)^{n_{i,j}} \right\}^{p_j}}{1 + \left\{ \sum_i (\bar{K}_{i,j} K_i^{\text{el}} c_i)^{n_{i,j}} \right\}^{p_j}} \right] \quad (4)$$

The value of T_j is a measure of the fraction of the empty sites or the reactivity of the carboxylic or phenolic groups of the organic molecules (Meeussen, 2003). Because the NICA model is essentially an approach that estimates the average conformation of the humic molecules on a statistical basis, the T_j value reflects in a way the possibility that the carboxylic or the phenolic sites are empty. If the possibility that the carboxylic type group is empty is T_1 and that for the phenolic type of group is T_2 , the possibility that both types of sites are empty is the product of T_1 and T_2 . In the LCD model, the reference-state of the fulvic acid in solution, FA^z , is defined as:

$$\text{FA}^z = \text{FA}_{\text{diss}} * T_1 * T_2 * f \quad (5)$$

In Eqn. 5, FA_{diss} (mol/L) stands for the concentration of fulvic acid in solution. f is an ionic strength correction factor, which is equated to the activity coefficient for an ion with the charge of fully dissociated fulvic acid molecule calculated using the adapted Davies equation. The reference-state of the organic molecules in the solution, in the case of fulvic acid, FA^z , is an output of the NICA-Donnan part of the LCD model. This result will be used in the second part of the LCD model, the CD-MUSIC model, to calculate the amount of organic matter adsorbed to the surface.

Table 1. Speciation of fulvic acid adsorbed on goethite interface and the charge distribution in the 0-plane (Δz_0) and d-plane (Δz_d). (Modified from Filius et al., 2003.) (# mineral surface; R the rest of fulvic acid molecule.)

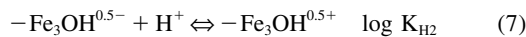
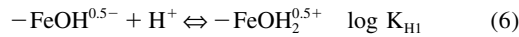
	Reaction	log K	Δz_0	Δz_d	Stoichiometry coefficient
1	# + RCOO ⁻ ⇌ #-RCOO ⁻	1	0	-1	—
2	# + RCOO ⁻ + H ⁺ ⇌ #-RCOOH ⁰	log $\tilde{K}_{H,1}$	0	0	c ₁
3	# + RCOO ⁻ + M ²⁺ ⇌ #-RCOOM ⁺	log $\tilde{K}_{M,1}$	0	1	d ₁
4	# + RCO ⁻ ⇌ #-RCO ⁻	1	0	-1	—
5	# + RCO ⁻ + H ⁺ ⇌ #-RCOH ⁰	log $\tilde{K}_{H,2}$	0	0	c ₂
6	# + RCO ⁻ + M ²⁺ ⇌ #-RCOM ⁺	log $\tilde{K}_{M,2}$	0	1	d ₂
7	-Fe ₁ OH ^{0.5-} + H ⁺ + RCOO ⁻ ⇌ -Fe ₁ -OOCR ^{0.5-} + H ₂ O	log \tilde{K}_{in}	+0.5	-0.5	a ₁
8	-Fe ₁ OH ^{0.5-} + H ⁺ + RCOO ⁻ ⇌ -Fe ₁ OH ₂ ·OOCR ^{0.5-}	log $\tilde{K}_{out,1}$ + log K _{H1}	+0.8	-0.8	b ₁
9	-Fe ₃ O ^{0.5-} + H ⁺ + RCOO ⁻ ⇌ -Fe ₃ OH·OOCR ^{0.5-}	log $\tilde{K}_{out,1}$ + log K _{H2}	+0.8	-0.8	b ₁
10	-Fe ₁ OH ^{0.5-} + H ⁺ + RCO ⁻ ⇌ -Fe ₁ OH ₂ ·OCR ^{0.5-}	log $\tilde{K}_{out,2}$ + log K _{H1}	+0.8	-0.8	b ₂₋₁
11	-Fe ₃ O ^{0.5-} + H ⁺ + RCO ⁻ ⇌ -Fe ₃ OH·OCR ^{0.5-}	log $\tilde{K}_{out,2}$ + log K _{H2}	+0.8	-0.8	b ₂₋₁
12	-Fe ₁ OH ^{0.5-} + H ⁺ + RCO ⁻ ⇌ -Fe ₁ OH·HOOCR ^{0.5-}	log $\tilde{K}_{out,3}$ + log K _{H1}	+0.2	-0.2	b ₂₋₂
13	-Fe ₃ O ^{0.5-} + H ⁺ + RCO ⁻ ⇌ -Fe ₃ O·HOOCR ^{0.5-}	log $\tilde{K}_{out,3}$ + log K _{H2}	+0.2	-0.2	b ₂₋₂

2.2. Part II. CD-MUSIC Model

The second part of the LCD model (II in Fig. 1) is the CD-MUSIC (Charge Distribution Multi Site Complexation) model (Hiemstra et al., 1989a,b; Hiemstra and Van Riemsdijk, 1996). In this part of the model the goethite surface and its reactions with the ions and functional ligands of the fulvic acids present in the system are central.

2.2.1. MUSIC and CD

A mineral surface has various types of surface sites, which are defined with the Multi Site Complexation (MUSIC) model. For goethite the basic charging is assumed to be caused by the protonation and deprotonation of the singly (-FeOH^{0.5-}) and triply (-Fe₃O^{0.5-}) coordinated surface oxygens:



Following Hiemstra and Van Riemsdijk (1996), the proton affinity constants (log K_{H1} and log K_{H2}) are assumed to be the same and equated to the PZC (point of zero charge) of the goethite.

The surface complexation model has to be accompanied by an electrostatic model, like the Basic Stern (BS) model. It comprises a diffuse double layer (DDL), separated from the surface by a Stern layer. The charge of the indifferent electrolyte ions bound is located at the head end of the DDL (*d*-plane).

Inner-sphere complexes have a spatial distribution of ligands. Some ligands of the adsorbed ion are common with the surface (0-plane) while the others remain at some distance from the surface. Therefore, the charge of the surface complex is taken to be distributed in the interface, which is described with the Charge Distribution (CD) approach.

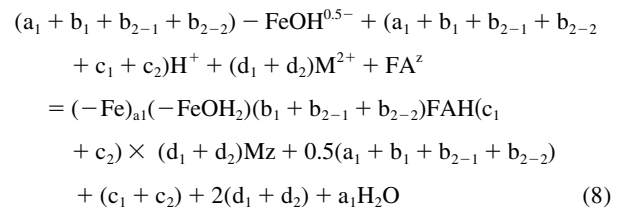
2.2.2. Surface complexes of the adsorbed fulvic acid

Because the molecules of fulvic acid are relatively small (<1 nm) in comparison with humic acids or synthetic polyelectrolytes, they will probably fit in the Stern layer at the oxide surface. Therefore in the LCD model, the charge carried by the bound fulvic acid molecules is assumed to be distributed be-

tween the surface plane and the *d*-plane. It is assumed that the carboxylic groups of fulvic acid can form inner-sphere complexes with singly coordinated surface sites (reaction 7 in Table 1). In addition, the carboxylic and phenolic groups can form outer-sphere complexes with singly and triply coordinated surface sites (reactions 8–13 of Table 1). The carboxylic and phenolic groups that are not involved in the surface complexation are located in the *d*-plane. They can be present in protonated and deprotonated forms and can also bind metal ions (reactions 1 to 6 of Table 1). The charge distributions of the inner-sphere and outer-sphere complexes over the 0-plane and *d*-plane are listed in Table 1.

2.2.3. Overall adsorption reaction

Taking into account the surface complexes described above, the macroscopic adsorption reaction for fulvic acid with the singly coordinated surface site can be written as:



The reaction for the triply coordinated surface site can be written in a similar way. In Eqn. 8, *a*, *b*, *c* and *d* express the average stoichiometry coefficients, which are calculated in the LD part of the model (see below). The coefficients *a* and *b* represent respectively the number of the inner-sphere complex (reaction 7 in Table 1) and outer-sphere complexes (reactions 8–13 of Table 1). The coefficients *c* and *d* represent the number of surface groups that are not involved in the surface complexation and are present respectively in protonated form (reactions 2 and 5 in Table 1) or are complexed with metal ions (reactions 3 and 6 in Table 1). In Eqn. 8, the first level of footnotes 1 and 2 refer to respectively the carboxylic and phenolic groups. The second level of footnotes 1 and 2 refer to respectively reaction 10 and 12 in Table 1.

The overall affinity constant of reaction in Eqn. 8 is composed of the constants for the formation of various surface

Table 2. Generic NICA-Donnan parameters (Milne et al., 2001, 2003).

	Carboxylic site	Phenolic site
Q_{\max} (mol/kg)	5.88	1.86
Q_{\max} (mol/mol)	4.02	1.27
p	0.59	0.70
$\log \tilde{K}_H$	2.34	8.60
n_H	0.66	0.76
$\log \tilde{K}_{Ca}$	-2.17	-3.29
n_{Ca}	0.85	0.83
b		0.57

complexes (Table 1) weighted by their stoichiometry coefficients. The amount of the adsorbed fulvic acid is calculated in the CD-MUSIC part of the model, and the output is used in the LD model to calculate the average speciation of the adsorbed molecules (see below).

2.3. Part III. LD Model

The Ligand Distribution (LD) model (III in Fig. 1) is the third part of the LCD model. In this part of the model, the adsorbed fulvic acid and its interactions with the surface sites of the mineral and the protons and cations are central. As has been pointed out by Filius et al. (2001), the possible number of surface species that can be formed between the mineral surface sites and the adsorbed organic molecules with multiple functional groups is large, which makes it impossible for all such species to be accounted for separately. Instead, in the LD model the statistical average distribution of the functional groups of adsorbed organic molecules over the surface species is calculated with the above-mentioned NICA approach (see 2.1.1). The essence of the use of the NICA concept in the LD model is that not only the protons and the metal ions but also the reactive surface sites of the mineral oxides compete for interaction with the reactive ligands of the adsorbed organic molecule.

The amount ($Q_{i,tot}$) of each species of the adsorbed organic molecules that is formed during the adsorption (Table 1) is calculated with the NICA equation (Eqn. 1) and is expressed in mol-complex/kg-organic molecule. In the calculation, the site density of the organic molecules ($Q_{j,max}$) and the heterogeneity parameter (p_j) are kept the same as for the organic molecules in the solution (Table 2). It is also assumed that the median affinity constants ($\tilde{K}_{i,j}$) and the nonideality parameters ($n_{i,j}$) for the protons and metal ions are the same for the organic molecules adsorbed and in the solution (Table 2). For the reaction with the surface sites ($-\text{FeOH}^{0.5-}$, $-\text{Fe}_3\text{O}^{0.5-}$), an assumption is made for the nonideality parameter. This parameter is set equal to $n_{i,j}$ for proton binding to the organic molecules, which means assuming a 1:1 stoichiometry in the binding of a reactive ligand on the fulvic acid molecule with a reactive site of the oxide surface (Table 2). The median affinity constants ($\tilde{K}_{i,j}$) for the adsorption of the surface sites are obtained by optimization using the adsorption data of the organic molecules on the oxides. The electrostatic contribution (K_i^{el}) is calculated using the Basic Stern model, which is part of the CD-MUSIC model (see 2.2.1).

The relative binding of the components (protons, metal ions

and surface sites) calculated with the NICA model as described above expresses the average stoichiometry of the overall reaction in Eqn. 8. The stoichiometry coefficients (a , b , c and d , expressed in mol-complex/mol-organic molecule) are calculated from the total amount of the different types of the surface species formed ($Q_{is,tot}$, $Q_{os,i,j,tot}$, $Q_{H,j,tot}$, $Q_{M,j,tot}$) for inner-sphere, outer-sphere, proton and metal ion complexes respectively:

$$\begin{aligned} a_1 &= M_{FA} * Q_{is,tot} \\ b_{i,j} &= M_{FA} * Q_{os,i,j,tot} \\ c_j &= M_{FA} * Q_{H,j,tot} \\ d_j &= M_{FA} * Q_{M,j,tot} \end{aligned} \quad (9)$$

in which M_{FA} is the average molecular weight of the organic molecule, in this case fulvic acid. The stoichiometry coefficients calculated in the LD model will be used in the CD-MUSIC part as input. The mean mode of the adsorbed organic molecules is not constant, but depends on the pH, ionic strength, surface coverage and the binding of other ions.

2.4. Calculation of the Three Parts of the LCD Model

Besides the input of known values such as pH, total amount of goethite and fulvic acid, the three parts of the LCD use the output of each other as essential model input. The final results can be achieved by iteration until all the equations are satisfied. The CD-MUSIC part (II in Fig. 1) calculates the adsorption of protons, metal ions and fulvic acid to goethite. Some of the output, such as the concentration of fulvic acid bound (FA_{ads}) and the surface sites, is used as input in the LD model (III in Fig. 1). Other output like the concentration of dissolved fulvic acid (FA_{diss}) is used as input for the NICA-Donnan model (I in Fig. 1). The LD model calculates the average conformation of the adsorbed organic molecules (a , b , c , and d in Eqn. 8), and the NICA-Donnan model calculates the solution speciation of the fulvic acid, including the concentration of the reference-state of the organic molecules (FA^*). Both in turn are used as input in the CD-MUSIC model (Fig. 1).

3. MATERIALS AND METHODS

3.1. Preparation of Goethite

The goethite preparation was based on the procedure of Atkinson et al. (1967) and was described in more detail by Hiemstra et al. (1989b). All solutions were prepared with ultra pure water. A freshly prepared 5 litre 0.5 M $\text{Fe}(\text{NO}_3)_3$ solution was titrated with 2.5 M NaOH to a pH of 12. The base was added at a low rate of 10 mL/min. The suspension formed was aged at 60°C for 90–110 h to obtain goethite. The aged suspension was dialyzed with ultra pure water until the electrical conductivity (EC) was lower than 10 $\mu\text{S}/\text{cm}$. After dialysis, the suspension of goethite was stored in a closed polyethylene container in refrigerator at 4°C. Before use, the dialyzed goethite suspension was adjusted to pH 5.3 by adding nitric acid, and continuously purged with clean, moist N_2 gas to remove CO_2 . The content of goethite in the suspension was determined by measuring the weight of a subsample of the material after being dried at 80 to 100°C. The specific surface area of the goethite material was determined using the BET- N_2 adsorption method.

3.2. Preparation of Fulvic Acid

The soil used was a Bs horizon from a peat soil (Strichen Soil Association, Scotland). Humic and fulvic acids were extracted using a

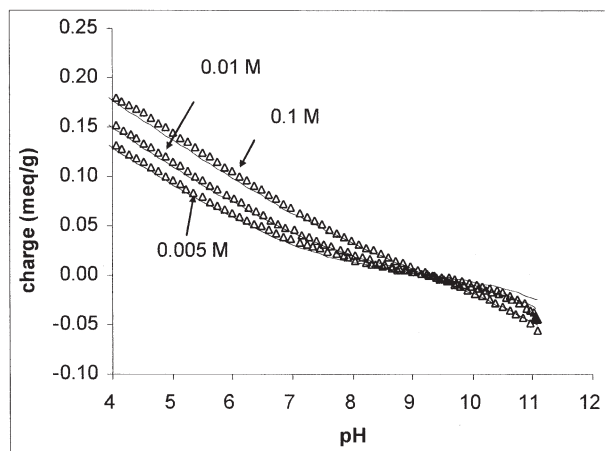


Fig. 2. Charge/pH curves of goethite at three NaNO_3 concentrations indicated in the figure. Symbols are derived from the acid-base titration data. Lines are the CD-MUSIC model predictions.

method based on those recommended by the International Humic Substances Society (Aiken et al., 1979; Swift, 1996). Detailed description of the extraction procedure can be found elsewhere (Filius et al., 2000). Purified fulvic acid material was freeze-dried and stored at room temperature and will be denoted as SFA (Strichen fulvic acid). The carbon content of SFA is 43%. This value will be used for the calculation of the amount of SFA in solution after adsorption using the total organic carbon concentration.

3.3. Acid-Base Titrations of Goethite

All the titrations mentioned in this work were performed using an automated titration set up (Kinniburgh et al., 1995) and the titration cell was kept under N_2 atmosphere at 20°C . The base and acid solutions that were used in the acid-base titration or pH stat titration were 0.100 M NaOH and HNO_3 . For the acid-base titration of goethite, 50 mL goethite suspension at the concentration of 15 g/L was prepared. The titration was performed for three electrolyte concentrations of 0.005 M, 0.015 M and 0.085 M by adding 1.0 M NaNO_3 solution to the suspension. The change of the charge of goethite was calculated from the difference of the amount of acid-base added and the mass balance of protons in the suspension. In the calculation, the adapted Davies equation was used to calculate the activity coefficients. The relative position of the titration curves at different electrolyte concentrations was determined by the change of pH measured after the addition of the electrolyte solution (NaNO_3). The absolute position of the curves was obtained by assuming that the common intersection point of the three titration curves at different NaNO_3 concentrations is the point of zero charge (PZC).

3.4. Acid-Base Titrations of SFA

The acid-base titrations of SFA were carried out at 1.1 g/L and four NaCl concentrations of 0.005, 0.010, 0.030 and 0.10 M (Filius et al., 2000). The change of the charge of fulvic acid was calculated from the difference of the amount of acid-base added and the mass balance of

protons in the suspension. The absolute charge of the fulvic acid was obtained by fitting the NICA-Donnan model.

3.5. Batch Ca and SFA Adsorption Experiments

The batch adsorption experiments of Ca and SFA on goethite were carried out in gas tight 20 mL polyethylene vessels with screw caps similarly as done by Rietra et al. (2001). During the filling procedure, the vessels were flushed with N_2 gas to minimize the influence of CO_2 . In the first series of the batch experiments, calcium adsorption on goethite was measured. Stock solution of $\text{Ca}(\text{NO}_3)_2$ was added to the suspensions, which contained 6.0 or 5.8 g/L goethite (carbonate free) in a background electrolyte solution of 0.10 M NaNO_3 , to achieve respectively a total Ca concentration of 0.0096 or 1.02 mM. A certain amount of acid or base solution (0.100 M NaOH and HNO_3) was added to the suspension to adjust the pH to selected values in the range of 3–11.

In the second series of the batch experiments, the adsorption of SFA to goethite was measured in suspensions with or without Ca. The final concentration of goethite was 5.8 g/L in a background electrolyte solution of 0.10 M NaNO_3 . For the Ca treatments the $\text{Ca}(\text{NO}_3)_2$ solution was added to achieve a total Ca concentration of 1.0 mM. For both treatments with or without Ca, four concentrations (total) of SFA, 75, 150, 300 and 450 mg/L, were studied by adding appropriate amounts of 2.0 g/L SFA stock solution. The solutions of NaNO_3 , $\text{Ca}(\text{NO}_3)_2$ and SFA were added almost simultaneously. Once this was done, a certain amount of acid or base solution (0.100 M NaOH and HNO_3) was added to the suspensions to adjust the pH to the desired values in the range of 3–11.

Thus prepared suspensions were shaken at 20°C for 3 d, the same reaction time as used by Filius et al. (2000), and then centrifuged at 18,000 g for 30 min. The concentration of Ca in the supernatant was measured using ICP-MS or ICP-AES. The concentration of dissolved C was measured with a TOC analyser. The final pH in the supernatant was measured using a pH meter.

3.6. pH Stat Titration of Goethite with SFA

Samples containing 10 g/L goethite suspension or 5 g/L SFA solution were titrated separately to pH 4.0, 5.5, or 7.0. Both the goethite and SFA samples had an electrolyte background of 0.10 M NaNO_3 , with or without 1.0 mM Ca. These samples were shaken at 20°C for 3 d. After shaking, the pH of the solutions was readjusted to the starting values.

Subsequently, 60 mL goethite suspension obtained in such a way was titrated with corresponding SFA solution with the same pH and metal composition using the automated titration set up (Kinniburgh et al., 1995). After the addition of each dose of SFA, pH was corrected to the initial value (4.0, 5.5 or 7.0) with acid or base (0.100 M HNO_3 and NaOH). A reaction time of at least 20 min and a maximum drift criterion of 0.002 pH units per minute were used between each addition of SFA in the titration. The total amount of added SFA was sufficiently small compared to the total surface area of the goethite to have more than 99% of SFA bound. The acid-base balance can be calculated from the amount of added acid and base.

3.7. Calculations

The CD-MUSIC model parameters for Ca adsorption on goethite were optimized using the computer code FIT (Kinniburgh, 1993), which is used in combination with the computer program ECOSAT (Keizer and Van Riemsdijk, 1994). The other model calculations were

Table 3. CD-MUSIC (basic Stern) model parameters.

Specific surface area (BET- N_2)	Capacitance of Stern layer*	Site density ^a		PZC					
		– $\text{FeOH}^{0.5-}$	– $\text{Fe}_3\text{O}^{0.5-}$	$\log K_{\text{H1}}$	$\log K_{\text{H2}}$	$\log K_{\text{Na1}^*}$	$\log K_{\text{HNO}_3-1^*}$	$\log K_{\text{Na2}^*}$	$\log K_{\text{HNO}_3-2^*}$
93.9 m^2/g	0.9 F/m^2	3.45/ nm^2	2.7/ nm^2	9.3	–1		8.3		

* From Hiemstra and Van Riemsdijk (1996).

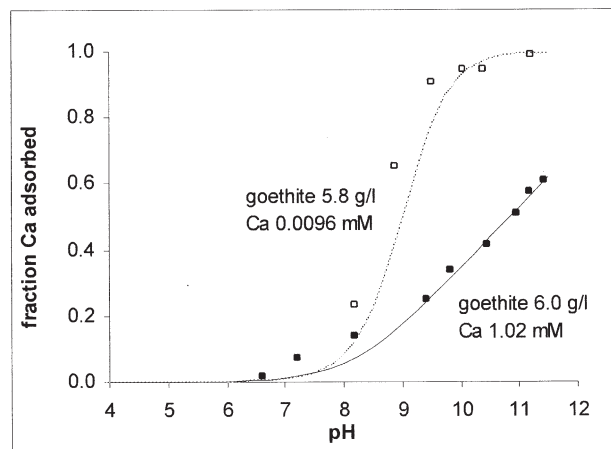


Fig. 3. Ca adsorption on goethite at 0.10 M NaNO₃ and two total Ca concentrations indicated in the figure. Symbols are experimental data. Lines are model predictions using CD-MUSIC.

carried out using the computer program ORCHESTRA (Meeussen, 2003).

4. RESULTS

4.1. Charging Behavior and Ca Adsorption on Goethite

The surface area of goethite determined by the BET-N₂ method was 93.9 m²/g, similar to the value reported by Filius et al. (2003). The charge/pH curves of goethite at three salt concentrations (0.005, 0.015 and 0.085 M) are given in Figure 2. From the common intersection point of the curves, the PZC of the goethite was determined as pH 9.3. Below this pH, the surface of goethite in an indifferent electrolyte solution is positively charged, whereas above this pH it becomes negatively charged. Lines in Figure 2 represent results calculated with the CD-MUSIC model using the parameters given in Table 3. The density of the singly and triply coordinated sites is taken from Hiemstra and Van Riemsdijk (1996). The protonation constants (logK_{H1}, logK_{H2}) of the two sites were assumed equal to the PZC (Hiemstra and Van Riemsdijk, 1996). The value of the capacitance of the Stern layer is 0.9 F/m², which has been fitted based on the charging behavior of goethite (Hiemstra and Van Riemsdijk, 1996). The ion pair formation constants for both Na⁺ and NO₃⁻ are assumed the same, logK_{Na} = logK_{NO3} = -1 (Hiemstra and Van Riemsdijk, 1996). The results are similar to those obtained by Venema et al. (1996).

Before the study of the ternary system, the adsorption of calcium on goethite in the binary system was first investigated using batch experiments. The symbols in Figure 3 show the measured adsorption edges of Ca on goethite at two total concentrations of Ca (0.0096 mM, 1.02 mM) in presence of

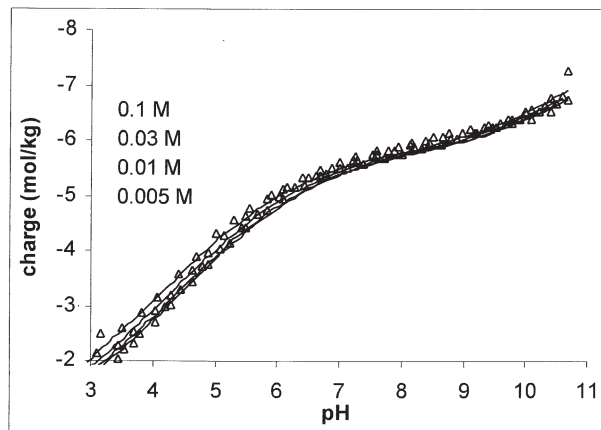


Fig. 4. Charging behavior of Strichen fulvic acid at four NaCl concentrations indicated in the figure. Symbols are the experimental data from Filius et al. (2003). Lines are the NICA-Donnan model prediction using the generic parameters of fulvic acid (Table 2).

0.10 M NaNO₃ as background electrolyte. The adsorption of Ca on goethite is relatively weak compared to that of many heavy metal ions. The adsorption is limited to the near neutral and alkaline pH range and increases with increasing pH. Similar Ca adsorption results have been found in other studies using goethite (Ali and Dzombak, 1996b; Rietra et al., 2001). The salt dependency of Ca adsorption on goethite has been found to be small in those publications.

To apply the CD-MUSIC model, assumptions as to the surface species of Ca and the charge distribution proposed by Rietra et al. (2001) have been followed: calcium forms a monodentate complex with the singly coordinated site on goethite (-FeOH^{0.5-}) and most of the charge of the adsorbed Ca is located in the *d*-plane (Table 4). The triply coordinated site (-Fe₃O^{0.5-}) does not contribute to the specific Ca binding. The other parameters of the CD-MUSIC model are the same as those used for the description of the charge/pH behavior (Table 3). Using the data obtained in this work, the CD-MUSIC parameters for Ca adsorption on goethite were optimized by fitting. The curve fitting was carried out in one time using the data at the two Ca concentrations studied. The obtained affinity constant (logK_{Ca} = 3.6) for the Ca complex is somewhat larger than that found by Rietra et al. (2001) (logK_{Ca} = 3.4). In Figure 3, the calculated results (lines) using the derived parameters are compared to the experimental data. The model fits the data reasonably well (R² = 0.98).

4.2. Charging Behavior and Ca Adsorption on SFA

The charging behavior of the Strichen fulvic acid at four NaCl concentrations has been measured in acid-base titration experiments and reported previously (Filius et al., 2003). The results are replotted in Figure 4. The charging behavior of SFA is pH dependent and very weakly ionic strength dependent.

Using available data from the literature, including the acid-base titration data of the Strichen fulvic acid, Milne et al. (2001, 2003) have derived two sets of generic NICA-Donnan model parameters for respectively a generalized fulvic acid and a generalized humic acid. Part of the parameter set for general-

Table 4. CD-MUSIC parameters for Ca adsorption on goethite.

Surface species	-FeOHCa ^{1.5+}
Charge distribution	Δz_0 0.4
	Δz_d 1.6
logK _{Ca} fitted	3.60

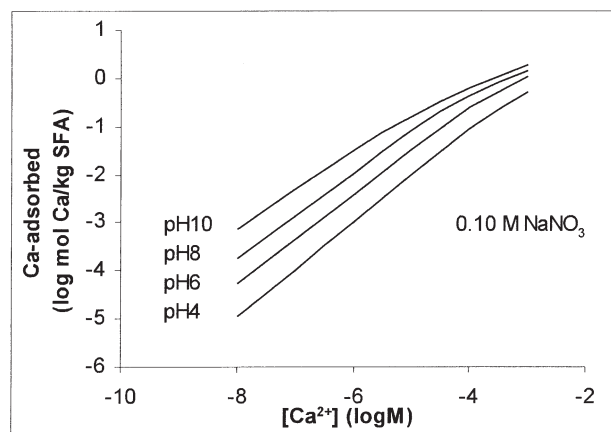


Fig. 5. Calculated adsorption isotherms of Ca to SFA at four pH values and 0.10 M NaNO_3 . The NICA-Donnan model is used with the generic parameter set shown in Table 2.

ized fulvic acid is given in Table 2. Figure 4 shows the model prediction of the charging behavior of SFA using this parameter set. The predictions are in good agreement with the experimental data. Filius et al. (2003) also used the NICA-Donnan model to describe the data, but they fitted the model specifically

to the data for SFA. Here the generic parameter set was used to show that the generic parameters also gave a good fit.

The adsorption of Ca on SFA was not measured. Compared to many other metal cations, the specific binding of calcium to the fulvic acid is weak (Milne et al., 2003). Most of the Ca is predicted to be electrostatically bound. Because the NICA-Donnan model with the generic parameter set provided a reasonable prediction of the charging behavior of the fulvic acid, it is expected that this model can also give a reasonable prediction of the Ca binding to SFA using the generic Ca affinity constants (Table 2). Figure 5 shows the predicted binding of Ca to SFA for four pH values and one background electrolyte concentration of 0.10 M NaNO_3 . Calculation shows that at pH 4, 78 and 94% of adsorbed Ca is predicted to be in the Donnan phase at a free Ca^{2+} concentration of 10^{-8} and 10^{-3} M respectively, whereas at pH 8 the fractions are respectively 16 and 65%. The calculation illustrates that most of the Ca is predicted to be electrostatically bound, especially at a relatively low pH and high Ca concentration.

4.3. Adsorption of SFA on Goethite without Ca

Adsorption of SFA on goethite in 0.10 M and 0.015 M NaNO_3 background electrolyte has been measured by Filius et al. (2003). The adsorption is pH dependent with less binding

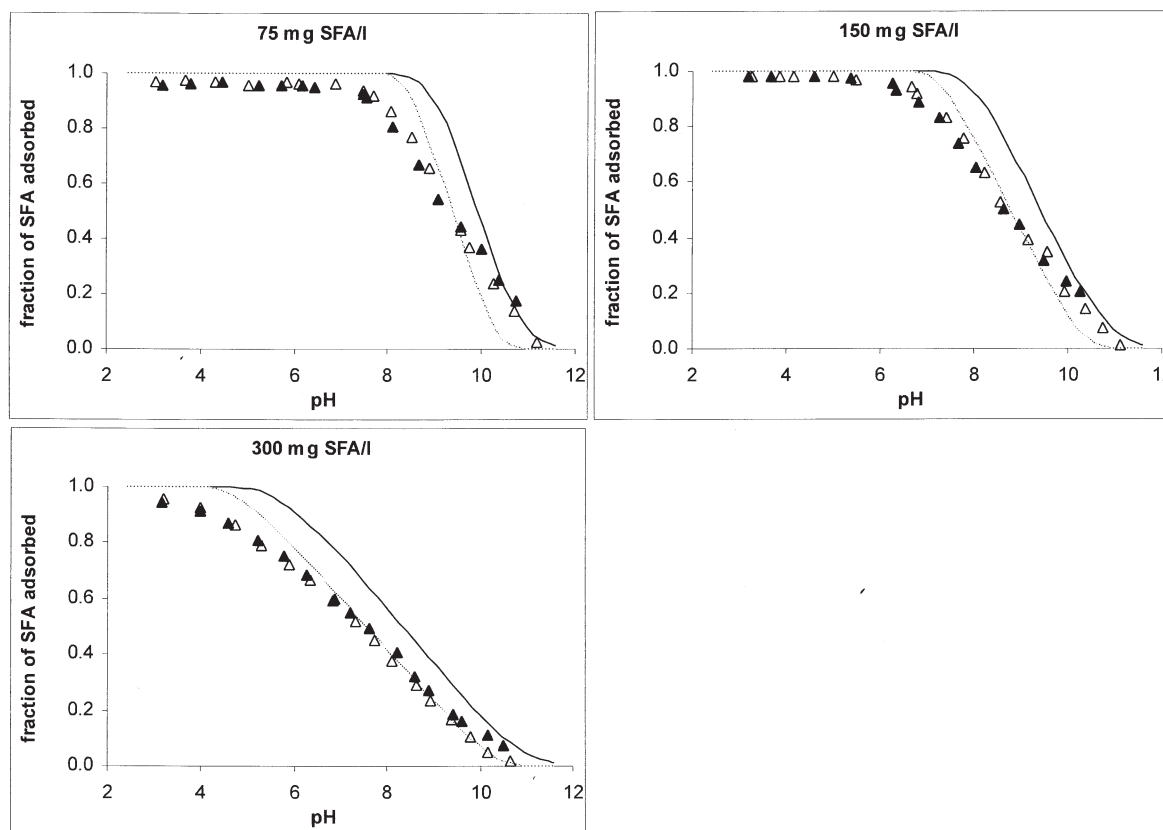


Fig. 6. Adsorption of SFA on goethite in 1:1 electrolyte. Symbols are the experimental data from Filius et al. (2003). Lines are the LCD model calculation without the salt correction factor ($f = 1$) using the generic NICA-Donnan parameters (Table 2) and the affinity constants for the surface complexes as presented by Filius et al. (2003) (Table 5). Empty symbols, gray lines: 0.015 M NaNO_3 ; solid symbols, black lines: 0.10 M NaNO_3 .

Table 5. Affinity constants of the surface species of adsorbed SFA and the molecular weight of SFA.

	Filius et al. (2003)	This work
$\log \tilde{K}_{in}$	-1	-1
$\log \tilde{K}_{out,1}$	0.75	0.4
$\log \tilde{K}_{out,2}$	4.0	5.4
$\log \tilde{K}_{out,3}$	3.35	6.5
Molecular weight SFA (g/mol)		683

at higher pH. Figure 6 shows the fraction of SFA adsorbed as a function of pH for the two salt concentrations. The goethite used in the experiment has a PZC of 9.2 (Filius et al., 2003). The solid symbols apply to the high and the open symbols to the low NaNO_3 concentrations. Clearly the effect of the salt concentration on the adsorption is rather small and barely noticeable.

The affinity constants of the surface complexes formed between SFA and goethite have been optimized by Filius et al. (2003) (Table 5), whereas the salt correction factor (f in Eqn. 5) was not taken into account in the calculation of the reference-state of fulvic acid (FA^z) ($f \equiv 1$). Lines in Figure 6 show the model calculation obtained with the LCD following their approach with $f = 1$ and using the generic NICA-Donnan parameters for fulvic acids (Table 2). The calculated results are

similar to those of Filius et al. (2003), who used the NICA-Donnan parameters specifically derived for the SFA. In both cases, the model gives correct trends, but compared to the experimental data, there are still serious discrepancies. First, the predicted slope of the pH dependency is somewhat steeper compared to the data. Second the model predicts a small salt concentration dependency, however, it is much larger than that observed experimentally. Most notably, the decrease of the SFA adsorption is predicted to occur at higher pH than the data show.

The fit between the model calculation and the data can be improved by including the salt correction factor f (see Eqn. 5) in calculating FA^z . Based on the site density of generic fulvic acid (Q_{max1} and Q_{max2}), the FA^z ion has an average charge of -5.3 per molecule (Table 2). In this case, the affinity constants for the adsorbed fulvic acid species also have to be optimized. The results are shown in the second column of Table 5. With these adjustments, the model description of the SFA adsorption is improved and both the pH and the salt dependency can now be described more successfully (see Fig. 7). At low pH nearly all SFA present is adsorbed independent of the SFA concentration. In this situation the goethite surface and the SFA molecules are oppositely charged. And due to the relatively low charge of the SFA molecules, there is little lateral repulsion that inhibits the adsorption. The adsorption of fulvic acid decreases with increasing pH. At high pH, both the goethite surface and

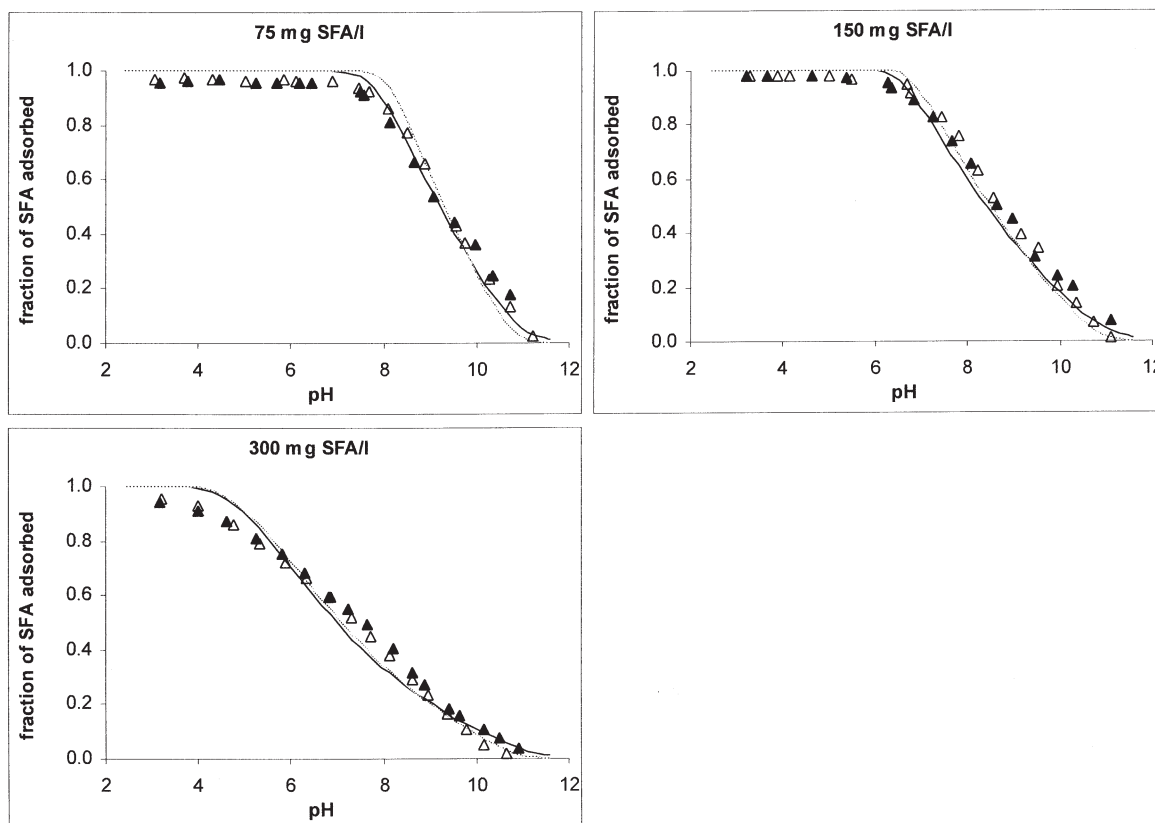


Fig. 7. Same adsorption data of SFA on goethite in 1:1 electrolyte as in Figure 6 (symbols). The lines are the LCD model calculation with the salt correction factor using the generic NICA-Donnan parameters (Table 2) and reoptimized affinity constants for the surface complexes (Table 5). Empty symbols, gray lines: 0.015 M NaNO_3 , solid symbols, black lines: 0.10 M NaNO_3 .

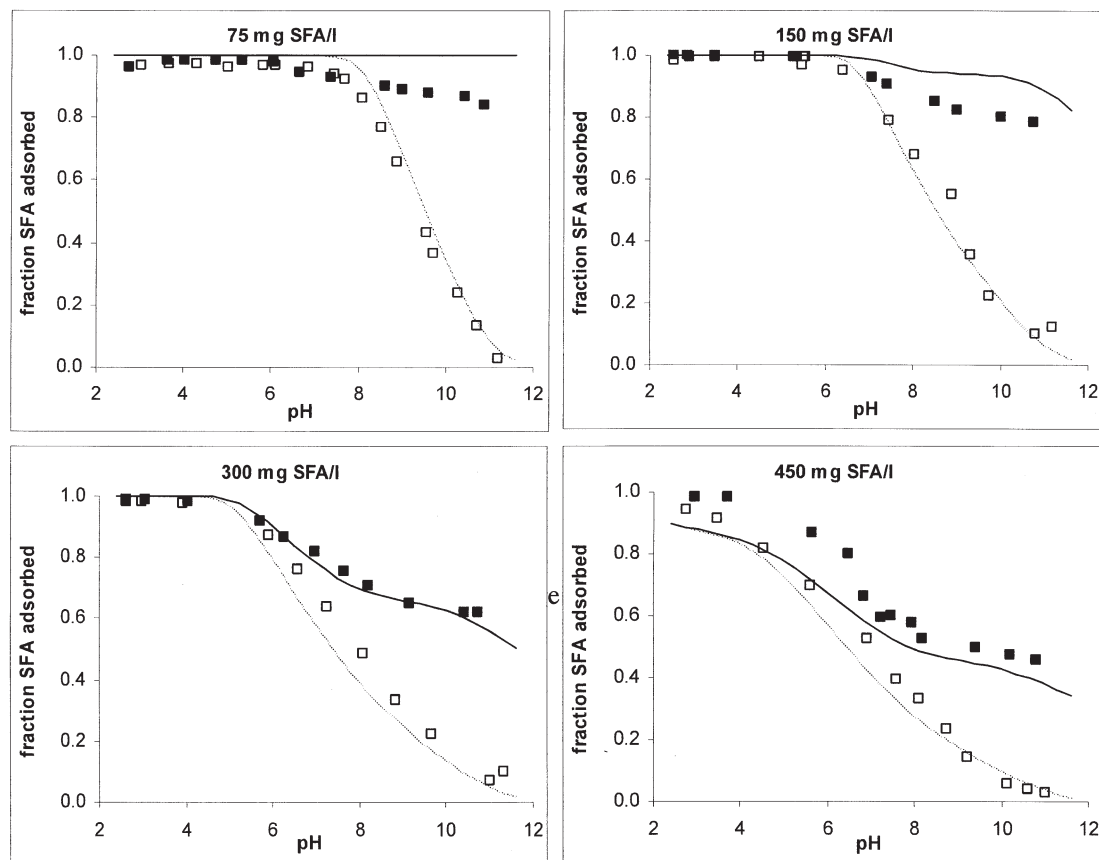


Fig. 8. Effects of Ca on SFA adsorption to goethite. Open symbols and gray lines indicate respectively the experimental data and model prediction for the control (no Ca added), whereas the solid symbols and the black lines are respectively the data and prediction for the treatments with Ca (1.0 mM). The suspension contains 5.8 g/L goethite in a background electrolyte of 0.10 M NaNO_3 .

the SFA molecules are negatively charged, and the negative charge of the fulvic acid increases with increasing pH. Hence both the electrostatic repulsion between the goethite surface and the SFA molecules and the lateral electrostatic repulsion between the bound SFA molecules are stronger at higher pH. The total SFA adsorption at pH 3 is close to 0.5 mg/m^2 goethite.

4.4. Effects of Ca on SFA Adsorption

The adsorption of SFA to goethite with or without the presence of 1.0 mM Ca measured in this work is shown in Figure 8. The results in the absence of Ca obtained in this study are comparable to those of Filius et al. (2003) under the same conditions, indicating no obvious difference of SFA adsorption to the goethite materials in these two studies. Compared to the control (no Ca), the addition of Ca enhanced the adsorption of SFA to goethite significantly at relatively high pH, where the SFA adsorption in the absence of Ca declines. The difference in the fraction of SFA bound between the control and the Ca treatment is larger the lower the SFA loading is.

The calculated fraction of SFA adsorbed with the LCD model is shown in Figure 8. The LCD predictions in the presence of Ca are based on the Ca binding parameters that

have been fitted using the data from the binary systems. Therefore the calculations in the presence of Ca are pure predictions. In accordance with the experimental data the LCD model predicts that addition of Ca increases the adsorption of SFA on goethite at high pH (black lines, Fig. 8). The model predictions for the Ca effects on SFA adsorption are reasonable at a high SFA loading. However, at low SFA loadings (75, 150 mg/L) the predicted SFA adsorption is larger than the experimental data. The discrepancy can be attributed to a too large Ca-SFA interaction predicted at the surface.

4.5. Effects of SFA on Ca Adsorption

The adsorption of Ca to the mixture of goethite and SFA is shown in Figure 9 (symbols), and it increases with increasing pH. The measured adsorption of Ca to the goethite-SFA complex is compared to the LCD model predictions (thick solid lines, Fig. 9). In the LCD approach the Ca adsorption is affected by the interactions between the fulvic acid and goethite. One interesting question is whether the Ca binding can also be predicted by assuming a separate reactivity of the SFA and goethite system, i.e., assuming linear additivity. The predicted Ca adsorption based on this assumption is also plotted in Figure 9 (thin solid line) for comparison with the experimental data.

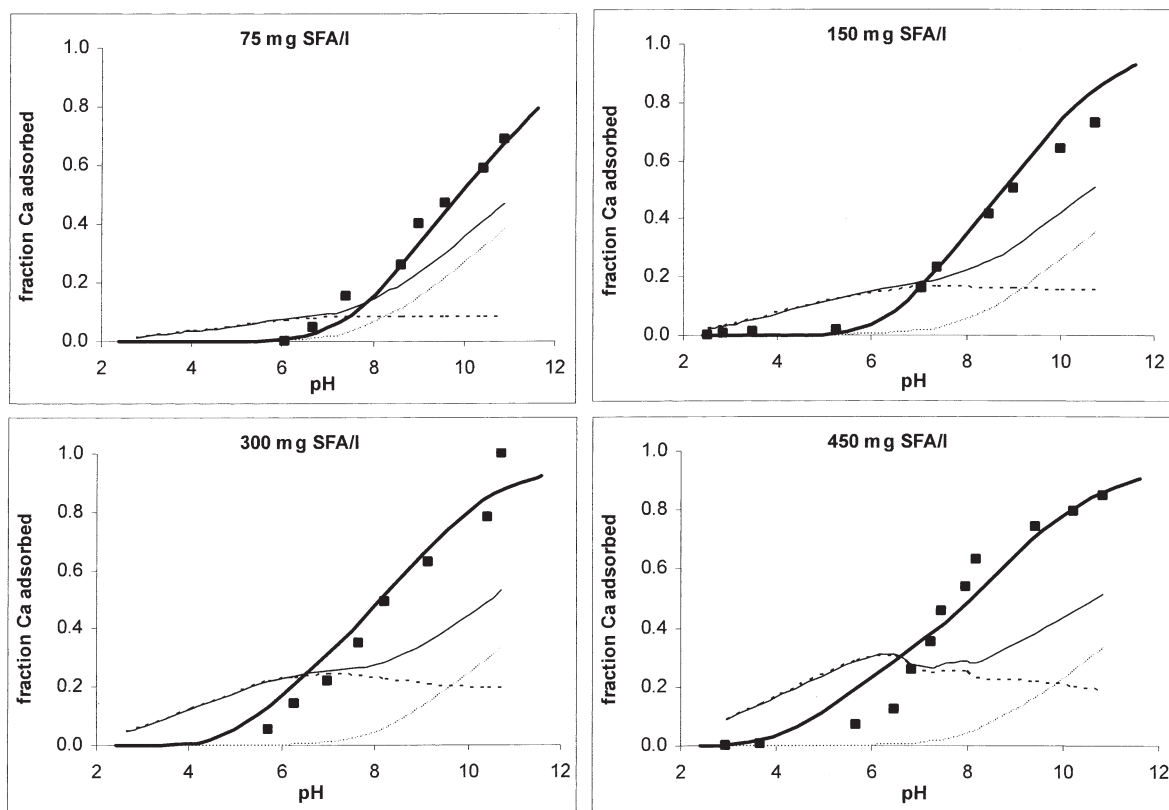


Fig. 9. Ca adsorption to goethite in the presence of SFA. Symbols are experimental data. Dotted, gray and thin solid black lines are respectively Ca bound to adsorbed SFA, goethite and the sum of the two predicted assuming no interactions (linear additivity). The thick solid black lines are the predictions using the LCD model.

In both calculations, i.e., LCD and linear additivity, the total amount of goethite, SFA, Ca and pH are given as input. In the LCD model, the distribution of SFA over the adsorbed and dissolved phase is calculated, whereas in the linear additivity model, the distribution of SFA measured has to be used as known value, because it can not be predicted by the linear additivity approach. From Figure 9, we see that the results of Ca adsorption are much better described with the LCD model (thick solid lines) than with the linear additivity model (thin solid lines). This indicates that the interaction between goethite and SFA affect Ca adsorption substantially.

Comparing the individual curves of the Ca adsorption to SFA (dotted lines, Fig. 9) and to goethite (gray lines, Fig. 9) with the experimental results for the complex shows that at low pH most of the Ca adsorbed to the SFA in solution is released once SFA is adsorbed to goethite. This is the reason that the linear additivity overestimates the overall Ca adsorption at this pH. At high pH, more Ca is adsorbed to goethite with SFA adsorption than to goethite and SFA together. Consequently linear additivity now underestimates the adsorption.

Vermeer et al. (1999) have found similar results for Cd adsorption to a hematite-humic acid complex. In their study on cadmium adsorption, it was found that at low pH less Cd was adsorbed to the complex than predicted by the linear additivity, and at high pH more Cd was adsorbed than predicted by the linear additivity. The authors suggested that the overall adsorption of a specific metal ion to the complex will be smaller than

predicted by the additivity postulate when the metal ion has a higher overall affinity for the humic substance than for the mineral oxide surface, whereas it will be larger than predicted by the additivity postulate when the metal ion has a higher overall affinity for the oxide surface than for humic substance.

Both the present results and those of Vermeer et al. (1999) indicate that assuming simple additivity with respect to the single reactive components can lead to wrong predictions. Therefore the more successful prediction with the LCD model of Ca and SFA adsorption to goethite is a promising step forward toward a more complete understanding of adsorptive interactions in these environmentally relevant ternary systems.

4.6. Proton Coadsorption

The proton coadsorption with SFA on goethite was measured with the pH stat SFA titrations at pH 4.0, 5.5 and 7.0. The experiment was designed in such a way that practically speaking all SFA added was adsorbed. The proton coadsorbed is calculated from the amount of acid-base added after each addition of SFA to keep the pH constant. The experiments were carried out in the absence of Ca and in the presence of 1.0 mM Ca.

The experimental data (symbols, Fig. 10) show that at pH 4.0 there is a net release of protons with the adsorption of SFA on goethite, whereas at pH 5.5 and 7.0 protons are adsorbed, both

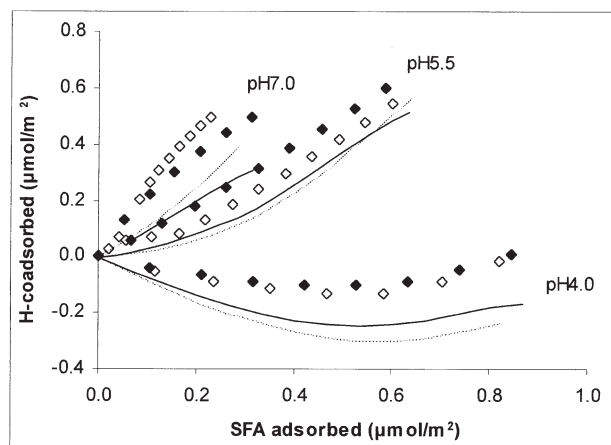


Fig. 10. Proton coadsorption. Symbols are experimental data. Lines are LCD model prediction. Open symbols and gray lines: no Ca; solid symbols and black lines: with 1.0 mM Ca.

in the absence (open symbol) and presence (solid symbol) of Ca. The effect of Ca on the amount of protons coadsorbed is small at pH 4.0 and 5.5, and somewhat larger at pH 7.0. At pH 4.0 and 5.5, Ca addition promoted net proton coadsorption, whereas at pH 7.0 proton coadsorption was decreased with Ca addition (Fig. 10).

Vermeer et al. (1999) and Saito et al. (2004) have studied the overall proton adsorption to a complex of humic acid and

hematite and goethite. It has been shown that the proton adsorption is affected by the interaction between humic acid and iron oxide. At low pH, protons are released (negative proton coadsorption) and at high pH, an increased proton adsorption occurs (positive proton coadsorption). The observed trends for humic acid and fulvic acid are thus the same.

The LCD model predictions for proton coadsorption with SFA show the right trends but the levels of proton coadsorption at pH 5.5 and 7.0 are somewhat too low and the level of proton release at pH 4.0 is overestimated (Fig. 10). The coadsorption data are a combination of two compensating contributions. Upon adsorption of the fulvic acid, the negatively charged molecules come under the influence of the positively charged surface. This weakens the binding of the protons bound by fulvic acid, which leads to release of protons. On the other hand, adsorption of the negatively charged fulvic acid acts positively on the binding of the protons to the goethite surface, because of the increased screening of the surface charge. Both effects can be quantified separately with the LCD model. The results of the calculations are shown in Figure 11. It follows that at all pH values, protons will be released from the SFA molecule once it is adsorbed to goethite. The release is larger the lower the pH is. The opposite occurs for goethite. The adsorption of the negatively charged SFA to the goethite surface induces proton coadsorption. Because the release and coadsorption of protons partially compensate each other, the net change in charge of the complex is small. At pH 4.0, the net change decreases slightly, whereas at pH 5.5 and 7.0, a small

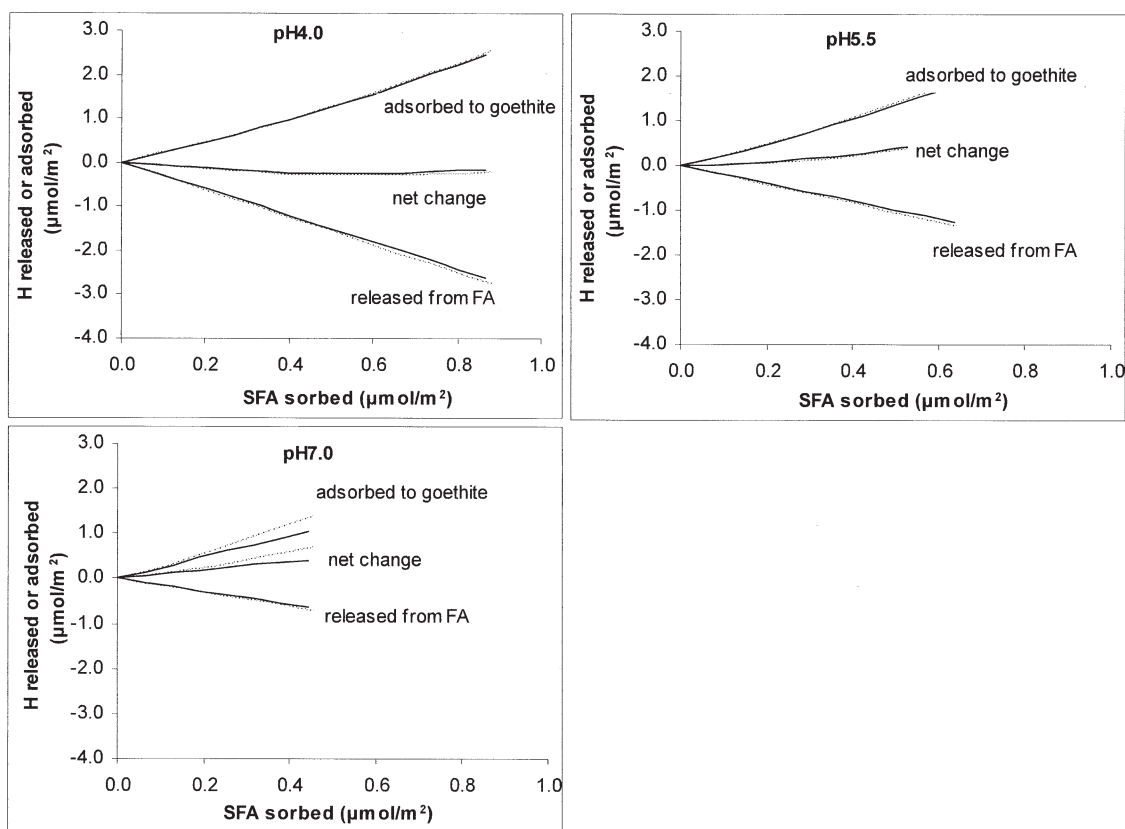


Fig. 11. Mass balance of protons calculated using the LCD model. Gray lines: no Ca; black lines: 1.0 mM Ca.

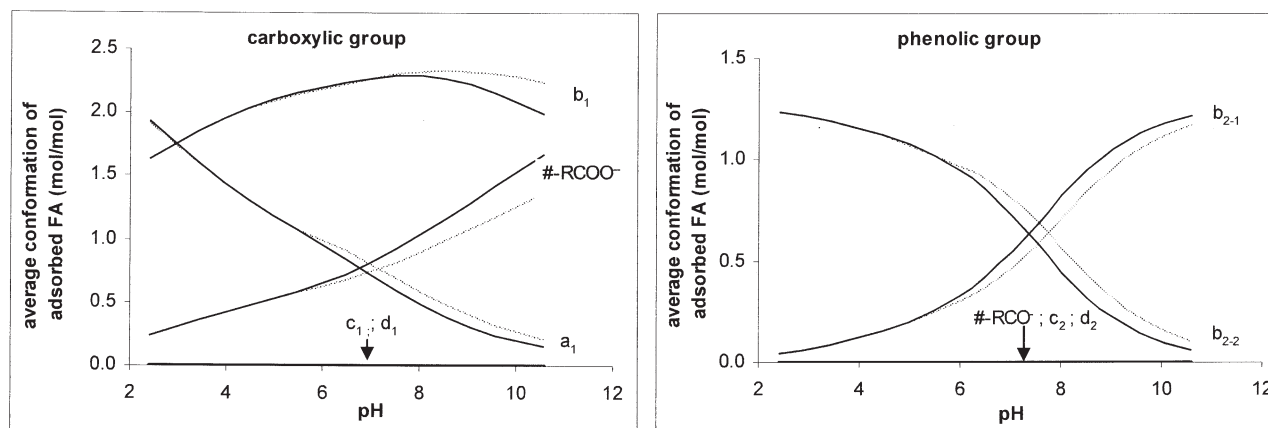


Fig. 12. The average conformation of the adsorbed SFA calculated using the LCD model for the treatment of 300 mg/L SFA, 5.8 g/L goethite, 0.10 M NaNO₃. Gray lines: no Ca; Black lines: 1.0 mM Ca.

increase in net charge is predicted. The effect of Ca on proton coadsorption to goethite is more significant at high pH (7.0). At this pH, the adsorption of Ca to goethite is stronger than at pH 5.5 and 4.0.

As has been pointed out by Filius et al. (2003), the experiment of proton coadsorption was carried out under the condition that almost all SFA added is adsorbed. Therefore the proton coadsorption data give information on the adsorption process that can not be obtained from interpretations of the SFA adsorption data because of the large slope of the adsorption isotherm.

5. DISCUSSION

At the oxide-water interface, metal ions and organic ligands may interact in different ways, (e.g., Ali and Dzombak, 1996b): 1) competing for surface sites; 2) forming nonsorbing or weakly sorbing complexes in solution; 3) forming ternary complexes at the surface; 4) altering the electrostatic properties at the oxide-water interface.

Tipping (1981), for instance, has postulated that cations and positive surface sites of minerals compete for the anionic groups in the humic molecules. The competition causes fewer contacts between the humic acid molecules and the surface, and according to Tipping, this leads to increased adsorption of the humics. Using the LCD model, the average conformation of the adsorbed SFA molecules can be calculated. An example of such a calculation is given in Figure 12 for a suspension containing 300 mg/L SFA, 5.8 g/L goethite in 0.10 M NaNO₃, with or without 1.0 mM Ca. The LCD model calculation shows that above pH 7 contacts between the ligands of fulvic acid molecules, especially the carboxylic groups, and the goethite surface sites decrease when Ca is added. This result supports the competition postulated by Tipping (Tipping, 1981), although this explanation is in our opinion not the major mechanism.

The mechanism proposed by Ali and Dzombak (1996b) is that the metal ions and the organic ligands form complexes in the solution, and that this will decrease the adsorption of the metal ions and the organics to the mineral surface. Formation of such complexes will certainly decrease the activity of both the

metal ions and the organic molecules. However, for calcium, our calculations predict that this effect is relatively small. This mechanism could however be more important for the metal ions that form much stronger complexes with the humic and fulvic acids than Ca.

A third mechanism that has been put forward is that ternary surface complexes are formed and that due to these complexes the adsorption of the organic ligands and metal ions to the mineral surfaces is promoted. In the system of metal ions, humic substances and minerals, generally two possible structures of the ternary complex are proposed (Stumm, 1992; Spark et al., 1997b). One is the mineral-metal ion-humics complex (goethite-Ca-SFA), which means the metal ion acts as a "bridge" between the mineral and the humics. The other is the mineral-humics-metal ion complex (goethite-SFA-Ca), in which the metal ion is bound to the mineral-humic complex through adsorption to the bound humics. In our calculations with the LCD model, the "bridging" structure is not included. For the cations such as calcium, which form relatively weak chemical bonds with the fulvic acid and goethite, the specific "bridging" mechanism seems unimportant. Our calculations show that an adequate description of the data can be obtained simply with the use of the goethite-SFA-Ca complex without taking the "bridging" species into account. Calculations of the contribution of the goethite-SFA-Ca complex to the total Ca binding shows that almost all of the Ca is bound directly to the surface sites of goethite as monodentate complex. An important reason is the high affinity of the functional groups of SFA for the surface sites of goethite. Therefore the functional groups prefer the mineral surface sites over the Ca²⁺ ion in their tendency to form complexes. As shown in Figure 12, only a minor amount of the ternary complex of goethite-SFA-Ca is formed. This means that the ternary complex formation is not an important mechanism in the interactions.

The fourth mechanism of the interaction is due to the electrostatic effects. When fulvic acid is adsorbed to goethite, the electrostatic potential of the *d*-plane becomes less positive or more negative. Adsorption of Ca adds positive charge to the interface, most of which is attributed to the *d*-plane. Due to the opposite effect that both adsorption processes have on the

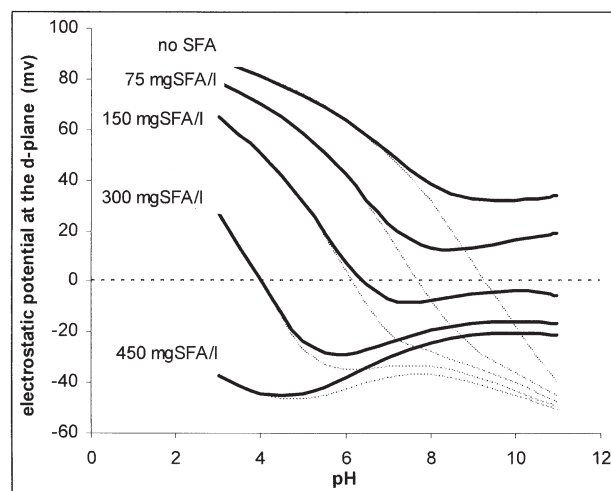


Fig. 13. Electrostatic potential in the d -plane on the surface of goethite calculated using the LCD model. Gray lines: no Ca. Black lines: with 1.0 mM Ca.

charge and potential of the d -plane, combined adsorption of fulvic acid and Ca leads to synergetic effects. To illustrate this in more detail, the calculated electrostatic potential at the d -plane is depicted in Figure 13. In a pure goethite suspension, the electrostatic potential is positive at low pH and becomes negative at a pH above the PZC. Addition of fulvic acid strongly decreases the potential at the d -plane. High loading of fulvic acid keeps the potential negative over the entire pH range. Addition of Ca diminishes the decrease of the d -plane potential at high pH. In the absence of or with low loading of SFA, the potential of the d -plane even remains positive for all pH values due to Ca adsorption. The difference between the d -plane potential in the absence or presence of Ca is larger at low loading of SFA than at high loading. These changes in the d -plane potential determine to a large extent the observed effects of the interactions on the adsorption of Ca and SFA to goethite.

As we have shown, the interactions between metal ions and humic substances at the oxide-water interface are complicated and the net effect is a complex function of many factors. Without a mechanistic model that can deal with this complexity in a consistent way, it is impossible to quantitatively predict the overall behavior. The LCD model can predict quantitatively the adsorption of fulvic acid and Ca in the ternary system and also provides qualitative insight in the mechanisms that govern the adsorption.

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