Pergamon

Modeling the binding of fulvic acid by goethite: The speciation of adsorbed FA molecules

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Abstract—Under natural conditions, the adsorption of ions at the solid–water interface may be strongly influenced by the adsorption of organic matter. In this paper, we describe the adsorption of fulvic acid (FA) by metal(hydr)oxide surfaces with a heterogeneous surface complexation model, the ligand and charge distribution (LCD) model. The model is a self-consistent combination of the nonideal competitive adsorption (NICA) equation and the CD-MUSIC model. The LCD model can describe simultaneously the concentration, pH, and salt dependency of the adsorption with a minimum of only three adjustable parameters. Furthermore, the model predicts the coadsorption of protons accurately for an extended range of conditions. Surface speciation calculations show that almost all hydroxyl groups of the adsorbed FA molecules are involved in outer sphere complexation reactions. The carboxylic groups of the adsorbed FA molecule form inner and outer sphere complexes. Furthermore, part of the carboxylate groups remain noncoordinated and deprotonated. *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

Natural organic matter (NOM) and metal(hydr)oxide surfaces can both be regarded as geo-colloids. Considerable attention has been and is still given to the understanding of the (surface) chemistry of these geo-colloids per se. NOM and metal(hydr)oxides are, for instance, very important for the chemical speciation and transport of nutrients and pollutants in the soil and sediment. In natural systems, both types of geo-colloids are simultaneously present and they will interact. The mutual interaction may influence their role as reactive surfaces in the natural environment. The interaction between organic matter and oxide surfaces can significantly alter the characteristics of both the organic matter and the oxide surface. Davis (1982) stated that a realistic representation of the surfaces of natural particulate matter might require a heterogeneous multisite model. To date, only a few attempts have been made to include NOM adsorption in surface speciation calculations (Vermeer et al., 1998; Karltun, 1998; Evanko and Dzombak, 1999; Filius et al., 2000). For such an important challenge, a fundamental understanding of the adsorption behavior of NOM by oxide surfaces is required to make progress.

Well-defined small organic acids have often been used as model compounds to study the adsorption of larger ill-defined natural organic acids. (Balistrieri and Murray, 1986; Ali and Dzombak, 1996; Filius et al., 1997, 2001; Boily et al., 2000). The description of the adsorption of these well-defined organic molecules has shown that three factors are essential: 1) the stoichiometry of the reaction, 2) the chemical affinity of the organic molecules for the oxide surface, and 3) electrostatic interactions between the charged organic molecules and the oxide surface. However, the description of the adsorption of large, ill-defined organic molecules (humic and fulvic acid; HA

and FA) is more complex for several reasons: (1) HA and FA are mixtures of molecules with different size, number of reactive groups, etc.; (2) FA and especially HA have many more reactive groups per molecule that can form bonds with the oxide surface; (3) the organic molecules and the metal(hydr)oxide surface have both a variable charge; and (4) HA and FA have a relatively large size.

In the studies of Karltun (1998), Evanko and Dzombak (1999), and Filius et al. (2000), the adsorption of FA by goethite is described assuming a discrete number of surface species. We refer to this type of modeling as "discrete modeling." In these studies, as well as in the present approach, FA is treated as a mixture of the same molecules with averaged properties.

Figure 1 shows three different schematic configurations of a bound FA molecule. The reactive groups (carboxylate and hydroxylate) of the FA molecule can react with mineral surface groups, may bind protons, or remain deprotonated. The configuration of the FA molecule bound by the oxide surface will vary widely with pH, salt level, surface loading, and other factors. In the discrete modeling, the varying configuration is introduced by defining different surface species. Filius et al. (2000) calculated that with such an approach a FA molecule with eight reactive groups can form potentially easily over a thousand different surface species. To reduce the number of adjustable parameters, the number of surface complexes used however has been minimized. Filius et al. (2000) only used four different surface species to describe the data. The limited number of surface species, is physically and chemically less realistic. For larger molecules, e.g., HA, the number of reactive groups is even larger than for FA and the number of possible surface species is almost infinite. Therefore, the discrete modeling approach is in our opinion not suitable for modeling the binding of molecules larger and more complex than FA molecules.

Recently, we developed the ligand and charge distribution (LCD) model (Filius et al., 2001) and described the adsorption

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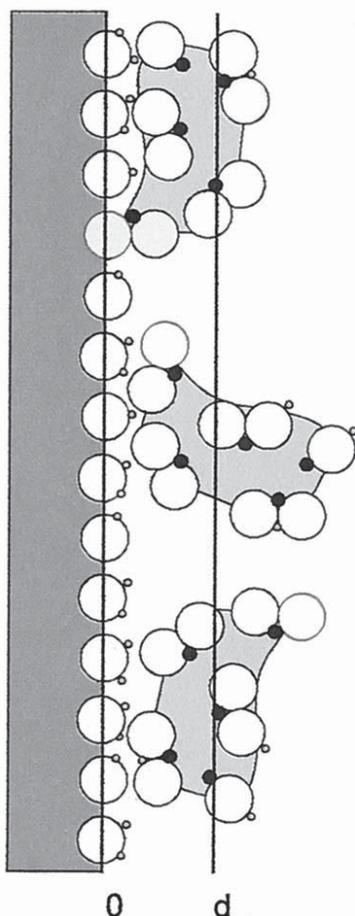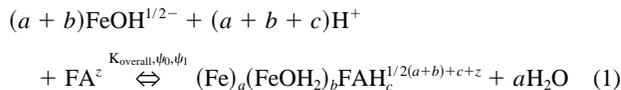
Fig. 1. A schematic representation of three possible configurations of an adsorbed FA molecule.

of multiple carboxylic acids by goethite. Using the CD (charge distributed complexation) model (Hiemstra and Van Riemsdijk, 1996) and the consistent nonideal competitive adsorption (NICA) equation (Koopal et al., 1994; Kinniburgh et al., 1999), the LCD model calculates the distribution of organic molecules over the mineral and the solution phase and the speciation (or configuration) of the adsorbed and dissolved molecules simultaneously and in a self-consistent way. Electrostatic effects on the speciation of the goethite and the adsorbed FA are taken into account with a united electrostatic model.

The aim of this study is to extend the model approach presented by Filius et al. (2001) to describe the adsorption of FA by goethite for a wide range of conditions (pH, ionic strength, and surface loading). As FA contains both carboxylic and hydroxylic groups, the original LCD model is extended taking the full speciation of the hydroxylate groups of the adsorbed FA molecules into account. The model is calibrated for the adsorption data of Strichen Fulvic Acid (SFA) by goethite. Furthermore, the model is tested predicting the coadsorption of protons as a function of the SFA adsorption by goethite at constant pH for conditions where almost 100% of the SFA molecules are adsorbed.

2. MODELING THE BINDING OF FA

In this study, the overall adsorption of FA by goethite is represented by the following overall reaction:

$$(a + b)\text{FeOH}^{1/2-} + (a + b + c)\text{H}^+$$

$$+ \text{FA}^z \overset{K_{overall}, \psi_0, \psi_1}{\Leftrightarrow} (\text{Fe})_a(\text{FeOH}_2)_b\text{FAH}_c^{1/2(a+b)+c+z} + a\text{H}_2\text{O} \quad (1)$$

in which FeOH represent the singly and triply coordinated surface groups of goethite, a is the number of surface groups forming inner sphere complexes, b the number of surface groups that will form outer sphere complexes with carboxylate (RCOO^-) and hydroxyl (RCOH) groups, and c the number of protons forming noncoordinated RCOOH and RCOH groups. z represents the charge of the fully deprotonated FA molecule.

The macroscopic adsorption reaction (Eqn. 1) is characterized by the stoichiometry coefficients a, b, and c, the overall affinity constant ($K_{overall}$), and the overall electrostatic interactions (ψ_0, ψ_1) between the oxide surface and the organic molecule. The calculation of these parameters and the details of this equation will be discussed later (see Table 1 and section 2.2.2). It should be mentioned that both singly and triply coordinated goethite surface groups are supposed to interact with the reactive groups of the FA molecule. However, in the text the reactions are only written for singly coordinated sites for reasons of simplicity.

The adsorption of FA by goethite is calculated with the LCD model (Filius et al., 2001). Figure 2 shows the basic structure of the LCD approach. The starting point for the iterative modeling is the calculation of the macroscopic distribution of FA over the solution (FA_{diss}) and the interface (FA_{ads}). This distribution is calculated with the CD-MUSIC models (I in Fig. 2). The CD-MUSIC model is fed by parameters gained from two submodels in which the ligand distribution at the surface is calculated (LD model) and the solution speciation of FA molecules is found (ND model). These two models are in turn based on the results of the CD model. The three models form a self-consistent iterative calculation scheme. A more detailed description of the model will be given below. We will start at the microscopic level before describing the FA adsorption at the macroscopic level.

2.1. Interaction of the Organic Groups with Protons and Surface Sites

2.1.1. In Solution

Table 1 shows the adsorption and protonation reactions of the carboxylic and hydroxylic groups of dissolved and adsorbed FA molecules. Reactions 1 and 2 of the table represent the protonation of the carboxylic and hydroxylic groups in solution respectively.

Reactions 3 through 6 of Table 1 represent the adsorption and protonation of a solution-oriented carboxyl or hydroxyl group of the bound FA molecule. The solution-oriented group does not have a direct interaction with the goethite surface groups, but is bound by the surface due to the complex formation of surface sites with other functional groups of the same adsorbed organic molecule. This structural feature is indicated by # in the reactions.

Table 1. Reaction equations for the reactions possible to occur on the surface with the corresponding affinity constants, change of charge (Δz_i) in plane i, and stoichiometry coefficients.

	Reactions	logK	Δz_0	Δz_d	St. coeff.
1	$RCOO^- + H^+ \Leftrightarrow RCOOH^0$	$\log \tilde{K}_{H,1}$	—	—	—
2	$RCO^- + H^+ \Leftrightarrow RCOH^0$	$\log \tilde{K}_{H,2}$	—	—	—
3	$\# + RCOO^- + H^+ \Leftrightarrow \#{-}RCOOH^0$	$\log \tilde{K}_{H,1}$	0	0	c_1
4	$\# + RCOO^- \Leftrightarrow \#{-}RCOO^-$	0	0	−1	$z_1 - a_1 - b_1 - c_1$
5	$\# + RCO^- + H^+ \Leftrightarrow \#{-}RCOH^0$	$\log \tilde{K}_{H,2}$	0	0	c_2
6	$\# + RCO^- \Leftrightarrow \#{-}RCO^-$	0	0	−1	$z_2 - a_2 - b_2 - c_2$
7	$-FeOH^{0.5-} + H^+ + RCOO^- \Leftrightarrow -Fe - OOCR]^{0.5-}$	$\log \tilde{K}_{in} + \log K_H$	+0.5	−0.5	a
8	$-FeOH^{0.5-} + H^+ + RCOO^- \Leftrightarrow -FeOH_2 \cdots OOCR]^{0.5-}$	$\log \tilde{K}_{out,1} + \log K_H$	+0.8	−0.8	$b_{1,1}$
9	$-FeOH^{0.5-} + H^+ + RCO^- \Leftrightarrow -FeOH_2 \cdots OCR]^{0.5-}$	$\log \tilde{K}_{out,2} + \log K_H$	+0.8	−0.8	$b_{2,1}$
10	$-FeOH^{0.5-} + H^+ + RCO^- \Leftrightarrow -FeOH \cdots HOCR]^{0.5-}$	$\log \tilde{K}_{out,2} +$ $\log \tilde{K}_{H,2}$	+0.2	−0.2	$b_{2,2}$

Note R represents the rest of the molecule. # indicates the adsorbed FA molecule of which the solution-orientated reactive groups can be protonated (reactions 3 and 5) or remain deprotonated (reactions 4 and 6). Note that the charge of the bound $RCOO^-$ and of the $RCOOH^0$ is located in the d-plane. In the modeling, outer sphere complexation reactions are assumed for both singly and triply coordinated groups. Here the reactions (reactions 8–10) are only written for singly coordinated groups. The charge distribution and affinity constant are assumed to be the same for outer sphere complexation with singly and triply coordinated groups. The stoichiometry coefficients in the table are related to the stoichiometry coefficients of Eqn. 1 by $b = b_1 + b2$; $b2 = b_{2,1} + b_{2,2}$; $c = c_1 + c_2$; and $z = z_1 + z_2$.

2.1.2. At the Interface

2.1.2.1. Carboxylic Groups
Based on spectroscopic evidence (Parfitt et al., 1977a, b; Gu et al., 1994; Kaiser et al., 1997; Boily et al., 2000), we assume in this study that the carboxylic groups of FA can form inner sphere complexes with the singly coordinated surface groups and outer sphere complexes with singly and triply coordinated surface groups. Inner sphere complexation (reaction 7 of Table 1) is characterized by the exchange of a surface water group of a singly coordinated surface group for one oxygen atom of the carboxylate group. We assume that the charge of the carboxylate groups (−1 valence unit; vu) is equally distributed over both oxygens (i.e., each oxygen −0.5 vu). In case of the exchange reaction, the charge of the iron in the solid (+0.5 vu) is fully neutralized by the charge of the carboxylate oxygen (−0.5 vu). Inner sphere coordination therefore results in an uncharged bonding oxygen. The charge of the second carboxylate oxygen is located in the d-plane.

In case of H bond formation, the −1 vu of the organic group is located in the d-plane (reaction 8 of Table 1). The proton involved attributes 0.8 vu of its charge to the surface plane. The remaining 0.2 vu is located in the d-plane together with the −1 vu of the carboxylate group. In the rest of the text, H bonding is described only for singly coordinated surface groups. In the modeling, the H bonding with triply coordinated groups is taken into account in the same manner as the H bonding with singly coordinated groups, with the same charge distribution and affinity constant.

2.1.2.2. Hydroxylic Groups
The hydroxylic groups, and other types of OH groups of FA with a high proton affinity are supposed to protonate and deprotonate and to form outer sphere complexes with singly and triply coordinated surface groups. The outer sphere complexes are formed due to H bonding (reactions 9 and 10 in Table 1). In case of H bonding, both the protonated reactive surface group and the hydroxylic group of the FA can, in principle, act as the proton donor. Figure 3 shows both options and indicates the different charge distribution of both types of outer sphere complexes over the interface. When the goethite surface site is the proton donor, 0.8 vu of the charge of the proton is located in the surface plane. The remaining 0.2 vu is located in the d-plane together with the –1 vu of the carboxylate or hydroxylate group (Fig. 3a; reaction 9 of Table 1). In case the reactive organic group is the proton donor, the 0.2 vu of the proton is located in the 0-plane. The remaining 0.8 vu is located in the d-plane together with the –1 vu of the carboxylate or hydroxylate group (Fig. 3b; reaction 10 of Table 1).

To determine which group is the actual proton donor, the intrinsic proton affinity of both groups as well as the electrostatic potential at the location of the reactive group should be taken into account. The overall affinity for the formation of the H bond in which the surface site is the donor is given by a combination of the protonation of the surface group (K_H), the formation of the H bond ($\tilde{K}_{out,2}$), and the electrostatic interactions ($e^{-0.8F\psi_0/RT} \cdot e^{+0.8F\psi_1/RT}$). The overall affinity for the formation of the H-bond in which the hydroxylic group is the donor is a combination of the protonation of the reactive FA group ($\tilde{K}_{H,2}$), the formation of the H bond ($\tilde{K}_{out,2}$), and the electrostatic interactions ($e^{-0.2F\psi_0/RT} \cdot e^{+0.2F\psi_1/RT}$). The surface site will therefore dominate as the H-bond donor in case $K_H \cdot e^{-0.8F\psi_0/RT} \cdot e^{+0.8F\psi_1/RT} > \tilde{K}_{H,2} \cdot e^{-0.2F\psi_0/RT} \cdot e^{+0.2\psi_1/RT}$ (reaction 9 of Table 1; Fig. 3a). The hydroxylic group will dominate as the H-bond donor in case $\tilde{K}_{H,2} \cdot e^{-0.2F\psi_0/RT} \cdot e^{+0.2F\psi_1/RT} > K_H \cdot e^{-0.8\psi_0/RT} \cdot e^{+0.8F\psi_1/RT}$ (reaction 10 of Table 1; Fig. 3b).

When the reactive surface group and the hydroxylate group have similar proton affinities, the relative presence of both types of H bond donors depends on the electrostatic potential in the 0- and d-plane.

Note that in principle the carboxylic groups can also form both types of H bonds. However, because $\log \tilde{K}_{H,1} \ll \log K_H$, the overall affinity for the formation of the H bond in which the carboxylate oxygen is the donor is much smaller than in case
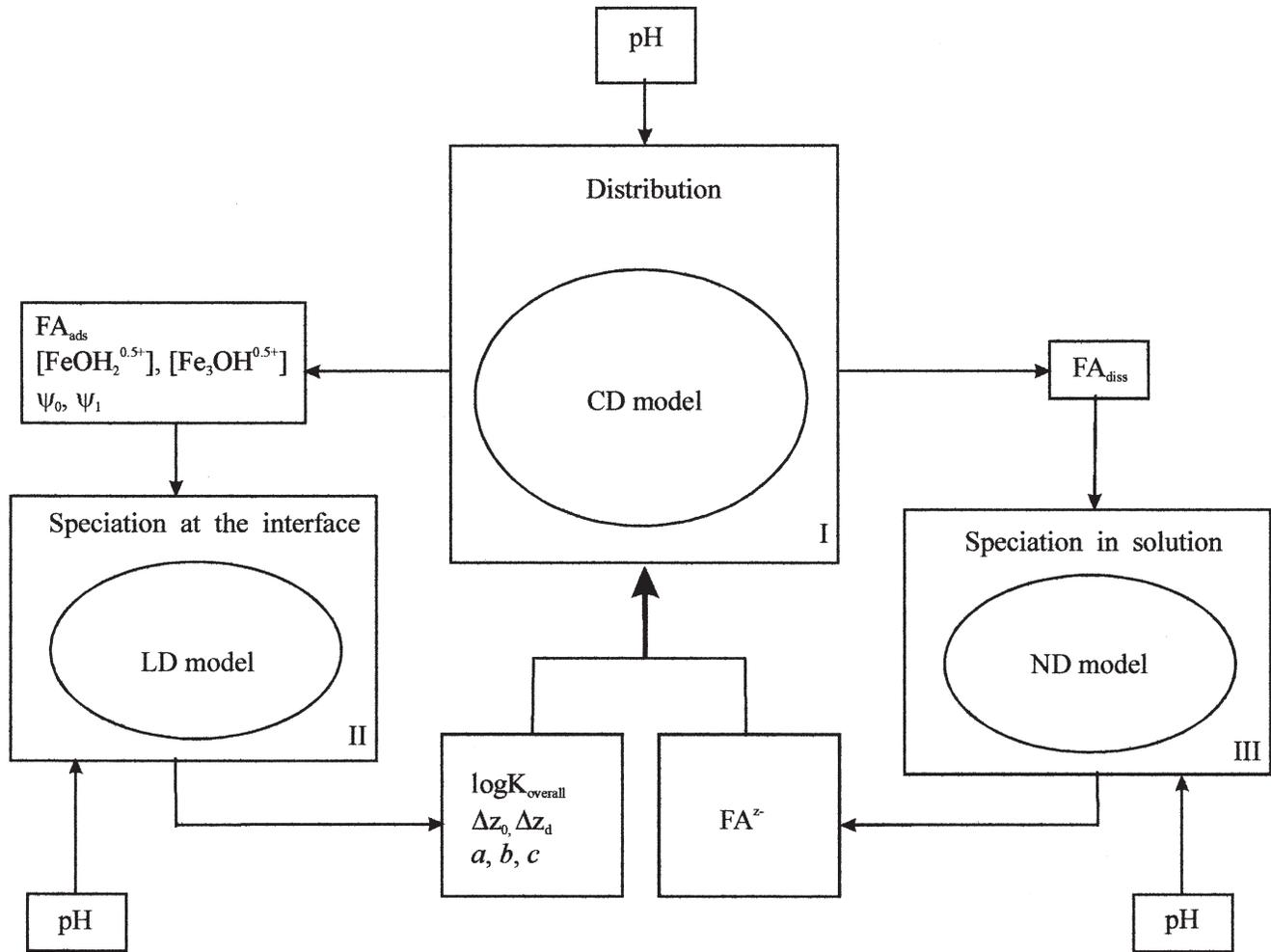
Fig. 2. Calculation scheme for the new model approach. (I) CD-MUSIC model calculates the distribution of the organic molecules over the solid and solution phase. (II) The LD model calculates the mean adsorption mode of the adsorbed organic molecules, which determines the input parameters for the CD-MUSIC model. (III) Converts the dissolved amount of FA into a reference species FA^{z-}, which is used as input for the CD-MUSIC model. The affinity constant ($\log K_{overall}$), charge distribution (Δz_0, Δz_1), stoichiometry coefficients (a, b, and c) of the reaction, and the activity of the FA in solution (FA^{z-}) are the input parameters for the CD&MUSIC model. The values of $\log K_{overall}$, Δz_0, Δz_d, and a, b, and c are also output of the speciation calculation of the adsorbed FA molecule.

the surface oxygen is the donor. Model calculations show that the carboxylic FA group will not act as the H bond donor for pH > 3.

2.1.3. Calculation of the FA Molecule Speciation: The Consistent NICA Model

In general, organic material contains functional groups with a wide range of affinities for protons, competing metal ions, and, in this case, reactive oxide surface groups. The NICA model is a site-binding model that takes heterogeneity and competition into account explicitly. For the calculation of the speciation of the adsorbed FA and the FA in solution (II and III in Fig. 2) the NICA model is used. The bimodal NICA equation is given by:

$$
Q_{i,t} = Q_{max1} \frac{n_{i,1}}{n_{H,1}} \frac{(\tilde{K}i,1c_{i,D})^{n_{i,1}}}{\sum_i (\tilde{K}_{i,1}c_{i,D})^{n_{i,1}}} \frac{\left\{ \sum_i (\tilde{K}_{i,1}c_{i,D})^{n_{i,1}} \right\}^{p_1}}{1 + \left\{ \sum_i (\tilde{K}_{i,1}c_{i,D})^{n_{i,1}} \right\}^{p_1}}
$$

$$
+ Q_{max2} \frac{n_{i,2}}{n_{H,2}} \frac{(\tilde{K}i,2c_{i,D})^{n_{i,2}}}{\sum_i (\tilde{K}_{i,2}c_{i,D})^{n_{i,2}}} \frac{\left\{ \sum_i (\tilde{K}_{i,2}c_{i,D})^{n_{i,2}} \right\}^{p_2}}{1 + \left\{ \sum_i (\tilde{K}_{i,2}c_{i,D})^{n_{i,2}} \right\}^{p_2}} \quad (2)
$$

where $Q_{i,t}$ is the total amount of component i bound to the humic substance, Q_{max} is the total site density (mol/kg), subscript 1 and 2 refer to the first and second type of sites in the affinity distribution, $\tilde{K}_i$ is a median affinity constant, and $c_{i,D}$ is
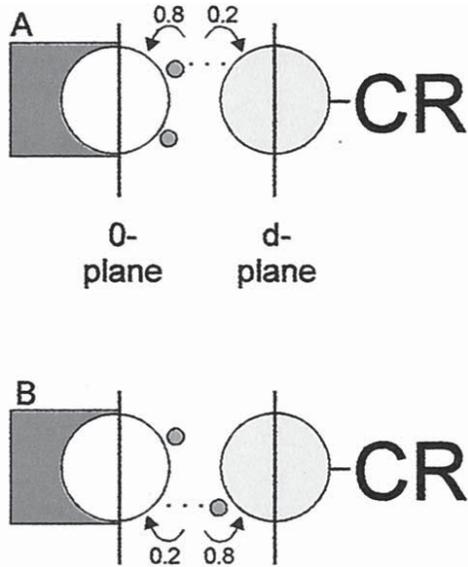
Fig. 3. Schematic representation of the formation of an H-bond between a hydroxylic group of a FA molecule and a singly coordinated reactive surface group of the goethite surface. (a) The reactive surface group acts as the H-bond donor; (b) the hydroxylic group acts as the H-bond donor.

the concentration of i in the Donnan phase. The value of p ($0 < p \leq 1$) accounts for the intrinsic chemical heterogeneity of the sorbent, which is the same for all components i. The parameter n_i accounts for the ion-specific heterogeneity or nonideality of component i that is not accounted for by intrinsic heterogeneity and/or the electrostatic model ($n \neq 1$ nonideal, $n = 1$ ideal).

2.1.3.1. Speciation of the Dissolved FA Molecules

For the conditions in solution as discussed in this paper, the NICA equation reduces to a simple LF equation because the proton is the only interacting component:

$$Q_H = Q_{max1} \frac{\{\tilde{K}_{H,1}[H]_D\}^{m_1}}{1 + \{\tilde{K}_{H,1}[H]_D\}^{m_1}} + Q_{max2} \frac{\{\tilde{K}_{H,2}[H]_D\}^{m_2}}{1 + \{\tilde{K}_{H,2}[H]_D\}^{m_2}} \quad (3)$$

in which m_i ($m = n_H p$) is a heterogeneity parameter that reflects the combined effect of the intrinsic heterogeneity (p) and the ion-specific heterogeneity (n_H).

A simple Donnan model can account for the nonspecific binding (Benedetti et al., 1996; Kinniburgh et al., 1999). The Donnan approach assumes that at each charge the overall electroneutrality is entirely preserved by the accumulation or depletion of salt ions in the gel phase.

$$q/v_D - \sum z_j c_j (e^{-z_j F \psi_D / RT} - 1) = 0 \quad (4)$$

where q is the charge of the fulvic acid in mol kg^{-1}, v_D is the specific volume of the gel phase in L/kg, and c_j is the concentration of ion j in the external solution in mol/L. $e^{-z_j F \psi_D / RT}$ is the Boltzmann factor in which subscript D indicates the potential in the Donnan phase.

For a given charge density and salt level, v_D is the only unknown parameter to solve Eqn. 4 for ψ_D. Kinniburgh et al.

(1999) introduced an empirical relation between v_D and the ionic strength:

$$\log v_D = k \cdot (1 - \log I) - 1 \quad (5)$$

Although this relation shows a variation in v_D with ionic strength which is much larger than can be expected based on structural models of fulvic acid (Langford et al., 1983; Avena et al., 1999; Lead et al., 2000), the Donnan model can mimic the salt effects on the charging very well. For more detail refer to Kinniburgh et al. (1999).

2.1.3.2. Speciation of the Adsorbed FA Molecules

So far, the NICA model has been used successfully to calculate the competitive binding between protons and metal ions for HA and FA (Christensen et al., 1998; Pinheiro et al., 1999; Kinniburgh et al., 1999; Berbel et al., 2001). Instead of metal ions, now surface sites compete for the binding sites of the FA. The NICA equation is combined with the basic Stern (BS) model, which accounts for the electrostatics near the surface (see CD-MUSIC model):

$$Q_{i,t}$$

$$= Q_{max1} \frac{n_{i,1}}{n_{H,1}} \frac{(\tilde{K}_{i,1} c_i X_{0,i} X_{d,i})^{n_{i,1}}}{\sum_i (\tilde{K}_{i,1} c_i X_{0,i} X_{d,i})^{n_{i,1}}} \frac{\left\{ \sum_i (\tilde{K}_{i,1} c_i X_{0,i} X_{d,i})^{n_{i,1}} \right\}^{p_1}}{1 + \left\{ \sum_i (\tilde{K}_{i,1} c_i X_{0,i} X_{d,i})^{n_{i,1}} \right\}^{p_1}}$$

$$+ Q_{max2} \frac{n_{i,2}}{n_{H,2}} \frac{(\tilde{K}_{i,2} c_i X_{0,i} X_{d,i})^{n_{i,1}}}{\sum_i (\tilde{K}_{i,2} c_i X_{0,i} X_{d,i})^{n_i}} \frac{\left\{ \sum_i (\tilde{K}_{i,2} c_i X_{0,i} X_{d,i})^{n_{i,2}} \right\}^{p_2}}{1 + \left\{ \sum_i (\tilde{K}_{i,2} c_i X_{0,i} X_{d,i})^{n_{i,2}} \right\}^{p_2}}$$

$$(6)$$

in which $X_{0,i}$ and $X_{d,i}$ indicate the Boltzmann factors ($e^{-\Delta z_0 F \psi_0 / RT}$, $e^{-\Delta z_d F \psi_1 / RT}$) for complex type i in the 0- and d-plane respectively. Note that in this equation the concentration of surface sites (c_i) is expressed in mol/L.

2.2. The Distribution of FA Over the Mineral Surface and Solution

In this study we assume that the reaction at the macroscopic level (Eqn. 1) is the result of all interactions at the microscopic level (Table 1). For the calculation of the distribution of FA molecules over the mineral surface and solution (I in Fig. 2) with the CD-MUSIC model (see Hiemstra et al., 1989a, b and Hiemstra and Van Riemsdijk, 1996 for details), the input parameters (reference state of the dissolved FA molecule, stoichiometry coefficients, overall affinity constant, and overall charge distribution) are obtained from the microscopic speciation calculation of the FA molecules. This will be described in more detail in the next sections.

2.2.1. The Reference State of the Dissolved FA

In this study we take the activity of the fully deprotonated species as the reference state of the FA molecules in solution.

Table 2. Basic physical chemical parameters used for the description of the charging behavior of FA with the NICA-Donnan model.

	$Qmax_i$ (mol/kg FA)	$\log\tilde{K}_{H,i}$	m
Carb. ($_1$)	6.11	2.33	0.33
Phen. ($_2$)	1.91	9.77	0.45
k	0.57		
M_m (g/mol)[a]	683		

[a] Van Zomeren and Comans (2002).

The activity of the fully deprotonated FA is not easy to derive from the NICA equation. For simplicity we assume that the activity of the fully deprotonated FA molecules is related to the total FA in solution according to:

$$[FA^z] = \theta_{FA^z} * FA_{diss} \tag{7}$$

in which FA_{diss} is the total concentration of FA in solution and θ_{FA^z} is the fraction of the deprotonated FA which can be defined as the product of the deprotonated fractions of the carboxylic (θ_{carb}^{fd}) and hydroxylic (θ_{hydr}^{fd}) groups:

$$\theta_{FA^z} = \theta_{carb}^{fd} * \theta_{phen}^{fd} \tag{8}$$

The individual fractions can be found from application of Eqn. 3 knowing that $\theta_{carb}^{fd} + \theta_{carb}^{H} = 1$ for the carboxylic groups, in which θ_{carb}^{H} is the fraction of the carboxylic groups of the FA molecule that is protonated. This yields:

$$\theta_{carb}^{fd} = \frac{1}{1 + (\tilde{K}_{H,1}[H^+]_D)^{m_1}} \tag{9}$$

for the carboxylic groups. θ_{phen}^{fd} can be calculated with Eqn. 9 using the constants of the second distribution ($\log\tilde{K}_{H,2}$ and m_2 of Table 2).

The activity of the fully deprotonated FA molecules can now be calculated according to:

$$[FA^z] = \frac{1}{1 + (\tilde{K}_{H,1}[H^+]_D)^{m_1}} * \frac{1}{1 + (\tilde{K}_{H,2}[H^+]_D)^{m_2}} * FA_{diss} \tag{10}$$

2.2.2. Stoichiometry Coefficients

In the LD model (III in Fig. 2), the mean speciation of the adsorbed FA molecule is calculated. In Eqn. 1, the stoichiometry coefficient for inner sphere complexation (see reaction 7 of Table 1) is given by a. The stoichiometry coefficient b in Eqn. 1 consists of the summation of the stoichiometry coefficients of the different types of outer sphere complexes as given by reactions 9 and 10 of Table 1, e.g.:

$$b = b_1 + b_2 \tag{11a}$$

$$b_1 = b_{1,1} + b_{1,2} \tag{11b}$$

$$b_2 = b_{2,1} + b_{2,2} \tag{11c}$$

in which the first subscript refers to either carboxylic groups (1) or hydroxylic groups (2). The second subscript discerns the two types of outer sphere complexes for hydroxylic groups. $b_{2,1}$

refers to the situation where the proton is closest to the reactive site of the goethite surface, whereas $b_{2,2}$ refers to the situation where the proton is closest to the hydroxylic group.

Finally, in Eqn. 1 c represents the stoichiometry coefficient of the proton complexes formed:

$$c = c_1 + c_2 \tag{12}$$

in which the index refers to carboxylic (1) or hydroxylic groups (2).

The microscopic stoichiometry coefficients (a, $b_{i,j}$, c_i; expressed in mol complex/mol FA) are related to the total amount of the different types of surface complexes formed ($Q_{is,t}$, $Q_{os_{i,j},t}$, $Q_{H_i,t}$) for inner sphere, outer sphere, and proton complexes respectively; e.g., the quantity of organic groups that forms a complex of type i expressed in mol complex/kg FA) and calculated with the NICA equation (Eqn. 6) by:

$$a = M_{FA} . Q_{is,t} \tag{13a}$$

$$b_{i,j} = M_{FA} . Q_{os_{i,j},t} \tag{13b}$$

$$c_i = M_{FA} . Q_{H_i,t} \tag{13c}$$

in which M_{FA} is the averaged molecular mass of the FA molecules (kg/mol). The subscripts i and j are the same as used for the stoichiometry coefficients b and c in the corresponding reactions in Table 1. Van Zomeren and Comans (2002) determined the M_{FA} for SFA to be 0.683 kg/mol (see Table 2).

Note that the stoichiometry coefficients are not constants, but depend on the pH, ionic strength, surface coverage, and so forth.

2.2.3. The Overall Reaction Constant

The overall affinity is composed of the constants for the formation of the different complexes weighed by their relative contribution:

$$\log K_{overall} = a . \log\tilde{K}_{in} + b_1 . \log\tilde{K}_{out,1} + b_2 . \log\tilde{K}_{out,2}$$
$$+ (a + b_1 + b_{2,1}) . \log K_H + c_1 . \log\tilde{K}_{H1}$$
$$+ (b_{2,2} + c_2) . \log\tilde{K}_{H2} \tag{14}$$

The different reaction stoichiometry coefficients (a, b, c) are defined in the previous section and in Table 1. The first three terms of the right-hand side of Eqn. 14 refer to the bonds formed between the FA groups and the surface, in which $\log\tilde{K}_{in}$ is the median affinity constant for the formation of inner sphere complexes and $\log\tilde{K}_{out,1}$ and $\log\tilde{K}_{out,2}$ are the median affinity constants for the formation of outer sphere complexes formed by carboxylic and hydroxylic groups respectively. The last three terms refer to the protonation reaction of the metal oxide surface groups ($\log K_H$), the free carboxylate groups of adsorbed FA ($\log\tilde{K}_{H1}$), and the free hydroxylate groups of adsorbed FA ($\log\tilde{K}_{H2}$) respectively.

Note that we have assumed that the affinity constants of the different outer sphere complexes are assumed to be the same for the reaction with singly and triply coordinated groups ($\log\tilde{K}_{out,2}$ for reactions 9 and 10 of Table 1).

2.2.4. The Overall Charge Distribution

The charge distribution can be calculated if we assume that the charge of the fully deprotonated adsorbed FA molecule is located in the d-plane except the charge of the FA groups that is located in the 0-plane due to the formation of inner (a), outer sphere (b) complexes (see charge distributions for reactions 7 to 10 in Table 1). The change in charge due to the protonation of the noncoordinated groups is assumed to take place in the d-plane. The charge distribution over the 0- and d-plane is therefore given by:

$$\Delta z_{0,FA} = (1 - 0.5)a + (+0.8)(b_1 + b_{2,1}) + (+0.2)b_{2,2} \tag{15a}$$

$$\Delta z_{d,FA} = z - (1 - 0.5)a - (+0.8)(b_1 + b_{2,1})$$
$$- (+0.2)b_{2,2} + c \tag{15b}$$

3. MATERIALS AND METHODS

3.1. Goethite

The goethite is prepared according to the procedure described in detail by Hiemstra et al. (1989b). The BET-N_2 surface area of the sample was 94 m^2 g^{-1}.

3.2. Fulvic Acid Extraction

Soil fulvic acid was extracted from a soil sample using methods based on those recommended by the International Humic Substances Society (Aiken et al., 1970; Swift, 1996). The soil material used was from a Bs horizon of a peaty podzol (Strichen association). The extraction is described in detail by Filius et al. (2000)

3.3. Data Analyses

The ionic strength is calculated for each data point explicitly taking into account both the background electrolyte ions and free H^+ and OH^-. From the calculated ionic strength (I), the activity coefficients (f) were determined using an adapted Davies equation:

$$-\log f = 0.51 * z^2 * \left\{ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 * I \right\} \tag{16}$$

Blank correction for each data point was carried out by calculating the amount of titrant required to increase the pH of an equivalent volume of background electrolyte solution. This was subtracted from the volume of titrant used for the sample.

3.4. Adsorption Experiments

The FA adsorption by goethite was measured in background electrolytes of 0.01 mol/L and 0.1 mol/L $NaNO_3$, using a batch equilibration procedure. The data are obtained from Filius et al. (2000).

3.5. Proton-Ion Titrations at Constant pH

Samples of 60 mL of a goethite suspension were titrated to pH 4, 5.5, or 7 and left overnight while purging with moist clean N_2. The samples have an electrolyte concentration of 0.01 mol/L or 0.1 mol/L $NaNO_3$. The goethite solution was titrated with a 5 g/L FA solution having the same pH and ionic strength as the goethite solution. Both goethite suspension and FA solution were kept under N_2 during the entire experiment. After each FA addition, the pH was corrected to the initial pH with acid or base. A reaction time of at least 20 min and a maximum drift criterion of 0.002 pH unit per minute were used between each addition of FA to reach equilibrium. The total amount of added FA was sufficiently small compared to the total surface area of the goethite to have more than 99% of the FA bound. The acid/base balance can be calculated from the amount of added acid and base because the pH was kept constant and virtually no FA remains in solution.

3.6. Model Calculations

The model calculations were carried out with the computer program ORCHESTRA (*O*bjects *R*epresenting *CHE*mical *Sp*eciation and *TRA*nsport; Meeussen et al., 2001) which was developed specifically to facilitate the implementation of advanced adsorption models. The most contrasting difference with any of the standard speciation algorithms is that in ORCHESTRA the model type definitions are completely separated from the calculation kernel, and even from the source code. Model types are defined in the form of objects in a separated database. This allows users to freely change or add new model definitions without changing the source code. The object-oriented structure of the model type definitions makes it possible to design a small set of fundamental object classes that can be used as building blocks for specific model implementations. This greatly simplifies the implementation of new chemical models and the combination of existing models as done in this study.

The ORCHESTRA model and the input file for the LCD model can be obtained from www.macaulay.ac/orchestra

4. RESULTS AND DISCUSSION

4.1. Basic Charging Behavior and FA Adsorption

The LCD model combines the charging characteristics of the oxide surface and the adsorbed FA. The basic charging behavior of the goethite surface and the FA molecules can be described using the individual fundamental models (CD-MUSIC for the metal oxide and NICA for the natural organic acid). The basic charging behavior of both components is determined in separate experiments. The charging behavior of goethite is very similar to the reported charging behavior of goethite by Venema et al. (1996) and Rietra et al. (2000). Table 3 gives the parameters used to describe this charging behavior with the CD-MUSIC model. Figure 4 shows the charging behavior of SFA in solution for four different electrolyte concentrations. The experimental setup is given in detail by Filius et al. (2000). The lines in Fig. 4 indicate the model calculations with the NICA-Donnan model. The fitting strategy of the experimental data to the NICA-Donnan model is described elsewhere (Kinniburgh et al., 1999). The parameters used to describe the charging behavior of SFA with the NICA-Donnan model are given in Table 2.

Figure 5 shows the adsorption envelopes for three different

Table 3. Basic physical chemical parameters used for the description of the charging behavior of the goethite.

$-FeOH^{0.5-} + H^+ \Leftrightarrow -FeOH_2^{0.5+}$	log K_H
$-Fe_3O^{0.5-} + H^+ \Leftrightarrow -FeOH^{0.5+}$	log K_H
A:	94 m^2/g
C:	0.9 F/m^2
N_s (FeOH):	3.45 sites/nm^2
N_s (Fe$_3$O):	2.7 sites/nm^2
log K_H = PPZC:	9.2
log K_{Na+}	-1
log K_{NO3-}	-1

total amounts of FA at constant goethite concentrations as determined in a previous study (Filius et al., 2000). The data show little salt dependency but the adsorption is strongly pH dependent. This type of sorption behavior is commonly found for FA and other fractions of NOM (Tipping, 1981; Becket and Le, 1990; Wang et al., 1997; Au et al., 1999).

The lines in Fig. 5 represent the model description. Table 4 lists the parameter values used to describe the adsorption data.

4.2. Number of Adjustable Parameters

In principle, two parameters are adjustable for each type of defined reaction; i.e., the median intrinsic affinity constant of the complex and the nonideality parameter n_i. In addition, the parameter p determines the width of the intrinsic affinity distributions of carboxylic and hydroxylic groups. However, the number of adjustable parameters can be reduced by a number of assumptions.

We assume a partial correlation between the distributions of the affinity constants of the different complexes. According to Rusch et al. (1997) the NICA model can be interpreted to relate to a partial correlation when the n-values for the different reactions are equal and smaller than 1. Therefore we assume: $n_i = n_{Hi} = n_{in} = n_{out,i.}$

Milne et al. (2001) determined the generic NICA-Donnan model parameters for 25 data sets. Their results show a variation in the value of the nonideality factor n_i. We have taken the

value for the n_H value of Milne et al. (2001) for our n parameter. The intrinsic chemical heterogeneity parameter p will follow in this approach from the n_H value taken from the generic parameter set and the distribution width ($m = n * p$) found from the interpretation of the H-titration data (Fig. 4). Therefore, the median affinity constants for each type of complex formed are the only adjustable parameters.

In the application of the LCD model, we assume further that the protonation of the adsorbed organic ligands can be described with the same parameters as found for the description of the basic charging behavior of FA in solution. Furthermore, the difference in affinity for the two types of outer sphere complexation reactions of the hydroxylic groups is assumed to be only due to the proton affinity of the hydroxyl group in case the hydroxyl group act as the proton donor (reactions 9 and 10 of Table 1).

Therefore, in the model approach used here only three adjustable parameters remain, i.e., log$\tilde{K}_{in}$, log$\tilde{K}_{out,1}$, and log$\tilde{K}_{out,2}$. The parameters that are taken from the generic data set (Milne et al., 2001) or independently obtained from curve fitting of solution titration data are given in Table 4. The number of adjustable parameters is comparable to the number often needed to describe the adsorption of much simpler anions, such as oxyanions (Bowden et al., 1980; Dzombak and Morel, 1990; Manning and Goldberg, 1996; Geelhoed et al., 1998).

With a minimum of the three adjustable affinity constants we are able to describe the data presented in Fig. 5 taking into account all reactions of Table 1.

4.3. Speciation of the Adsorbed FA

Based on the description of the data we can analyze the adsorption behavior of FA. The adsorption of FA by goethite is largely determined by the speciation of the adsorbed FA molecules. In Fig. 6, the speciation of the adsorbed FA molecules is given for the highest FA:goethite ratio presented in Fig. 5c. In a large range of pH values (pH 4 to 12), Fig. 6 represents the speciation of the bound FA at the "pseudoplateau" of the adsorption isotherms. Figure 6a shows the fate of the carbox-
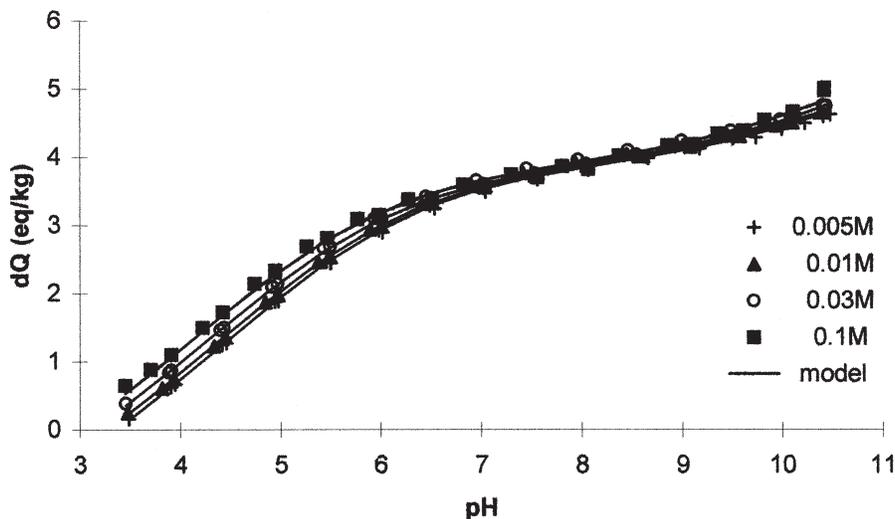

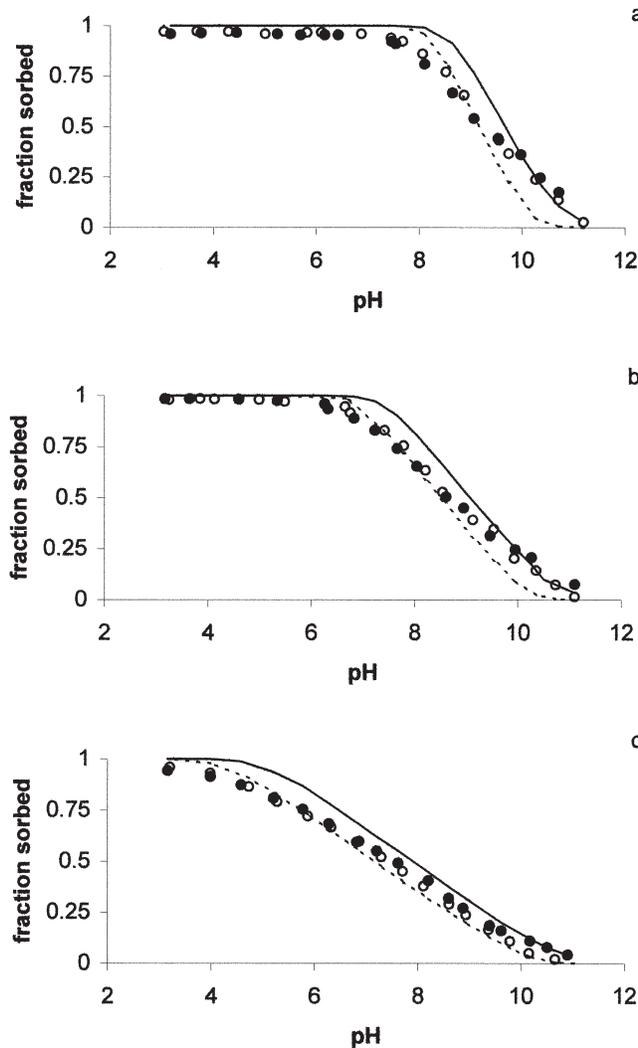Fig. 4. Basic charging behaviour of SFA in solution at four salt levels.

Fig. 5. The adsorption envelopes of SFA by goethite in 0.01 mol/L (open symbols and dotted lines) and 0.1 mol/L NaNO$_3$ (solid symbols and full lines). The suspension density of goethite is 5 g/L and three different total FA concentrations: (a) 75 mg/L; (b) 150 mg/L; (c) 300 mg/L.

Table 4. Parameters for the NICA model used for the calculation of the speciation of the adsorbed FA molecules.

$\log\tilde{K}_{in}$	-1	Fitted
$\log\tilde{K}_{out,1}$	0.75	Fitted
$\log\tilde{K}_{out,2}$	3.5	Fitted
n_1	0.66	Generic data set[a]
n_2	0.76	Generic data set[a]
p_1	0.50	$m = n_H \cdot p$
p_2	0.59	$m = n_H \cdot p$

[a] Milne et al., 2001.

ylic groups of an adsorbed FA molecule. Under the conditions of apparent maximal adsorption, model calculations show that the carboxylic groups react predominantly via outer sphere complexes. At low pH, inner sphere complexes become more important owing to their favorable charge distribution. With increasing pH, the electrostatic interactions will increasingly favor outer over inner sphere complexation. Over the entire pH range, part of the carboxylic groups is dissociated. Only a small fraction of the carboxylic groups becomes protonated at low pH.

This behavior agrees with the findings of Boily et al. (2000) who studied the binding of three carboxylic acids. They inferred from spectroscopic data that outer sphere complexes are important at high pH, whereas inner sphere complex formation becomes significant at low pH. For multiple carboxylic acid (e.g., pyromellitic acid) Boily et al. found that the protonated reactive groups become noticeable.

Figure 6b shows the fate of the hydroxylic groups. Almost all

hydroxylic groups are involved in the complexation reactions with the goethite surface over a wide pH range. The differences in charge distribution of the two hydroxylic outer sphere complexes cause a preferential formation of the complex in which the hydroxylic FA group acts as the H-bond donor at low pH. With increasing pH, the complex is replaced by the goethite surface group as the proton donor. At low pH, the speciation calculations show that the hydroxylic groups that are not associated with the surface start to become noticeable. According to the calculations, these groups are protonated. To date, no spectroscopic data are available to verify the presented speciation calculations for the hydroxylic groups presented in Fig. 6b.

In the present model, the main parameters determining the speciation are the median affinity constant, the nonideality coefficient, and the charge distribution of the different complexes. As was found by Filius et al. (2000, 2001), the median affinity constants for the formation of outer sphere complexes are much higher than for the formation of inner sphere complexes. This indicates that the replacement of a water molecule in case of inner sphere complex formation is not necessarily favorable. The higher affinity constant for the formation of outer sphere complexes involving a hydroxylic group compared to carboxylic groups corresponds with the larger undersaturation of the hydroxylate oxygen (-1 per O) compared to the carboxylate oxygens (-0.5 per O) of the organic molecule.

4.4. Verification of the LCD Model

To verify the LCD model, we predict the coadsorption of protons in case >99% of the added FA is adsorbed. Recently, Rietra et al. (1999) pointed out that proton-ion titrations at constant pH and a high solid/liquid ratio provide additional information under these conditions. The adsorbed amount of FA (x-axis) in such experiments follows directly from the added total amount. The number of protons that coadsorb/desorb (y-axis) follows from the amount of acid (or base) added to maintain a constant pH. The coadsorption of protons is measured as the extra amount of protons consumed upon the adsorption of FA at constant pH.

In this study, we have measured the proton-FA adsorption stoichiometry for three different pH values and two electrolyte concentrations. Figure 7 shows the results of the proton-ion titrations. The lines in the figure indicate model predictions. Note that the model is calibrated on the FA adsorption data of Fig. 5 where the goethite has a relatively high FA loading. The FA:goethite ratio used in the proton-ion titrations is much lower than the ratios used in the adsorption experiments (pH 7: 18 to 180 μg FA/m^2 and 60 to 630 μg FA/m^2 respectively).
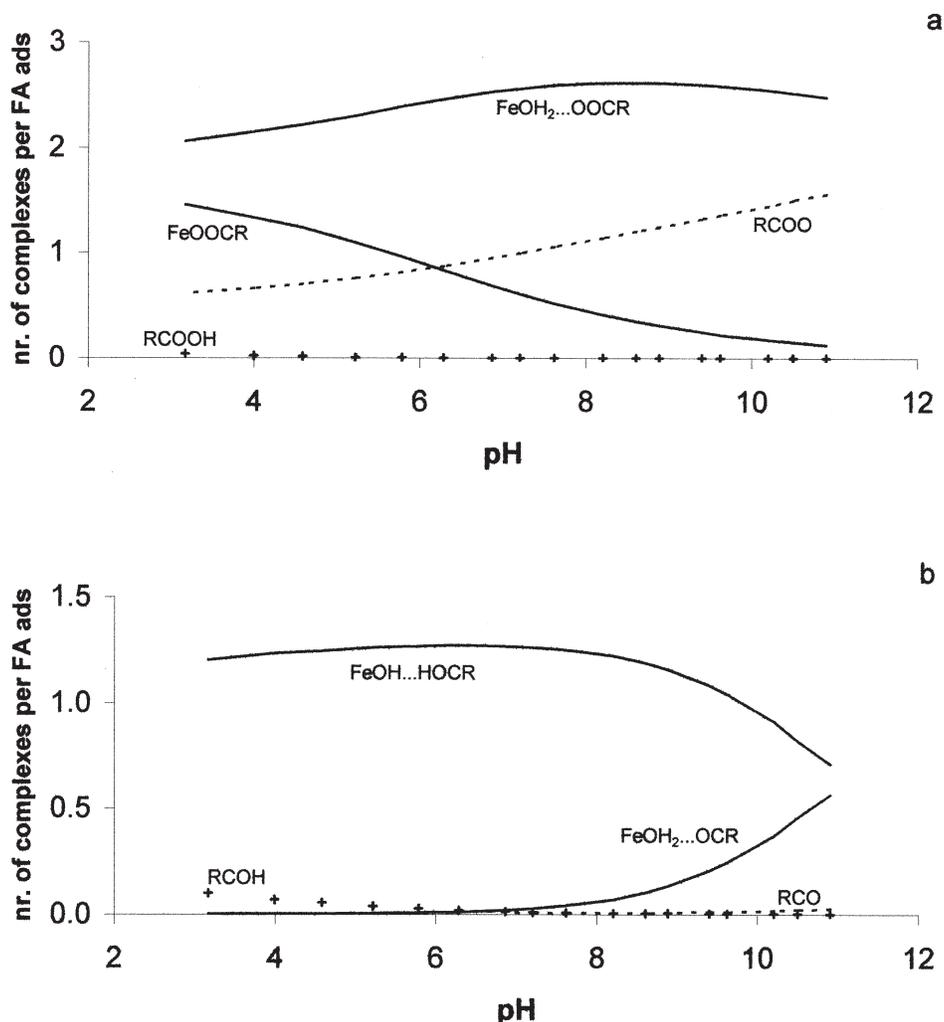
Fig. 6. The speciation of adsorbed FA molecules on the goethite surface expressed in number of complexes per adsorbed FA molecule (FA ads) plotted as function of pH at the highest goethite:FA ratio of Fig. 5. (a) The speciation of the adsorbed carboxylic groups; (b) the speciation of the adsorbed hydroxylic groups. Note that the number of complexes per adsorbed FA molecule is equivalent to the stoichiometry coefficient of that particular complex.

The calculations of the proton coadsorption are therefore pure predictions for situations which are extrapolations compared to Fig. 5 and not interpolations. The effects of pH, ionic strength, and surface loading on the proton adsorption are predicted quite accurately.

5. CONCLUSIONS

The LCD model enables the simultaneous description of the concentration, pH, and salt dependency of FA adsorption and the related charge phenomena: basic proton charging, coadsorption of protons upon FA adsorption. The model exhibits different levels of detail.

At a microscopic scale, the types of complexes between protons and the reactive groups of FA and the surface are defined. The structures of the complexes are, if possible based on information obtained from spectroscopic studies. Protons in solution and reactive surface groups compete for the same reactive groups of the FA molecule. The interactions result in a speciation of the adsorbed FA molecule that depends on pH,

ionic strength, surface loading, and so forth. This level of detail is comparable to the binding of protons and heavy metals by humic materials.

The speciation of the adsorbed FA molecules is calculated using the NICA model. The speciation of the adsorbed FA molecule implicitly determines the most important factors for NOM binding by oxide surfaces, e.g., the overall binding affinity, the charge distribution near the surface, and the stoichiometry of an adsorbed FA molecule.

The macroscopic distribution of FA over the dissolved and adsorbed state is calculated using the CD-MUSIC model. The coupling of the NICA equation and the CD-MUSIC model is self-consistent. This means that the speciation of the bound FA determines the overall affinity constant, the overall charge distribution, and the stoichiometry of the adsorption reaction and vice versa. For the calculation of the speciation of the bound FA, as well as in the calculation of the overall adsorption of FA by goethite, the electrostatic interactions are taken into account using the BS approach.
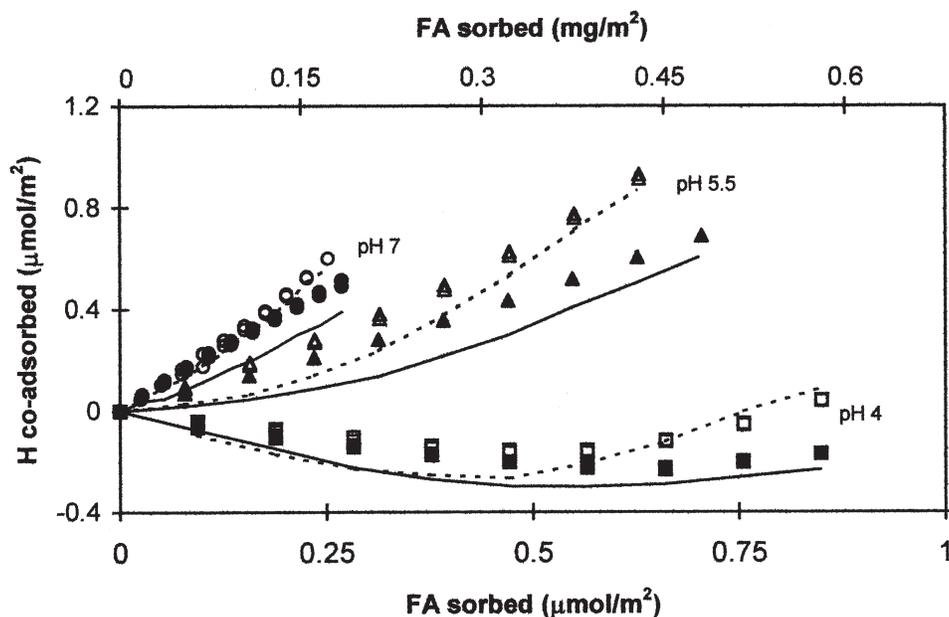
Fig. 7. The coadsorption of protons as function of the adsorbed amount of FA at three pH values and two ionic strengths. The open symbols and dotted lines represent the data at 0.01 mol/L $NaNO_3$ and the solid symbols and solid lines the data at 0.1 mol/L $NaNO_3$. The model lines are pure predictions.

Because of the complex nature of the interactions between organic materials and oxide surfaces, spectroscopy studies give at present little information about the speciation of the adsorbed organic molecules. The spectroscopic data provide quantitative information about the types of complexes formed between the reactive groups of the surface and of the organic molecule. This information corresponds to the microscopic level of detail of the present approach and constrains the types of complexes used in the model.

The calculated surface speciation of the adsorbed FA molecule (Fig. 6) shows that almost all hydroxylic groups are involved in surface complexation reactions. The noncoordinated groups of adsorbed FA molecules are predominantly deprotonated carboxylate groups. The model calculations show that the carboxylic groups are important for the FA binding at low pH, whereas the hydroxylic groups are relatively more important at high pH. This is in agreement with studies determining the sorption of small, well-defined, weak organic carboxylic and hydroxylic acids. Inner sphere complexes become important at low pH; outer sphere complexes are important at high pH. This is in agreement with the complex formation inferred from spectroscopy studies of small organic acids. The advantage of the model approach presented here is that it can also be applied or extended for larger, complex molecules like humic acids.

For the adsorption of molecules larger than humic acid (e.g., large polyelectrolytes), the conformational changes due to a variation in the formation of so-called loops and tails with changes in pH and salt level are important. As entropic and hydrophobic contributions are taken into account only implicitly in the LCD model, the model is less suitable for describing the adsorption of the polyelectrolyte molecules with very large molecular weight.

In the near future, the LCD model will be used to test how far the approach will give satisfactory results for complex systems in which oxyanions and polyvalent cations will be simultaneously present together with the oxide and the FA.

Associate editor: S. J. Traina

REFERENCES

Aiken G. R., Thurman E. M., Malcolm R. L., and Walton H. F. (1970) Comparison of XAD macroporous resins for the concentration of fulvic acid from aqueous solution. *Anal. Chim. Acta* **51,** 1799–1803.

Ali M. A. and Dzombak D. A. (1996) Competitive sorption of simple organic acids and sulfate on goethite. *Environ. Sci. Technol.* **26,** 2357–2364.

Atkinson et al., 1967; Evanko and Dzombak 1998; and Gu et al., 1995; Milne 2000.

Au K-K., Penisson A. C., Yang S., and O'Melia C. R. (1999) Natural organic matter at oxide/water interfaces: Complexation and conformation. *Geochim. Cosmochim. Acta* **63,** 2903–2917.

Avena M. J., Vermeer A. W. P., and Koopal L. K. (1999) Volume and structure of humic acids studied by viscometry: pH and electrolyte concentration effects. *Colloids Surfaces A* **151,** 213–224.

Balistrieri L. S. and Murray J. W. (1986) The influence of the major ions of seawater on the adsorption of simple organic acids by goethite. *Geochim. Cosmochim. Acta* **51,** 1151–1160.

Beckett R. and Le N. P. (1990) The role of organic matter and ionic composition in determining the surface charge of suspended particles in natural waters. *Colloids Surfaces* **44,** 35–49.

Benedetti M. F., Van Riemsdijk W. H., and Koopal L. K. (1996) Humic substances considered as a heterogeneous Donnan gel phase. *Environ. Sci. Technol.* **30,** 1805–1813.

Berbel F., Díaz-Cruz J. M., Ariño C., Esteban M., Mas F., Garcés J. L., and Puy J. (2001) Voltammetric analysis of heterogeneity in metal ion binding by humics. *Environ. Sci. Technol.* **35,** 1097–1102.

Boily J. F., Persson P., and Sjoberg S. (2000) Benzenecarboxylate surface complexation at the goethite (a-FeOOH)/water interface: II. Linking IR spectroscopic observations to mechanistic surface com-

plexation models for phthalate, trimellitate and pyromellitate. *Geochim. Cosmochim. Acta* **64,** 3453–3470.

Bowden J. W., Nagarajah S., Barrow N. J., Posner A. M., and Quirk J. P. (1980) Describing the adsorption of phosphate, citrate and selenite on a variable-charge mineral surface. *Aust. J. Soil Res.* **18,** 49–60.

Christensen J. B., Tipping E., Kinniburgh D. G., Gron C., and Christensen T. H. (1998) Proton binding by groundwater fulvic acids of different age, origins, and structure modeled with the model V and NICA-Donnan model. *Environ. Sci. Technol.* **32,** 3346–3355.

Davis J. A. (1982) Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochim. Cosmochim. Acta* **46,** 2381–2393.

Dzombak D. A. and Morel F. M. M. (1990) *Surface Complexation Modeling: Hydrous Ferric Oxide.* Wiley, New York.

Evanko C. R. and Dzombak D. A. (1999) Surface complexation modeling of organic acid sorption to goethite. *J. Colloid Interface Sci.* **214,** 189–206.

Filius J. D., Hiemstra T., and Van Riemsdijk W. H. (1997) Adsorption of small weak organic acids on goethite: Modeling of mechanisms. *J. Colloid Interface Sci.* **195,** 368–380.

Filius J. D., Lumsdon D. G., Meeussen J. C. L., Hiemstra T., and Van Riemsdijk W. H. (2000) Adsorption of fulvic acid on goethite. *Geochim. Cosmochim. Acta* **64,** 51–60.

Filius J. D., Meeussen J. C. L., Hiemstra T., and Van Riemsdijk W. H. (2001) Modelling the binding of benzenecarboxylates by goethite: The speciation of adsorbed organic molecules. *J. Colloid Interface Sci.* **244,** 31–42.

Geelhoed J. S., Hiemstra T., and Van Riemsdijk W. H. (1998) Competitive interaction between phosphate and citrate on goethite. *Environ. Sci. Technol.* **32,** 2119–2123.

Gu B., Schmitt J., Chem Z., Liang L., and McCarthy J. F. (1994) Adsorption and desorption of natural organic matter on iron oxide: Mechanisms and models. *Environ. Sci. Technol.* **28,** 38–46.

Gu B., Schmitt J., Chem Z., Liang L., and McCarthy J. F. (1995) Adsorption and desorption of different organic matter fractions on iron oxide. *Geochim. Cosmochim. Acta* **59,** 219–229.

Hiemstra T., Van Riemsdijk W. H., and Bolt G. H. (1989a) Multisite proton modeling at the solid/water interface of (hydr)oxides: A new approach. I. Model description and evaluation of intrinsic reaction constants. *J. Colloid Interface Sci.* **133,** 91–104.

Hiemstra T., De Wit J. C. M., and Van Riemsdijk W. H. (1989b) Multisite proton adsorption modeling at the solid/solution interface of (hydr)oxides: A new approach, II. Application to various important (hydr)oxides. *J. Colloid Interface Sci.* **133,** 488–508.

Hiemstra T. and Van Riemsdijk W. H. (1996) A structural approach to ion adsorption: The charge distribution model. *J. Colloid Interface Sci.* **179,** 105–117.

Kaiser K., Guggenberger G., Haumaier L., and Zech W. (1997) Dissolved organic matter sorption on subsoils and minerals studied by 13C-NMR and DRIFT spectroscopy. *Eur. J. Soil Sci.* **48,** 301–310.

Karltun E. (1998) Modelling SO_4^{2-} surface complexation on variable charge minerals. II. Competition between SO_4^{2-}, oxalate and fulvate. *Eur. J. Soil Sci.* **49,** 113–120.

Kinniburgh D. K., Van Riemsdijk W. H., Koopal L. K., Borkovec M., Benedetti M. F., and Avena M. J. (1999) Ion binding to natural organic matter: Competition, heterogeneity, stoichiometry, and thermodynamic consistency. *Colloids Surfaces A* **151,** 147–166.

Koopal L. K., Van Riemsdijk W. H., De Wit J. C. M., and Benedetti M. F. (1994) Analytical isotherm equations for multicomponent adsorption to heterogeneous surfaces. *J. Colloid Interface Sci.* **166,** 51–60.

Langford C. H., Gamble D. S., Underdown A. W., and Lee S. (1983) Interactions of metal ions with a well characterized fulvic acid. In *Aquatic and Terrestrial Humic Materials* (eds. R. F. Chistman and E. T. Gjessing), pp. 219–237. Ann Arbor Science, Ann Arbor, MI.

Lead J. R., Wilkinson D. J., Starchev K., Canonica S., and Buffle J. (2000) Determination of diffusion coefficients of humic substances by fluorescence correlation spectroscopy: Role of solution conditions. *Environ. Sci. Technol.* **34,** 1365–1369.

Manning B. A. and Goldberg S. (1996) Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. *Soil Sci. Soc. Am. J.* **60,** 121–131.

Meeussen J. C. L. (2001) ORCHESTRA, a new object-oriented framework for implementing chemical equilibrium models. *Environ. Sci. Technol.* (submitted).

Milne C. J., Kinniburgh D. G., and Tipping E. (2001) Generic NICA-Donnan model parameters for proton binding by humic substances. *Environ. Sci. Technol.* **35,** 2049–2059.

Parfitt R. L., Fraser A. R., and Farmer V. C. (1977a) Adsorption on hydrous oxides. I. Oxalate and benzoate on goethite. *J. Soil Sci.* **28,** 29–39.

Parfitt R. L., Fraser A. R., and Farmer V. C. (1977b) Adsorption on hydrous oxides. III. Fulvic acid and humic acid on goethite, gibbsite and imogolite. *J. Soil Sci.* **28,** 289–296.

Pinheiro J. P., Mota A. M., and Benedetti M. F. (1999) Lead and calcium binding to fulvic acids: Salt effect and competition. *Environ. Sci. Technol.* **33,** 3398–3404.

Rietra R. P. J. J., Hiemstra T., and Van Riemsdijk W. H. (1999) Sulfate adsorption on goethite. *J. Colloid Interface Sci.* **218,** 511–521.

Rietra R. P. J. J., Hiemstra T., and Van Riemsdijk W. H. (2000) Electrolyte anion affinity and its effect on oxyanion adsorption on goethite. *J. Colloid Interface Sci.* **229,** 199–206.

Rusch U., Borkovec M., Daicic J., and Van Riemsdijk W. H. (1997) Interpretation of competitive adsorption isotherms in terms of affinity distributions. *J. Colloid Interface Sci.* **191,** 247–255.

Swift R. S. (1996) Organic matter characterization. In *Methods of Soil Analysis. Part 3. Chemical Methods* (eds. D. L. Sparks, et al.), pp. 1018–1020. Soil Sci. Soc. Am. Book Series: 5 Soil Science Society of America, Madison, WI.

Tipping E. (1981) The adsorption of aquatic humic substances by iron oxides. *Geochim. Cosmochim. Acta* **45,** 191–199.

Van Zomeren A. and Comans R. N. J. Characterisation of dissolved organic carbon in leachates from MSWI bottom ash (in preparation).

Venema P., Hiemstra T., and Van Riemsdijk W. H. (1996) Multi site adsorption of cadmium on goethite. *J. Colloid Interface Sci.* **183,** 515–527.

Vermeer A. W. P., Van Riemsdijk W. H., and Koopal L. K. (1998) Adsorption of humic acid to mineral particles. 1. Specific and electrostatic interactions. *Langmuir* **14,** 2810–2819.

Wang L., Chin Y. P., and Traina S. J. (1997) Adsorption of (poly)maleic acid and an aquatic fulvic acid by goethite. *Geochim. Cosmochim. Acta* **61,** 5313–5324.