



PII S0016-7037(99)00176-3

## Adsorption of fulvic acid on goethite

JEROEN D. FILIUS,<sup>1</sup> DAVID G. LUMSDON,<sup>2,\*</sup> JOHANNES C. L. MEEUSSEN,<sup>2</sup> TJSSE HIEMSTRA,<sup>1</sup> and WILLEM H. VAN RIEMSDIJK<sup>1,\*</sup><sup>1</sup>Department of Environmental Sciences, Sub-department Soil Science and Plant Nutrition, Wageningen Agricultural University, Wageningen, The Netherlands<sup>2</sup>Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen, Scotland

(Received August 11, 1998; accepted in revised form May 7, 1999)

**Abstract**—The adsorption of fulvic acid by goethite was determined experimentally as a function of concentration, pH, and ionic strength. The data were described with the CD-MUSIC model of Hiemstra and Van Riemsdijk (1996), which allows the distribution of charge of the bound fulvate molecule over a surface region. Simultaneously, the concentration, pH, and salt dependency of the binding of fulvic acid can be described. Using the same parameters, the basic charging behavior of the goethite in the absence of fulvic acid could be described well. The surface species used in the model indicate that inner sphere coordination of carboxylic groups of the fulvate molecule is important at low pH, whereas at high pH the outer sphere coordination with reactive groups of the fulvate molecule with high proton affinity is important. *Copyright* © 1999 Elsevier Science Ltd

### 1. INTRODUCTION

Metal (hydr)oxides play an important role in the adsorption and transport of organic substances in many natural aquatic systems. Retention of organic acids by geo colloids influences the mobility of organic matter and also the physical/chemical behavior of the geo colloids. In the last two decades, a considerable amount of work has been published on the binding of weak organic acids (Balistrieri and Murray, 1986; Ali and Dzombak, 1996; Filius et al., 1997) and organic matter by minerals (Parfitt et al., 1977b; Tipping, 1981; Davis, 1982; Jardine et al., 1989; Gu et al., 1994 and 1995; Wershaw et al., 1995). The results show that the adsorption of organic acids by mineral surfaces is dependent on pH and electrolyte concentration. The organic acids are bound over a large pH range, even at pH values well above the point of zero charge (PZC) of the adsorbing surface.

Gu et al. (1995) investigated the binding of natural organic matter (NOM) by hematite using FTIR spectroscopy. They found that both carboxylic and hydroxyl groups are involved in the binding of NOM by hematite. Kaiser et al. (1997) showed similar results for organic matter binding by goethite. In order to provide further insight into the mechanisms and functional groups that are involved in the interactions, Gu et al. (1995) and Evanko and Dzombak (1998) studied the pH-dependent adsorption of organic acids containing carboxylic or phenolic groups. Compounds with carboxylic groups show an adsorption maximum at low pH, whereas compounds containing phenolic groups show a maximum at high pH. This suggests that carboxylic groups are relatively important for the binding of NOM at low pH, whereas hydroxyl groups are relatively important at high pH. Similar conclusions follow from the work of Kummert and Stumm (1980) on the adsorption of catechol and benzoic acid on Al<sub>2</sub>O<sub>3</sub>.

Only a few attempts were made to model the adsorption of NOM. To date, most studies modeling NOM sorption by mineral surfaces employ sorption isotherms (Tipping, 1981; Gu et

al., 1994; Van de Weerd et al., 1999). This approach is quite limiting in the sense that the model is only applicable under limited conditions (e.g., constant pH, ionic strength, and competing ion concentration). A first attempt to include the charging and binding of NOM in speciation calculations is made by Karlton (1998). However his study discusses the binding of fulvic acid (FA) for a rather small set of data (1 adsorption edge with or without SO<sub>4</sub><sup>2-</sup> present at constant ionic strength). Vermeer et al. (1998) simulated the binding of humic acid by hematite by using polyelectrolyte adsorption theory. Their model calculations suggest internal induction of charge, resulting in a more positively charged oxide surface and more negatively charged humic acid. This suggests the proton reactive groups of the humics and the hematite internally titrate each other.

In this paper, the adsorption of FA by goethite is studied. FA was chosen as a model compound for NOM because FA molecules are highly soluble and relatively small. This enables distinction between the different functional groups of the acid. The aim of the present study is to include the pH- and salt-dependent binding of FA by goethite in speciation calculations. For this purpose, the binding of FA by goethite is measured in batch equilibration experiments as a function of pH, FA concentration, and ionic strength. The approach we use here is built upon the insights gained from the description of the binding of relatively small, well-defined weak organic acids by goethite (Filius et al., 1997).

#### 1.1. Model Description

##### 1.1.1. The CD-MUSIC model

In this study, we will use the CD-MUSIC (Charge Distributed Multi Site Complexation) approach in order to describe the binding of FA by goethite. For more details about this approach, refer to Hiemstra and Van Riemsdijk (1996).

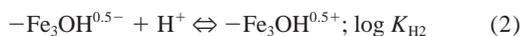
Following Hiemstra and Van Riemsdijk (1996), the charging behavior of the goethite in absence of FA can be described

\* Authors to whom correspondence should be addressed: (Willem. VanRiemsdijk@bodschenben.wau.nl); or (D.Lumsdon@mluri.sari.ac.uk).

Table 1. Basic physical chemical parameters used for the description of the charging behavior of the goethite.

A:	94 m <sup>2</sup> /g
C:	0.9 F/m <sup>2</sup>
N <sub>s</sub> (FeOH):	3.45 s/nm <sup>2</sup>
N <sub>s</sub> (Fe <sub>3</sub> O):	2.7 s/nm <sup>2</sup>
PPZC:	9.2
log K <sub>Na+</sub>	-1
log K <sub>NO<sub>3</sub>-</sub>	-1

assuming the protonation of singly and triply coordinated surface groups according to:



The proton affinity constants ( $K_{\text{H1}}$  and  $K_{\text{H2}}$ ) are set equal to the pristine point of zero charge (PPZC) of the goethite.

In addition to the protonation of surface groups, the formation of ion pairs influences the charging behavior of the surface.

The charging behavior of goethite can be described using the Basic Stern model. Protons are located in the surface plane (0-plane), whereas the ion pair formers are present at the head end of the diffuse double layer (1-plane) (Hiemstra and Van Riemsdijk, 1996.). The Stern layer has a capacitance,  $C$ , which for goethite is approximately 0.9 F/m<sup>2</sup>. This capacitance is found by fitting the model to the charging curves of the goethite. It is possible to interpret the capacitance value in terms of a distance,  $d$ , if the dielectric constant is known. Both are related according to:

$$C = \frac{\epsilon_0 \epsilon_r}{d} \quad (3)$$

At the interface, the dielectric properties change from a high value at the solution side ( $\epsilon_r$ , water = 80) to a low value in the solid ( $\epsilon_r$ , goethite = 11). Assuming an average relative dielectric constant between the 0- and 1-plane of 45 the separation between the 0- and 1-plane is 0.44 nm, approximately 1½ water molecule.

Table 1 lists the parameters used for the description of the charging behavior of the goethite used.

## 1.2. The Binding of Organic Anions

Filius et al. (1997) were able to describe the binding of several well-defined weak organic acids with the CD-MUSIC model. Based on the size and structure of the adsorbed polyprotic weak organic acids, a distribution of charge of the

complexed organic molecule over three electrostatic planes was assumed. Filius et al. (1997) distinguished between the formation of inner sphere complexes and outer sphere complexes. The carboxylic groups are assumed to bind as inner sphere complexes with singly coordinated surface groups (Parfitt, 1977a; reaction 1 of Table 2) or outer sphere complexes with both singly and triply coordinated surface groups (reactions 2 and 3 of Table 2). Hydroxyl groups bind only as outer sphere complexes (reactions 4 and 5 of Table 2). An equal distribution of the charge from a carboxylate group ( $\text{COO}^{-1}$ ) over both oxygens was assumed. Each oxygen of a carboxylate thus carries half a unit negative charge ( $-0.5$  vu). Inner sphere complex formation of the carboxylate oxygen with a Fe ion in the surface leads to a full neutralization of the bridged oxygen since the Pauling charge (Pauling, 1929) of a Fe–O bond equals  $+0.5$  vu. Filius et al. (1997) did not assume inner sphere interaction with organic hydroxyl groups (R–COH) because this leads to undersaturation of the common ligand charge ( $-0.5$  vu) if Fe–O–C–R is formed or overcompensation if Fe–OH–C–R is formed ( $+0.5$  vu). For cases in which inner sphere formation occurs, an oxygen of the carboxylate group exchanges for a singly coordinated surface group (Parfitt et al. 1977a). In the ligand exchange process,  $-0.5$  vu of the coordinating carboxylate oxygen is located in the 0-plane. The  $-0.5$  vu of the second carboxylate oxygen is located in the 1-plane (see Table 2).

Outer sphere complexes can be formed as a result of H-bond formation between carboxylate and hydroxyl groups of the organic molecule and singly and triply coordinated surface groups. In the present MUSIC model, the charge of the surface proton is fully attributed to the surface oxygen, although H-bonds may transfer charge between, for instance, the oxygens of the surface and water molecules in solution (Hiemstra et al., 1996). This simplification can be accepted as long as the strength of the H-bonds is not changed in the adsorption process. According to Brown (1978), the H-bond involved in organic complexes can be stronger than the H-bond between water molecules. This implies that extra charge will be transferred between the surface and the 1-plane due to the stronger H-bond. This extra charge transfer agrees with the infrared spectra of adsorbed catechol (Gu et al., 1995), salicylate, and NOM bound by goethite (Yost et al., 1990; Gu et al., 1995; Kaiser et al., 1997). In these spectra, a strong single band appears around 1270/cm. Novack (1974) showed empirically that low infrared frequencies are correlated with smaller O–O distances, which leads to more symmetrical H-bonds. If the band around 1270/cm is attributed to H-bonds, we estimate that the H-bond transfers between 0.2 (H-bond with H<sub>2</sub>O) and 0.5

Table 2. Reaction equations for the reactions possible to occur on the surface with the corresponding change of charge ( $\Delta z_i$ ) in plane<sub>*i*</sub>.

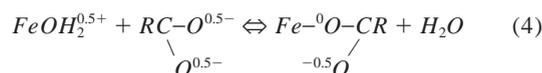
	Reactions	$\Delta z_0$	$\Delta z_i$
1	$-\text{FeOH}^{0.5-} + \text{H}^+ + \text{RCOO}^- \Leftrightarrow -\text{FeOOCR}^{0.5-} + \text{H}_2\text{O}$	+0.5	-0.5
2	$-\text{FeOH}^{0.5-} + \text{H}^+ + \text{RCOO}^- \Leftrightarrow -\text{FeOH}_2 \cdot \cdot \text{OOCR}^{0.5-}$	+0.8	-0.8
3	$-\text{Fe}_3\text{O}^{0.5-} + \text{H}^+ + \text{RCOO}^- \Leftrightarrow -\text{Fe}_3\text{OH} \cdot \cdot \text{OOCR}^{0.5-}$	+0.8	-0.8
4	$-\text{FeOH}^{0.5-} + \text{H}^+ + \text{RCO}^- \Leftrightarrow -\text{FeOH}_2 \cdot \cdot \text{OCR}^{0.5-}$	+0.8	-0.8
5	$-\text{Fe}_3\text{O}^{0.5-} + \text{H}^+ + \text{RCO}^- \Leftrightarrow -\text{Fe}_3\text{OH} \cdot \cdot \text{OCR}^{0.5-}$	+0.8	-0.8

In the change of charge in the 0-plane ( $\Delta z_0$ ), the charge of the proton is also included.

vu (symmetrical H-bond). According to Filius et al. (1997), this extra charge transfer equals about 0.2 vu. It means that in case of H-bonding, the charge contribution of the proton to the surface plane will be 0.2 vu smaller. A value of 0.2 vu flows to the 1-plane (see Table 2).

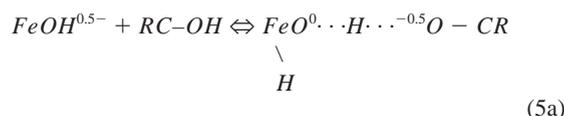
Gu et al. (1995) and Evanko and Dzombak (1998) studied the binding of anions containing carboxylic and/or phenolic groups. Both studies show that compounds containing carboxylic groups have their adsorption maximum at low pH, whereas compounds containing phenolic groups have their adsorption maximum at high pH. This adsorption behavior is similar to adsorption behavior of anions and cations, respectively. The pH dependence of ion adsorption is directly related to the macroscopic "exchange" with protons. Co-adsorption of protons leads to a decrease of the adsorption with increasing pH, whereas release of protons leads to an increase of adsorption with increasing pH.

At low pH, the goethite surface is positively charged. In solution carboxylic groups can be deprotonated even at low pH. Therefore carboxylic groups can bind as anions according to:

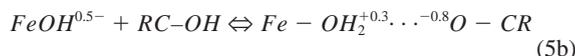


This reaction will cause a co-adsorption of protons (or release of OH<sup>-</sup>) due to the near-Nernstian behavior of the surface.

The opposite holds for the binding of phenolic groups to the goethite surface. At high pH, the surface is negatively charged and the phenolic group in solution is uncharged. The adsorption behavior of a phenolic group can be explained assuming that the proton from the hydroxyl group of the catechol molecule protonates (or "titrates") a surface hydroxyl groups forming an H-bond:



or



In Eqn. 5a, the depicted H-bond is symmetrical. In this study, the charge distribution of the H-bond is based on the extra transfer of charge due to differences in the strength of the H-bonds between the surface and organic complexes or H<sub>2</sub>O (see Eqn. 5b).

Part of the positive charge of the proton is now attributed to the surface plane. Due to the near-Nernstian behavior of the surface charge this will result in a net release of protons.

## 2. MATERIALS AND METHODS

### 2.1. Goethite

Goethite preparation was based on the procedure of Atkinson et al. (1967) and is described in more detail by Hiemstra et al. (1989). The BET-N<sub>2</sub> surface area of the sample was 94 m<sup>2</sup>/g.

### 2.2. Fulvic Acid Extraction

Soil humic and fulvic acids were extracted from a soil by using methods based on those recommended by the International Humic Substances Society (Aiken et al., 1979; Swift, 1996). The soil used was a Bs horizon from a peaty podzol (Strichen association). Soil, 1 kg, was extracted in 10 dm<sup>3</sup> of redistilled 1 M hydrochloric acid for 24 h and then centrifuged at 10,000 × *g* using a Alpha Laval centrifugal separator. The supernatant was retained and pumped onto a column of XAD-8 resin [poly(methyl methacrylate)]. The column was then water-washed and the FA fraction 1 was removed from the column using 0.1 M NaOH. The recovered material (FA fraction 1) was acidified and retained for further treatment.

The soil residue was rolled in 10 dm<sup>3</sup> of 0.1 M NaOH for 4 h and then left to stand overnight. The suspension containing the extracted humic material was removed from the remaining sediment and centrifuged to remove additional mineral material. The suspension was then acidified to pH 1.3 by using 6 M hydrochloric acid and left to stand for up to 48 h to allow the precipitated humic acid fraction to settle. The supernatant remaining after precipitation of the humic acid (FA fraction 2) was removed from the humic acid and pumped onto the XAD-8 column. The column was water-washed and FA fraction 2 was back eluted from the column with 0.1 M NaOH then acidified with 6 M HCl. At this stage, both FA fractions were combined and pumped onto the XAD-8 column. Following removal from the XAD-8 the Strichen fulvic acid (SFA) was treated with Amberlite resin 120 in the H<sup>+</sup> form (1 h), pH 2.3, then freeze-dried and stored for further use.

### 2.3 Potentiometric Titrations

Potentiometric titrations were carried out at two electrolyte concentrations (0.01 and 0.1 M NaCl) by using the automated Wallingford titrator (Kinniburgh et al., 1995). Fifty-five milligrams of SFA was dissolved in 50 mL Milli-Q water giving a concentration of 1.1 g/L. Carbon dioxide was excluded by using a thermostated reaction vessel under a nitrogen atmosphere. The pH was read by a pH electrode calibrated with pH 4.005 and 6.857 buffers before and after each titration. A single calomel reference electrode was connected to the vessel via an electrolyte bridge (0.1 M KNO<sub>3</sub>). The electrode readings were stable within drifts of 0.2 mV/min. The titration of the FA included 2 up and down cycles carried out at increasing ionic strength. Before the start of the first titration cycle, the solution was titrated with 0.1 M NaOH to approximately pH 10.5. NaCl was added to obtain the initial ionic strength. Data points were collected at approximately 5 mV intervals in the range of -200 mV to 200 mV (pH range 3.8–10.6). After finishing the first acid and base titration, NaCl was added to obtain the ionic strength for the second cycle.

### 2.4 Data Analyses

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

$$\log f = 0.51 * z^2 * \left\{ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 * I \right\} \quad (6)$$

Blank correction was carried out by calculating, for each data point, 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.

### 2.5 Adsorption Experiments

The FA adsorption by goethite was measured in background electrolytes of 0.01 M and 0.1 M NaNO<sub>3</sub>, using a batch equilibration procedure. Samples for equilibration were prepared by adding 1 mL of NaNO<sub>3</sub> (0.2 or 2 M) to a series of polyethylene vessels, followed by 1.5, 3, or 6 mL of a FA stock solution containing 1 g of FA/L. The pH was adjusted by adding various amounts of 0.1 M HNO<sub>3</sub> to give pH values in the range from 3 to 11. Then ultrapure water (UV-oxidized) was added to bring the volume in the vessels to 10 mL. Finally, 10 mL

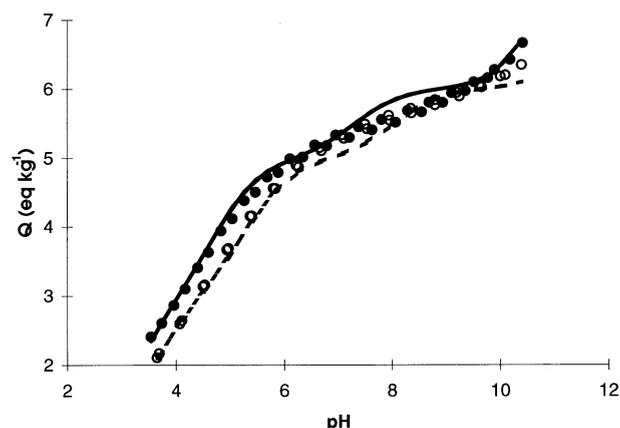


Fig. 1. Charging behavior of SFA in 0.1 (solid line and symbols) and 0.01M (dotted line and open symbols) NaCl. The lines are fitted using 8 discrete log  $K_H$  values for the different sites.

of a goethite suspension (10 g/L) was added to each vessel to bring the total volume to 20 mL. During each addition, the vessels were  $N_2$ -sparged to avoid  $CO_2$  contamination. The suspensions were equilibrated for 72 h in an end-over-end shaker in the dark. To avoid possible artefacts introduced from filtering, the equilibrium supernatant was separated from the solid phase by centrifugation ( $26,500 \times g$  for 30 min). Samples of the supernatant were taken for total organic carbon (TOC) analysis (samples were acidified and immediately analyzed with a Skalar SK12 Organic Carbon Analyzer). The pH of the solutions was measured in the remaining supernatant using an electrode that was calibrated (EMF–pH relationship) with standard pH 4.00 and 7.01 buffers (Merck, Darmstadt, Germany, accurate to  $\pm 0.01$ ). The amount of FA adsorbed was determined from the difference between the initial and final FA concentrations in the equilibrating solution. The initial FA solution concentration was calculated from experimental blanks treated as above, but in the absence of goethite.

The model calculations were carried out with the computer program Orchestra (Meeussen et al., 1997).

### 3. RESULTS

#### 3.1. Fulvic Acid in Solution

The charging behavior of the SFA is given in Figure 1. Similar charging behavior of FA was found in several studies (Ephraim et al., 1986; Christensen et al., 1998). The data show an increase in negative charge of the FA with increasing pH. Furthermore the data show very little salt dependency.

Often the charging behavior of FA in solution is described using a site-binding model with a continuous distribution of affinity constants. The site-binding model is combined with a double layer model that accounts for electrostatic effects (De Wit et al., 1993b; Milne et al., 1995; Benedetti et al., 1996). According to De Wit et al. (1993a) FAs are relatively small molecules, which can easily be seen as small rigid particles. Based on their small size and small ionic strength-dependent charging behavior we will treat the FA in this study as small molecules (like citrate or EDTA). Although FA is a mixture of molecules with a range of molecular sizes and number of reactive groups, we assume a constant molecular weight and a constant, discrete number of reactive groups of the FA molecules. The molecular weight is set to 1000 Dalton (Hansen and Schnitzer, 1969; Aiken et al., 1985; Xu et al., 1989). The total number of reactive groups of the FA is estimated using the

Table 3. Number of carboxylic and phenolic groups of the SFA.

	NICA-Donnan <sup>a</sup> (meq/g)	%	This study <sup>b</sup> (mol eq/mol)
Total	8.38	100	8
Carboxylic	5.56	66	5
Phenolic	2.82	33	3

1 meq/g equals 1 mol eq/mol because the molar mass of FA is taken as 1000 g/mol. Therefore, 1 meq/g is equal to 1 group per FA molecule.

<sup>a</sup> Fitted with the NICA-Donnan model, <sup>b</sup> used in the present study.

NICA-Donnan model (Benedetti et al., 1996). Table 3 shows the number of reactive groups used in the NICA-Donnan model required to fit the charging behavior of the SFA. The numbers used in the present study are presented in the last column of Table 3. The numbers found agree with the numbers obtained by Christensen et al. (1998).

The proton affinity constants (Table 4) are fitted to the FA charge data using the speciation program ECOSAT (Keizer and Van Riemsdijk, 1994) coupled with Kinniburgh's FIT software (Kinniburgh, 1993). In this approach, the proton affinity constants depend on the type of activity correction used for the FA. For simplicity, the activity coefficients of salt ions, protons, and FA in solution are calculated using the Davies equation (Eqn. 6). The Davies equation is often used to calculate the activity coefficient of small ions. With this simplified approach it is possible to get a reasonable agreement between data and model description using the Davies equation. The lines in Figure 1 represent the model description.

In this approach, the FA contributes to the ionic strength. The presence of the FA (1.1 g/L  $\approx$  1.1 mmol/L) affects the ionic strength up to a factor 4 at low salt levels. However, model calculations using low FA concentrations (not affecting the ionic strength) show that the change in ionic strength due to FA only affects the charging behavior of FA significantly at pH > 10.

#### 3.2. Adsorption of FA by Goethite

Figure 2 shows the binding of SFA by goethite. The data set covers a broad range of conditions.

Over the whole pH range investigated, sorption of FA by goethite was found. At pH values below the PZC (PZC = 9.2), the goethite surface and the FA have an opposite charge. This

Table 4. Protonation reactions of FA-reactive groups in solution and corresponding affinity constants.

$FAH^{8-} + H^+ \Leftrightarrow FAH_1^{7-}$	$\log K_{H1} = 12.45$
$FAH_1^{7-} + H^+ \Leftrightarrow FAH_2^{6-}$	$\log K_{H2} = 11.97$
$FAH_2^{6-} + H^+ \Leftrightarrow FAH_3^{5-}$	$\log K_{H3} = 8.54$
-----	
$FAH_3^{5-} + H^+ \Leftrightarrow FAH_4^{4-}$	$\log K_{H4} = 6.07$
$FAH_4^{4-} + H^+ \Leftrightarrow FAH_5^{3-}$	$\log K_{H5} = 5.30$
$FAH_5^{3-} + H^+ \Leftrightarrow FAH_6^{2-}$	$\log K_{H6} = 4.12$
$FAH_6^{2-} + H^+ \Leftrightarrow FAH_7^{1-}$	$\log K_{H7} = 3.40$
$FAH_7^{1-} + H^+ \Leftrightarrow FAH_8^0$	$\log K_{H8} = 1.67$

The reactive groups above the dashed line are believed to be hydroxyl groups. The reactive groups below the dashed line are believed to be carboxylic groups.

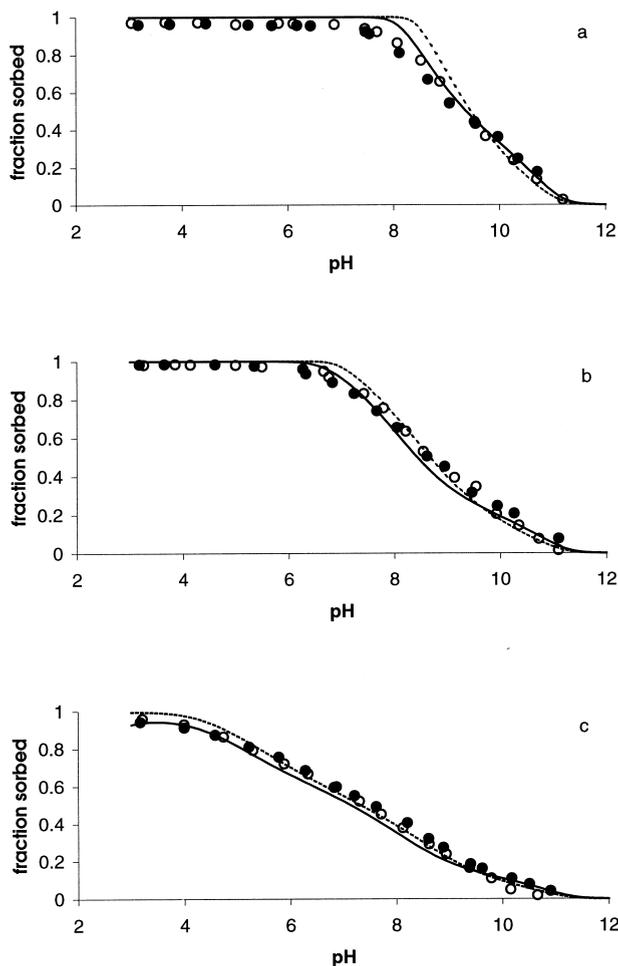


Fig. 2. Adsorption envelopes of SFA binding by goethite in 0.01 M (open symbols and dotted lines) and 0.1 M  $\text{NaNO}_3$  (solid symbols and full lines). The suspension density of goethite is 5 g/L and three total concentration of FA are used: (1) 75 mg/L; (2) 150 mg/L; and (3) 300 mg/L. The lines indicate model calculations.

results in a high adsorption of FA. At pH values above the PZC, the goethite surface and the FA are both negatively charged. Despite the electrostatic repulsion a considerable amount of FA is adsorbed by the goethite.

The salt dependency of the FA binding by goethite is negligible within the experimental error of the data over the entire pH range.

### 3.3. Modeling the Sorption Data

Mechanistic modeling requires the introduction of the basic physical chemical surface characteristics. The description of the FA adsorption by goethite is built upon the framework that describes both the charging behavior of the goethite surface and the charging behavior of the FA in solution. The same parameter values as given in Tables 1 and 4 are used in the description of SFA adsorption. Furthermore, it is assumed that the charging behavior of the reactive groups of adsorbed FA can be described using the same proton affinity constants as in solution (Table 4).

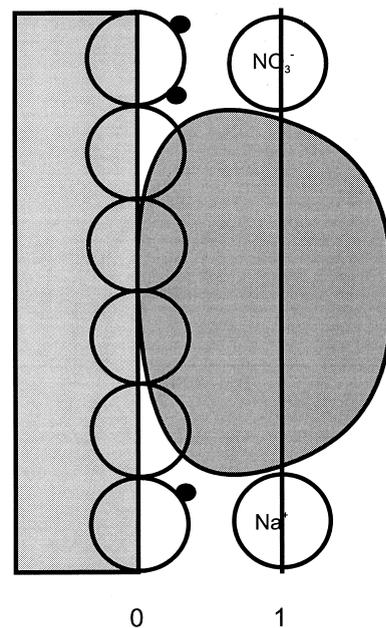


Fig. 3. Schematic representation of adsorbed fulvic acid on the goethite surface. The lines (0- and 1-plane) indicate the boundaries of the Stern layer.

Compared to the size of a proton, the FA is a large molecule with a considerable number of reactive groups. If one is interested to model the adsorption with surface species that may have physical significance it is obvious that the charge of the bound FA should not be regarded as being a point charge. The charge of the bound molecule is distributed to some extent into solution (Fig. 3). There are no experimental data available that quantify this distance. De Wit et al. (1993a,b) estimated an average spherical radius for FA in solution of 0.75 nm. This value is in agreement with the radii deduced from viscometry by Avena et al. (1999). The extent to which the adsorbed fulvate molecule will protrude into the solution is at the most similar in magnitude to the diameter of the molecule in solution. However, the configuration of the FA molecule is likely to be flattened as a result of the coordination with the surface. Vermeer et al. (1998) suggested that humic acid molecules adsorb relatively flat on the mineral surface at high pH and have a reduced contact with the surface at low pH. Due to this reduced contact it is expected that the bound FA molecules will protrude further into solution at low pH. However, the charge of these noncoordinated groups is low due to the protonation of the reactive groups at low pH. Therefore, we assume that only a limited amount of charge protrudes into solution. In the present study, the negative charge of groups on the fulvate molecule that are not directly involved in the inner and outer sphere coordination to the surface is located in the 1-plane.

### 3.4. Affinity Constants

Following Filius et al. (1997) we assume that the FA molecules can become bound by the surface due to ligand exchange or H-bond formation. The overall log  $K$  of the surface complexation reaction of FA consists of the summation of the

Table 5. Affinity constants for ligand exchange and H-bonding.

$\log K_{\text{exch}}$ :	-0.45
$\log K_{\text{h-b,carb}}$ :	1.26
$\log K_{\text{h-b,phen}}$ :	5.21

affinities of the protonation of the coordinating surface groups, the formation of inner and outer sphere complexes, and the protonation of noncoordinated fulvate groups. An example of the calculation of the overall  $\log K$  is given in Appendix A.

- The affinity constants for the ligand exchange reaction and H-bond formation (reactions 1–5 of Table 2, respectively) are assumed to be constant. The constants are found by curve fitting and listed in Table 5.
- The intrinsic proton affinity for the reactive groups of the fulvate molecule are the same on the surface as they are in solution (see Table 4).
- The FA groups with the highest proton affinity may become protonated.
- H-bonds are formed between surface groups and FA groups. It is assumed that the FA group with the highest proton affinity will be preferred in H-bond forming with the surface except the groups orientated towards the solution that are protonated (see previous point).

### 3.5. Degrees of Freedom and Constraints

There are several degrees of freedom left in the modeling:

- the affinity constants for ligand exchange and the formation of an H-bond,
- the number of groups involved in ligand exchange ( $k$ ),
- the number of groups forming an H-bond ( $l$ ),
- the number of noncoordinated groups that may become protonated ( $n$ ),

where  $k$ ,  $l$ , and  $n$  refer to the coefficients used in Table 6 in order to calculate the change in charge in the electrostatic planes.

However, there is a constraint to the degrees of freedom mentioned:

- the total number of reactive groups per fulvate molecule equals 8.

This gives a total of four degrees of freedom in the model.

Table 6. Calculation scheme for the change of charge in the electrostatic planes of the CD MUSIC model.

$$\Delta z_0 = k \cdot z_{\text{O}} + (k + 1) \cdot z_{\text{H}} - 1 \cdot \Delta s_{\text{O} \cdots \text{H}}$$

$$\Delta z_1 = m \cdot z_{\text{O}} + n \cdot z_{\text{H}} + 1 \cdot \Delta s_{\text{O} \cdots \text{H}}$$

$\Delta z_i$ , change of charge in plane  $i$ ;  $z_{\text{O}}$ ,  $z_{\text{H}}$ , charge of, respectively, carboxylate or hydroxyl oxygens and protons;  $\Delta s_{\text{O} \cdots \text{H}}$ , change of charge due to change in strength of H-bonds;  $k$ ,  $n$ , coefficients corresponding to the various quantities. Note that  $z_{\text{O}}$  is  $-0.5$  for a carboxylate oxygen and  $-1$  for a hydroxyl oxygen.

### 3.6. Number of Surface Species

FA molecules can bind in many different configurations to the surface. The total number of possible surface species is approximately 10,000. However, in case of inner or outer sphere complexation, the model cannot differentiate between the reactive groups that are deprotonated. Still, the model can distinguish between more than 1000 different surface species. To limit this number, we assume that the reactive FA groups will form complexes in the order of: protons > outer sphere > inner sphere. This means that in the surface complexation of a FA molecule with 1 inner sphere complex, 1 outer sphere complex, and 1 protonated group, the reactive group with the highest proton affinity is protonated, the second highest proton affinity group forms an outer sphere complex, and one of the rest of the groups forms an inner sphere complex. This assumption limits the number of possible surface species to approximately 100.

The number of possible species is further limited by the chemical characteristics of the FA binding. The protonation of the noncoordinated FA groups will be influenced by the electric field near the surface. At low pH, protons are repelled from the positively charged surface. The pH near the surface ( $\text{pH}_s$ ) is higher than in solution. At high pH,  $\text{pH}_s$  is lower than in solution due to the attraction of protons. This electrostatic effect results in a smaller pH window near the surface than in solution. At low pH, fewer reactive groups of the bound FA will be protonated than in solution. At high pH, the opposite holds. This reduces the number of possible surface species. Also, at high pH the electrostatic repulsion has to be overcome by the chemical energy of the H-bond formation. In cases in which more H-bonds are formed, more chemical energy is involved.

For model purposes it is not convenient to use a large number of surface species. Therefore, we try to model the data with a minimum number of species. In this study, we will try to determine the most important surface species that can account for the effect of concentration, pH, and salt on the binding of fulvate molecules. Apart from simplicity, the chosen approach will also give more insight in the main factors that dominate the binding behavior of FA on variable charge minerals.

### 3.7. Model Results

The lines in Figure 2 represent the model description of the data. Four surface species are required to obtain a satisfactory description. The assumed surface species, charge distribution, and affinity constants for the model description are given in Table 7. Using this set of surface species the adsorption of FA as function of pH, FA concentration, and ionic strength is described well. Figure 4 shows the relative contribution of the different surface species to the total binding of the fulvate by goethite.

At  $\text{pH} > 5$ , the binding is described using a surface species with 4 H-bonds. Note that it has been assumed that the groups with the highest proton affinity are considered to participate in the H-bond formation. At high pH, the rest of the reactive groups are deprotonated. At lower pH, the two phenolic groups with highest proton affinities are not involved in H-bonding

Table 7. Surface species assumed for describing the adsorption of Strichen fulvic acid by goethite.

Species	Surface site	H	FA	logK	$\Delta z_0$	$\Delta z_1$
$\text{Fe}_{(4)}(\text{OH}_2)_3\text{FAH}_3^{-3}$	1 + 3	7	1	73.0	2.9	-3.9
$\text{Fe}_{(4)}(\text{OH}_2)_4\text{FAH}_2^{-4}$	0 + 4	6	1	70.2	3.2	-5.2
$\text{Fe}_{(4)}(\text{OH}_2)_4\text{FAH}^{-5}$	0 + 4	5	1	62.2	3.2	-6.2
$\text{Fe}_{(4)}(\text{OH}_2)_4\text{FA}^{-6}$	0 + 4	4	1	53.7	3.2	-7.2

**Note:** The subscripts between brackets indicate the number of goethite surface groups involved in the goethite-fulvate complex. The subscript after (OH<sub>2</sub>) indicates the number of outer sphere complexes. The difference between both subscripts is the number of inner sphere complexes.  $\text{Fe}_{(4)}(\text{OH}_2)_3\text{FAH}_3$ , 4 outer and 1 inner sphere bond, the hydroxyl groups remain protonated;  $\text{Fe}_{(4)}(\text{OH}_2)_4\text{FAH}_2$ , 4 outer sphere bonds, two hydroxyl groups with highest  $\log K_H$  remain protonated;  $\text{Fe}_{(4)}(\text{OH}_2)_4\text{FAH}$ , 4 outer sphere bonds, hydroxyl group with highest  $\log K_H$  remains protonated (see also Appendix A).

with the surface, but are assumed to be orientated towards the solution and to be protonated.

At  $\text{pH} < 5$ , the data give little information because the two lowest FA additions are almost fully adsorbed by the goethite. The adsorption of the highest FA addition can be modeled assuming one inner and three outer sphere complexes and all phenolic groups protonated.

#### 4. DISCUSSION

The surface species used to describe the SFA binding data are based on three macroscopic binding characteristics: (1) pH dependency; (2) concentration dependency; and (3) salt dependency. These three characteristics are strongly related to the structure of the adsorbed species and the electrostatic potential profile near the surface.

Figure 4 shows that at low pH the surface species with inner and outer sphere complexation are important whereas at high pH outer sphere complexation is important. The pH dependence of the formation of inner and outer sphere complexes might be explained by the differences in the change of the

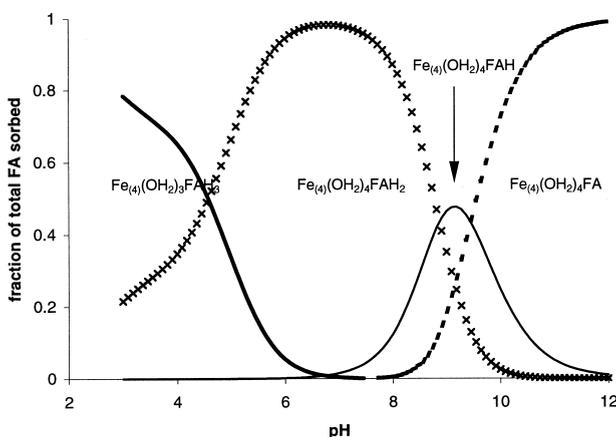


Fig. 4. The contribution to the total adsorption of the three surface species used to describe the FA binding by goethite for a  $\text{FA}_{\text{tot}}$  concentration of 300 mg/L and a background electrolyte concentration of 0.1 M.

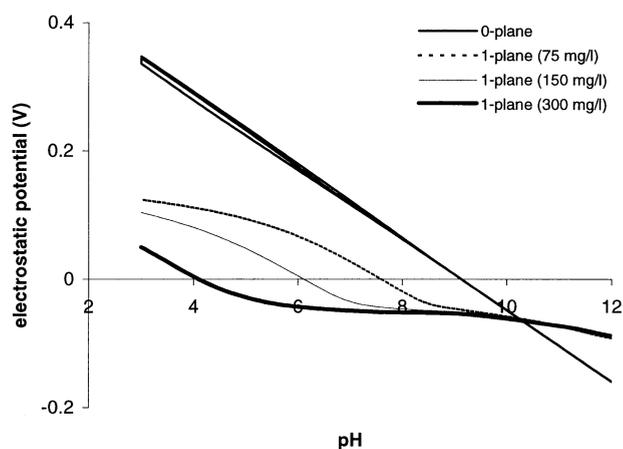


Fig. 5. Electrostatic potential of the 0- and 1-plane as function of pH for the three FA additions and a background electrolyte concentration of 0.1 M. Legend is in the same order as the model lines. The calculation of the 0-plane shows the three lines for the different FA additions.

standard Gibbs free energy ( $\Delta G_r^0$ ) and the electrical energy ( $\Delta G_{e1}$ ) of the reactions.

The change in standard Gibbs free energy can be related to the intrinsic affinity constant of the reaction ( $\log K_{\text{int}} \equiv -\Delta G_r^0 / 2.3RT$ ) and the change in electrical energy is determined by the electrostatic potential ( $\Delta G_{e1}$ ). The intrinsic affinity constants for the formation of inner and outer sphere complexes are constants (Table 5), whereas the electrostatic potential is a variable that depends on pH, ionic strength, and surface coverage. Figure 5 shows the electrostatic potential in the 0- and 1-plane. The potential in the 0-plane shows near-Nernstian behavior. At low pH, there is a high positive potential which decreases with increasing pH. The potential in the 1-plane depends on pH, ionic strength, and surface coverage.

The intrinsic affinity for the formation of outer sphere FA-surface complexes is much higher than for inner sphere complexes. Nevertheless, at low pH inner sphere complexes are found to be important for the binding of organic material (Gu et al., 1995; Kaiser et al., 1997; Nordin et al., 1998). This can be explained by the changes in electrical energy. In both inner and outer sphere complexation negative charge of the anion is distributed over the 0- and 1-plane. At low pH, the positive potential of the 0-plane is much higher than in the 1-plane. In the case of inner sphere complexation, more negative charge is located in the 0-plane. Therefore, the electrical energy gained during inner sphere complexation is much larger than for outer sphere complexation. At low pH the sum of the change in standard Gibbs free energy and the electric energy ( $\Delta G_r^0 + \Delta G_{e1}$ ) is higher for inner sphere complexation than for outer sphere complexation. With increasing pH the difference between the electrostatic potential in the 0- and 1-plane decreases strongly. This means that less electric energy is gained by the location of negative charge in the 0-plane instead of the 1-plane. Therefore, its larger intrinsic affinity favors the formation of outer sphere complexes.

At pH values above the PZC the electrostatic potential in both planes is negative. For adsorption the electrostatic repulsion between surface and FA molecule has to be overcome. The

intrinsic affinity of phenolic FA groups for outer sphere complexation is large (see Table 5). Furthermore, the electrical energy gained by the location of the proton of the phenolic group in the negative 0-plane is larger than the loss of energy due to the corresponding negative charge of the phenolate group in the 1-plane. This results in a reduced electrostatic repulsion.

#### 4.1. pH Dependency

The binding of FA by goethite is strongly dependent on pH. In systems with FA and goethite present there are three types of reactions involving protons: (1) protonation of FA in solution; (2) protonation of reactive goethite surface groups; and (3) proton co-adsorption/desorption upon FA adsorption.

The description of the first two types of reactions is determined by the charging behavior of the FA in solution and the goethite in absence of FA. The co-adsorption/desorption of protons upon the adsorption of FA is the only unknown type of reaction and is directly related to the pH dependency of the adsorption.

Several authors (Fokkink et al., 1987; Venema et al., 1996; Rietra et al., 1999) discussed the proton (or hydroxyl) exchange ratio of ion adsorption. They showed that the exchange ratio depends on the charge of the ion and the location of the charge at a finite distance from the surface. The charge and charge distribution of adsorbed FA molecules are determined by the number of inner and outer sphere complexes formed and the protonation of non-coordinated reactive groups of the sorbed FA. It is assumed that the proton affinity of the non-coordinated reactive groups of the sorbed FA is the same as in solution. Therefore the number of inner and outer sphere complexes of each surface species and the relative contribution of each surface species to the total adsorption (determined by the affinity constants of inner and outer sphere complexes) determines the proton exchange ratio and the pH dependence of FA adsorption.

#### 4.2. Concentration Dependency

In Figure 6, adsorption isotherms of fulvate by goethite are given at three pH values and two ionic strengths. The data in Figure 6 are obtained from using smooth interpolation of the adsorption envelopes. The lines are model descriptions based on the parameters obtained in this study. Figure 6 illustrates the high-affinity character of the binding at low FA concentrations. For weak organic acids Filius et al. (1997) showed that the increase in the slope of the adsorption isotherms at low concentrations is related to the number of reactive acid functional groups involved in the binding between organic anion and the surface. The FA adsorption data reveal a steeper adsorption isotherm than for the citrate data of Filius et al., which is consistent with the proposed number of coordinating groups assumed for the FA.

After the high affinity part, the adsorption isotherm in Figure 6 shows a plateau. The effects of elevated surface loading and/or electrostatics might explain the observed adsorption plateau. With increasing adsorption more of the goethite surface becomes covered by FA. Therefore, each additional FA molecule has less surface to which it can bind. Statistically, this

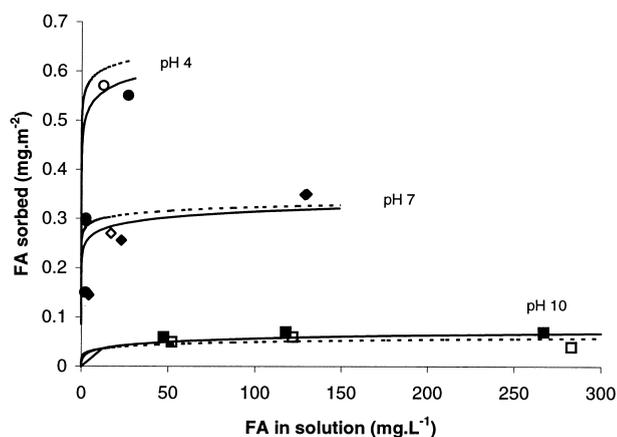


Fig. 6. Model predicted adsorption isotherms for FA adsorption by goethite at different pH values. Open symbols show experimental data at 0.01 M (model calculated, dashed line) and closed symbols data at 0.1 M (model, solid line).

means that the chance an additional FA molecule can bind becomes smaller. This effect results in a reduced slope of the adsorption isotherm with increasing surface loading. At high surface loading an adsorption plateau can occur long before the surface is physically saturated with FA molecules. In our model this effect is accounted for by multiplying the overall affinity constant by the term  $(1 - \theta)^n$ , in which  $\theta$  is the surface coverage (number of sites involved in inner or outer sphere formation as fraction of the total number of sites) and  $n$  is the number of inner and outer sphere complexes formed per bound molecule. At pH 4 and highest FA concentration, the surface coverage is approximately 0.25 times the theoretical maximum. Note that the adsorbed molecule covers most probably a larger area than the  $n$  sites due to the physical size of the molecule. This affects the binding statistics. In the present approach, this is not taken into account.

A second cause of the adsorption plateau is the behavior of the surface charge. Due to the sorption of FA the surface becomes less positive (or more negative). Therefore, each additional molecule is less attracted (or more repelled) by the goethite surface. With increasing adsorption this means a reduced slope of the adsorption isotherm. This effect can cause an adsorption plateau in case of charge reversal. In our model calculations we don't observe charge reversal at low pH. Therefore, the observed plateau cannot solely be explained by electrostatics. Most likely a combination of increased surface loading and electrostatics cause the observed adsorption plateau.

#### 4.3. Salt Dependency

In case of FA adsorption by goethite we can distinguish between two situations: (1) the FA and goethite are both charged negatively (high pH); and (2) the FA and goethite are charged oppositely (low pH). When both components are charged equally, the adsorption is favored by a higher background electrolyte concentration. The charge of both components is screened more effectively. This will result in less electrostatic repulsion between the two components. In case FA and goethite are oppositely charged the goethite surface charge

can either be neutralized by bound FA or by  $\text{NO}_3^-$  pair formation.

The experimental data do not show any salt dependency. Due to the strong adsorption at low pH, all FA is adsorbed at the two lowest FA additions. This gives little information about the salt dependency. For the highest FA addition the electrostatic potential in the 1-plane is very low. This might explain the lack of salt dependency observed in the data at low pH. Model calculations show (data not shown) that at high pH the protonation of the solution-orientated reactive groups increases at decreasing ionic strength. When the charge reduction near the surface due to protonation of the solution-orientated groups is in the same order of magnitude as the reduction of charge due to the difference in ion pair formation this might explain the absence of the salt dependency at high pH.

The model describes the salt dependency adequately at both low and high pH as illustrated in Figures 2 and 6.

## 5. CONCLUSIONS

FA is bound over a wide range of pH values reaching well above the PZC of the goethite. The adsorption of FA by goethite can be described well with the CD-MUSIC model.

The data set of FA binding is relatively large although little information can be gained from the data at low pH. Regardful of the assumptions made, the data can be described with only four surface species. Interpretation of the charge distribution of the assumed surface species is consistent with the assumption of outer sphere coordination at high pH and inner sphere coordination at low pH. The same types of mechanisms are proposed for the binding of compounds containing carboxylic and phenolic groups respectively.

The affinity constant for the ligand exchange of a carboxylate oxygen of the fulvate molecule and a surface water group is very low, indicating a low chemical affinity and a strong electrostatic interaction at low pH. The intrinsic affinity constant for the formation of H-bonds is higher and the electrostatic interaction is less than for the inner sphere complexes. At high pH (weak electrostatic attraction or repulsion) outer sphere formation in the FA-surface complex out-competes the inner sphere formation due to the high chemical energy involved in outer sphere complexation. At low pH the reverse is the case because the electrostatic contribution of inner sphere complexes is stronger dependent on pH. Therefore at low pH the combination of a low intrinsic affinity and a high electrostatic contribution of inner sphere complexes out-competes the formation of outer sphere complexes.

The fulvate adsorption isotherms show a steep slope at low FA concentrations followed by a pseudo plateau at higher concentrations. The effects of increased surface loading and electrostatics most probably cause the plateau.

The FA adsorption data show little salt dependency. The model describes the salt dependency accurately.

*Acknowledgments*—The authors thank Pat Cooper and Stefan Jansen for their assistance with the experiments and preliminary interpretation of the results. This research was partly funded by the Scottish Office Agriculture, Environment and Fisheries Department (SOAEFD) as part of its Soils and the Environment program. The reviewers of *Geochimica et Cosmochimica Acta* are gratefully acknowledged for their helpful comments on the manuscript.

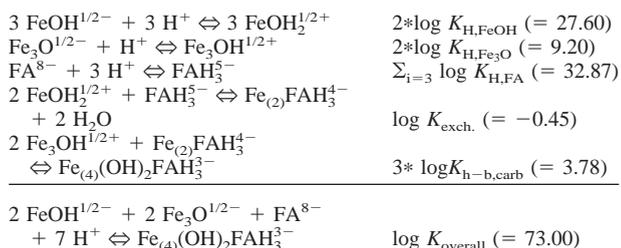
## REFERENCES

- Ali M. A. and Dzombak D. A. (1996) Competitive sorption of simple organic acids and sulfate on goethite. *Environ. Sci. Technol.* **26**, 2357–2364.
- Aiken G. R., Thurman E. M., Malcolm R. L., and Walton H. F. (1979) Comparison of XAD macroporous resins for the concentration of fulvic acid from aqueous solution. *Anal. Chim. Acta* **51**, 1799–1803.
- Aiken G. R., McKnight D. M., Wershaw R. L., and MacCarthy P. (1985) *Humic Substances in Soil, Sediment, and Water*. Wiley Interscience.
- Atkinson R. J., Posner A. M., and Quirk J. P. (1967) Adsorption of potential-determining ions at the ferric oxide-aqueous electrolyte interface. *J. Phys. Chem.* **71**, 550–558.
- Avena M. J., Koopal L. K., and Van Riemsdijk W. H. (1999) Proton binding to humic acids. Electrostatic and specific interactions. *J. Colloid Interface Sci.* **217**, 37–48.
- Balistreri 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.
- 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.
- Brown E. D. (1978) Bond Valence: A simple structural model for inorganic chemistry. *Chem. Soc. Rev.* **7**, 359–376.
- Christensen J. B., Tipping E., Kinniburgh D. G., Gron C., and Christensen T. H. (1998) Proton binding by groundwater fulvic acids of different age, origin and structure modelled 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.
- De Wit J. C. M., Van Riemsdijk W. H., and Koopal, L. K. (1993a) Proton binding to humic substances: 1. Electrostatic effects. *Environ. Sci. Technol.* **27**, 2005–2014.
- De Wit J. C. M., Van Riemsdijk W. H., and Koopal, L. K. (1993b) Proton binding to humic substances: 2. Chemical heterogeneity and adsorption models. *Environ. Sci. Technol.* **27**, 2015–2022.
- Ephraim J., Alegret S., Mathuthu A., Bicking M., Malcolm R. L., and Marinsky J. A. (1986) A united physicochemical description of the protonation and metal ion complexation equilibria of natural organic acids (humic and fulvic acids). 2. Influence of polyelectrolyte properties and functional group heterogeneity on the proton equilibria of fulvic acid. *Environ. Sci. Technol.* **20**, 354–366.
- Evanko C. R. and Dzombak D. A. (1998) Influence of structural features on sorption of NOM-analogue organic acids to goethite. *Environ. Sci. Technol.* **32**, 2846–2855.
- 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.
- Fokink L. G. J., de Keizer A., and Lyklema J. (1987) Specific ion adsorption on oxides. *J. Colloid Interface Sci.* **118**, 454–462.
- 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.
- Hansen E. H. and Schnitzer M. (1969) Molecular weight measurements of polycarboxylic acids in water by vapor pressure osmometry. *Anal. Chim. Acta* **46**, 247–254.
- Hiemstra T. and Van Riemsdijk W. H. (1996) A structural approach to ion adsorption: The charge distribution model. *J. Colloid Interface Sci.* **179**, 488–508.
- Hiemstra T., De Wit J. C. M., and Van Riemsdijk W. H. (1989) 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**, 105–117.
- Hiemstra T., Venema P., and Van Riemsdijk W. H. (1996) Intrinsic proton affinity of reactive surface groups of Metal (hydr)oxides: Application to Iron (hydr)oxides. *J. Colloid Interface Sci.* **184**, 680–692.
- Jardine P. M., Weber N. L., and McCarthy J. F. (1989) Mechanisms of

- dissolved organic carbon adsorption on soil. *Soil Sci. Soc. Am. J.* **53**, 1378–1385.
- Kaiser K., Guggenberger G., Haumaier L., and Zech W. (1997) Dissolved organic matter sorption on subsoils and minerals studied by <sup>13</sup>C-NMR and DRIFT spectroscopy. *Europ. J. Soil Sci.* **48**, 301–310.
- Karltun E. (1998) Modelling SO<sub>4</sub><sup>2-</sup> surface complexation on variable charge minerals. II. Competition between SO<sub>4</sub><sup>2-</sup>, oxalate and fulvate. *Europ. J. Soil Sci.* **49**, 113–120.
- Keizer M. G. and Van Riemsdijk W. H. (1994) ECOSAT; Technical report of the Department of Soil Science and Plant Nutrition; Wageningen Agricultural University.
- Kinniburgh D. G., Milne C. J., and Venema P. (1995) Design and construction of a personal-computer based automatic titrator. *Soil Sci. Soc. Am. J.* **59**, 417–422.
- Kinniburgh D. G. (1993) Technical Report WD/93/23: FIT User Guide. British Geological Survey.
- Kummert R. and Stumm W. (1980) The surface complexation of organic acids on hydrous γ-Al<sub>2</sub>O<sub>3</sub>. *J. Colloid Interface Sci.* **75**, 373–385.
- Meeussen J. C. L., Meeussen V. C. S., and Lumsdon D. G. (1997) An efficient object orientated numerical approach for calculating chemical equilibria in combination with transport. In *Hydroinformatics '96*. (ed. A. Mueller), pp. 557–564. Balkema.
- Milne C. J., Kinniburgh D. G., De Wit J. C. M., Van Riemsdijk W. H., and Koopal L. K. (1995) Analysis of metal-ion binding by Peat Humic Acid using a simple electrostatic model. *J. Colloid Interface Sci.* **175**, 448–460.
- Nordin J., Persson P., Nordin A., and Sjöberg S. (1998) Inner-sphere and outer-sphere complexation of a polycarboxylic acid at the water-boehmite (γ-AlOOH) interface: A combined potentiometric and IR spectroscopic study. *Langmuir* **14**, 3655–3662.
- Novack A. (1974) Hydrogen bonding in solids. Correlation of spectroscopic and crystallographic data. In *Structure and Bonding* (ed. J. D. Dunitz, P. Hemmerich, J. A. Ibers, J. B. Neilands, R. J. P. Williams), Vol. 18, pp. 177–216. Springer Verlag.
- 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.
- Pauling L. (1929) The principles determining the structure of complex ionic crystals. *J. Am. Chem. Soc.* **51**, 1010–1026.
- Rietra R. P. J., Hiemstra T., and Van Riemsdijk W. H. (1999) The relationship between molecular structure and ion adsorption on variable charge minerals. *Geochim. Cosmochim. Acta*, in press
- Swift R. S. (1996) Organic matter characterization. In *Methods of Soil Analysis. Part 3. Chemical Methods—SSSA Book Series no 5*, pp. 1011–1069. Soil Science Society of America and American Society of Agronomy.
- Tipping E. (1981) The adsorption of aquatic humic substances by iron oxides. *Geochim. Cosmochim. Acta* **45**, 191–199.
- Van de Weerd H., Leijnse A., and Van Riemsdijk W. H. (1999) Modeling the dynamic adsorption/desorption of a NOM mixture: Effects of physical and chemical heterogeneity. *Environ. Sci. Technol.* **33**, 1675–1681.
- 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. I. Specific and electrostatic interactions. *Langmuir* **14**, 2810–2819.
- Wershaw R. L., Leenheer J. A., Sperline R. P., Song Y., Noll L. A., Melvin R. L., Rigatti G. P. (1995) Mechanisms of formation of humus coatings on mineral surfaces 3. Composition of adsorbed organic acids from compost leachate on alumina. *Colloids Surf.* **96**, 93–104.
- Xu H., Ephraim J., Ledin A., and Allard B. (1989) Effects of fulvic acid on the adsorption of Cd(II) on aluminol. *Sci. Total Environ.* **81/82**, 653–660.
- Yost E. C., Tejedor-Tejedor M. I., and Anderson M. A. (1990) In situ CIR-FTIR characterization of salicylate complexes at the goethite/aqueous solution interface. *Environ. Sci. Technol.* **24**, 822–828.

## APPENDIX

For the first surface species of Table 7, we show how we calculated the overall affinity constant.



The subscripts between brackets indicate the number of goethite surface groups involved in the goethite–fulvate complex, not the number of Fe atoms involved. Note that the formation of H-bonds is represented here by bonds with triply coordinated sites, although it is assumed also to take place with singly coordinated sites. In our equilibrium calculation scheme, we accounted for the formation of H-bonds with two different surface groups by defining a surface species with H-bonds with singly coordinated groups and an additional surface species with H-bonds with triply coordinated groups. Defining surface species with mixed H-bonds did not change the results. Therefore these species are disregarded.