*Colloids and Surfaces*, 2 (1980) 2 (1981) 101—117
© Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

# THE INTERACTION OF ANIONS AND WEAK ACIDS WITH THE HYDROUS GOETHITE (α-FeOOH) SURFACE

**LAURA SIGG and WERNER STUMM**

*Institute of Aquatic Sciences (EAWAG), Swiss Federal Institute of Technology, Zürich (Switzerland)*

(Received August 20th, 1979; accepted in final form February 19th, 1980)

## ABSTRACT

Adsorption of $F^-$, $SO_4^{2-}$, acetate, $H_2SiO_4^{2-}$, $PO_4^{3-}$ and their conjugate acids on the surface of α-FeOOH (goethite) has been investigated with acid—base titrations and adsorption experiments. A surface complexation model is used to describe the dependence of the extent of adsorption on pH and other solution variables. A set of equilibrium constants has been determined which permits calculation of the amount bound to the surface and of the surface charge as a function of pH and total concentrations. The equilibrium constants for the adsorption of a series of ligands on the α-FeOOH surface can be correlated with the complex formation constants of the same ligands with $Fe^{3+}$ in solution.

## INTRODUCTION

Reactions of oxides in water systems with cations and anions are of importance (1) in regulating the concentration of certain components in natural waters; (2) in geochemical processes (congruent and incongruent dissolution processes, weathering, nucleation and precipitation reactions); and (3) in characterizing the colloid chemistry, especially the colloid stability of dispersed oxides. Naturally occurring oxides, like those of Si, Al and Fe(III) have large specific surface areas and have been shown to adsorb significant quantities of cations and anions. Thus they are believed to play a role for the transport of heavy metals and of anions like phosphate into the sediments.

Hydrous oxide surfaces contain surface hydroxyl groups (4—10 OH groups per $nm^2$) which exhibit amphoteric behavior, they can be compared at least operationally with amphoteric polyelectrolytes [1—3]

$$\equiv MeOH_2^+ \rightleftarrows \equiv MeOH + H^+; \qquad K^s_{a_1} \tag{1}$$

$$\equiv MeOH \rightleftarrows \equiv MeO^- + H^+; \qquad K^s_{a_2} \tag{2}$$

The OH-group on a hydrous oxide surface has a complex-forming oxygen donor group like $OH^-$ or OH or O groups attached to other elements (such as in phosphate, silicate, carboxylate). Thus, metal ions may, at least operationally, coordinate with the coordinating sites of the surface.

EXHIBIT
tabbies
78

$$\equiv\mathrm{MeOH} + \mathrm{M}^{z+} \rightleftarrows \equiv\mathrm{MeOM}^{(z-1)} + \mathrm{H}^{+}; \qquad K_1^s \qquad (3)$$

$$\begin{matrix}=\mathrm{MeOH}\\=\mathrm{MeOH}\end{matrix} + \mathrm{M}^{z+} \rightleftarrows \begin{matrix}=\mathrm{MeO}\\=\mathrm{MeO}\end{matrix}\!> \mathrm{M}^{(z-2)} + 2\mathrm{H}^{+}; \qquad \beta_2^s \qquad (4)$$

Surface coordination equilibrium constants have been used to describe quantitatively the interaction of cations with oxide surfaces. Similarly the metal ion at the oxide surface may be treated as a Lewis acid; the $\mathrm{OH}^-$ ion may then be replaced by other coordinating ligands (ligand exchange)

$$\equiv\mathrm{MeOH} + \mathrm{A}^{z-} \rightleftarrows \equiv\mathrm{MeA}^{(z-1)} + \mathrm{OH}^{-} \qquad (5)$$

$$\begin{matrix}=\mathrm{MeOH}\\=\mathrm{MeOH}\end{matrix} + \mathrm{A}^{z-} \rightleftarrows \begin{matrix}=\mathrm{Me}\\=\mathrm{Me}\end{matrix}\!>\mathrm{A}^{(z-2)} + 2\mathrm{OH}^{-} \qquad (6)$$

The objective of this paper is to illustrate that this simple ligand-exchange model is able to explain and predict, at least semi-quantitatively, the main features of the anion adsorption (extent of adsorption as a function of pH and solution variables) at the hydrous oxide surface. $\alpha$-FeOOH (goethite) was chosen as a model oxide surface representative of interfaces encountered in natural waters; it has a zero point of charge $\mathrm{pH_{zpc}} \approx 7$, so that adsorption on positive and negative surfaces can be examined. Its interaction with acetic acid, silicic acid, sulfate, phosphate and fluoride was investigated. These anions and weak acids were selected because they offer a range of acid—base properties ($\mathrm{p}K_a$ values) and different coordinating tendencies and numbers of protons and because they are representative of substances indigeneously present in natural waters.

Several authors have investigated the adsorption of anions and proposed different models for its description. Quirk et al. investigated different anions and weak acids at the $\alpha$-FeOOH surface [4—8]; they showed a relationship between the $\mathrm{p}K_a$ of weak acids and the pH optimum of adsorption. Anderson [9] treated the adsorption of arsenate on $\gamma$-$\mathrm{Al_2O_3}$ as a process involving electrostatic and chemical interaction; electrophoretic measurements and determination of adsorbed quantities at zero surface charge allow a distinction between the chemical and the electrostatic contribution to the adsorption energy. Huang [10] applied the James-Healy model of adsorption [11] to the adsorption of phosphate at the $\gamma$-$\mathrm{Al_2O_3}$ surface, while Gupta [12] interpreted the binding of phosphate to iron oxide with a coordination model similar to that presented in this paper. Yates and Healy [14] studied the adsorption of nitrate, sulfate and phosphate on goethite and $\alpha$-chromia surfaces and examined whether anion adsorption in these systems involves ligand exchange with surface groups. The work described here is based in part on the Ph.D. Thesis of L. Sigg [15].

## EXPERIMENTAL METHODS

### *Materials*

$\alpha$-FeOOH has been prepared according to the procedure given by Quirk [8]. The resulting suspension was washed by centrifugation. $\alpha$-FeOOH was identified by X-ray diffraction. The specific surface area, determined by BET measurement was 29 $m^2$ $g^{-1}$ for $\alpha$-FeOOH I and 28 $m^2$ $g^{-1}$ for preparation II ($\alpha$-FeOOH II). (These samples were prepared at different times.)

### *Titration curves*

$\alpha$-FeOOH was titrated acidimetrically (and/or alkalimetrically) in the presence of an inert electrolyte medium (0.1 M $NaClO_4$) and in the absence and presence of specifically adsorbing anions. As equilibration of surface reactions is a slow process, the titrations were performed as batch experiments, i.e., to aliquots of goethite suspensions contained in a multitude of volumetric flasks various increments of strong acid or base were added. During the equilibration time the flasks remained stoppered (without air space above the solution) to avoid contamination with $CO_2$. For each point of the titration curve a separate sample of total volume $V$ = 25 ml was prepared, containing: 1—6 g $l^{-1}$ $\alpha$-FeOOH(s); 0.1 M $NaClO_4$; various concentrations of strong acid, $c_A$, or base, $c_B$, respectively, and in the case of adsorption experiments with an anion, the anion concentration was varied between $1 \cdot 10^{-4}$—$1 \cdot 10^{-3}$ M.

pH was measured potentiometrically by a glass electrode, using an electrolyte bridge and an Ag/AgCl reference electrode.

### *Total exchange capacity*

The total exchange capacity, ($\equiv FeOH_T$), i.e., the maximum number of exchangeable OH groups at the surface, was determined by two different procedures. (1) To an $\alpha$-FeOOH suspension an excess of strong acid or base was added; after equilibration the solid phase was separated, and the remaining acid (or base) in the supernatant was back-titrated. This procedure gives $\equiv FeOH_T = 2 \cdot 10^{-4}$ mol $g^{-1}$ $\simeq$ 4 OH-groups per $nm^2$. (2) An excess of fluoride was added to an $\alpha$-FeOOH suspension; the pH was maintained constant at 5.5. After equilibration either the remaining $F^-$ in the solution or the quantity of $F^-$ bound to the surface (desorption by raising the pH to 7.5) was measured. This method gives $\equiv FeOH_T = 3.5 \cdot 10^{-4}$ mol $g^{-1}$ $\simeq$ 6—7 OH-groups per $nm^2$.

Both experimentally obtained values are lower than the theoretically calculated ones [16]. Since different kinds of OH groups may belong to the surface, depending on the coordination type and geometric situation, their reactivity may differ. For calculations the value $2 \cdot 10^{-4}$ mol $g^{-1}$ was used, which may be the most realistic one for exchange with cations and anions.

### *Adsorption measurements*

Adsorption of fluoride, sulfate, acetate, silicate and phosphate has been investigated as a function of pH and total concentrations of specifically adsorbable anions. The samples were prepared as described for the titration curves. After measurement of the equilibrium pH, the solid phase was separated by filtration through a 0.45-μm filter, and the remaining concentration of the anion was measured in the supernatant solution.

$F^-$ was measured directly in the suspension with an $F^-$ selective electrode; $SO_4^{2-}$ was measured by the methyl thymol blue method [17]; acetate was determined by gas chromatography. Because of small differences in concentration, the extent of adsorption could not be measured very precisely; silicate was determined by the molybdate blue method (adsorption at 660 nm); phosphate was determined by the molybdate blue method; the absorption was measured at 700 nm.

*Kinetics*

The adsorption of fluoride at a constant pH (=6) was measured as a function of time. After about five minutes the equilibrium concentration was nearly reached. The adsorbed quantities can be desorbed in the same time by raising the pH of the suspension.

The adsorption of phosphate is a slower reaction. A reasonably constant concentration is reached after about 48 h; this concentration is taken as the equilibrium concentration. A very slow reaction, especially at high pH values, is still going on after three weeks, giving some hints that after the adsorption step a new phase may be forming on the surface.

## THEORY AND DATA EVALUATION

In the model developed by Stumm et al. [1] and Schindler et al. [3], the specific adsorption of cations and anions is described as a surface coordination reaction in which cations substitute $H^+$ in the surface-OH groups (eqns (3), (4)) and anions bind directly to the metal ions of the metal oxide surface by replacing $OH^-$ (eqns (5), (6)). The free energy of the surface coordination reactions, as well as the acid—base properties of the surface OH-groups, are described with a set of equilibrium constants (Table 1).

These *equilibrium constants* were determined by measuring at various pH values and solute concentrations the extent of adsorption (surface coordination). The extent of adsorption can also be determined by comparing alkalimetric (or acidimetric) titration curves obtained in the presence and absence of the specifically adsorbable species (Tables 2 and 3).

On the basis of some evidences considered later, it is postulated that specifically adsorbed ligands are bound directly to the surface ("inner sphere complexes"); thus, these ligands are assumed to contribute to the surface charge in the same way as $H^+$ and $OH^-$ ions bound to the surface.

The *surface charge* and thus also the pH of the isoelectric point ($pH_{iep}$) and its displacement by specific adsorption can be determined directly from the titration curve (which gives that portion of the charge caused by the proton balance at the surface) *and* the extent of adsorption (which gives the

TABLE 1

Protolysis and ligand exchange equilibria of α-FeOOH

| | | | Intrinsic constant[a] (22°C) log $K$ | |
|---|---|---|---|---|
| $\equiv FeOH_2^+$ | $\rightleftarrows$ | $\equiv FeOH + H^+$ | − 6,4 | (1) |
| $\equiv FeOH$ | $\rightleftarrows$ | $\equiv FeO^- + H^+$ | − 9,25 | (2) |
| $\equiv FeOH + F^-$ | $\rightleftarrows$ | $\equiv FeF + OH^-$ | − 4.8 | (3) |
| $\equiv FeOH + SO_4^{2-}$ | $\rightleftarrows$ | $=FeSO_4^- + OH^-$ | − 5.8 | (4) |
| $2{=}FeOH + SO_4^{2-}$ | $\rightleftarrows$ | $=Fe_2SO_4 + 2OH^-$ | −13.5 | (5) |
| $=FeOH + HAc$ | $\rightleftarrows$ | $=FeAc + H_2O$ | 2.9 | (6) |
| $=FeOH + H_4SiO_4$ | $\rightleftarrows$ | $=FeSiO_4H_3 + H_2O$ | 4.1 | (7) |
| $=FeOH + H_4SiO_4$ | $\rightleftarrows$ | $=FeSiO_4H_2^- + H_3O^+$ | − 3.3 | (8) |
| $=FeOH + H_3PO_4$ | $\rightleftarrows$ | $=FePO_4H_2 + H_2O$ | 9.5 | (9) |
| $=FeOH + H_3PO_4$ | $\rightleftarrows$ | $=FePO_4H^- + H_3O^+$ | 5.1 | (10) |
| $=FeOH + H_3PO_4$ | $\rightleftarrows$ | $=FePO_4^{2-} + 2H^+ + H_2O$ | − 1.5 | (11) |
| $2{=}FeOH + H_3PO_4$ | $\rightleftarrows$ | $=Fe_2PO_4H + 2H_2O$ | 8.5[b] | (12) |
| $2{=}FeOH + H_3PO_4$ | $\rightleftarrows$ | $\equiv Fe_2PO_4^- + H^+ + 2H_2O$ | 4.5 | (13) |

[a] Equilibrium constants are defined as for example:

$$K_{a1}^s = \frac{[\equiv FeOH]\,[H^+]}{[\equiv FeOH_2^+]}$$

All concentrations are given in mol dm$^{-3}$.

[b] Bidentate equilibria are defined as:

$$K = \frac{[\equiv Fe_2PO_4H]}{[\equiv FeOH]\,[H_3PO_4]}.$$

charge caused by the bound anions) (Tables 2 and 3)

$$\sigma_0 = (\{\equiv MeOH_2^+\} - \{\equiv MeO^-\} - \Sigma\{\equiv MeA^{z-}\}) \cdot \frac{F}{S} \tag{7}$$

$$\sigma_0 = F(\Gamma_H - \Gamma_{OH} - (z-1)\Gamma_{A^{z-}}) \tag{8}$$

where $F$ is Faraday constant (C mol$^{-1}$), $\Gamma_H$, $\Gamma_{OH}$ and $\Gamma_{A^{z-}}$ are the adsorption densities (mol m$^{-2}$) of $H^+$ (and its complexes) of $OH^-$ and of the deprotonated anion, respectively, $\Sigma\{\equiv MeA^{z-}\}$ is the equivalent sum of ligand bound to the surface; $S$ is the specific surface area m$^2$ g$^{-1}$; the concentration of surface species (e.g., $\{\equiv MeOH_2^+\}$, $\{\equiv MeO^-\}$, $\{\equiv MeA^-\}$ are given in mol g$^{-1}$. (The concentration of surface species may also be expressed in mol per dm$^3$ solution: if no bidentate complexes are formed, equilibrium constants are independent of the choice of the units for the surface complexes*.

---

*In a bidentate reaction (6), the constant may be expressed as:

$$K = \frac{[\equiv Me_2A]\,[OH^-]^2}{[\equiv MeOH]^m\,[A^{z-}]}$$

$m = 2$ would mean that the formation of a second bond may occur with every other OH group.

$m = 1$ means that only one possibility of a second bond exists.

$1 < m < 2$ would be realistic; $m = 1$ was used in the calculations.

TABLE 2

**Displacement of titration curve**

All concentrations, also those of the surface species, are given in mol dm$^{-3}$; concentrations with a * are those in the presence of specifically adsorbable species.

Charge balance in absence of [F$^-$]:

$$C_A - C_B - [H^+] + [OH^-] = [\equiv FeOH_2^+] - [\equiv FeO^-] \qquad (1)$$

Charge balance in presence of adsorbed [F$^-$]:

$$^*C_A - {}^*C_B - [H^+] + [OH^-] - ([F^-]_T - [F^-]) = {}^*[\equiv FeOH_2^+] - {}^*[\equiv FeO^-] \qquad (2)$$

where $[F^-]_T - [F^-] = [\equiv FeF]$

Mass balance in presence of [F]:

$$[\equiv FeOH]_T = {}^*[\equiv FeOH] + {}^*[\equiv FeO^-] + {}^*[\equiv FeOH_2^+] + [\equiv FeF] \qquad (3)$$

Degree of protolysis:

$$^*\alpha_o = \frac{[\equiv FeOH_2^+]}{([\equiv FeOH]_T - [\equiv FeF])} \qquad {}^*\alpha_1 = \frac{[\equiv FeOH]}{([\equiv FeOH]_T - [\equiv FeF])}$$

$$^*\alpha_2 = \frac{[\equiv FeO^-]}{([\equiv FeOH]_T - [\equiv FeF])} \qquad (4)$$

$$\boxed{\Delta C = {}^*C_A - {}^*C_B - (C_A - C_B) = (1 + \alpha_2 - \alpha_o)\,[\equiv FeF]} \qquad (5)$$

TABLE 3

**Equations used in calculating the equilibria constants for the interaction with $H_4SiO_4$**

Concentrations given in { } have the units mol kg$^{-1}$. $a$ = quantity of oxide used (kg dm$^{-3}$).

$$[\equiv FeOH]_T = [\equiv FeOH_2^+] + [\equiv FeO^-] + [\equiv FeOH] + [\equiv FeH_3SiO_4] + [\equiv FeH_2SiO_4^-] \qquad (1)$$

$$[H_4SiO_4]_T = [H_4SiO_4] + [H_3SiO_4^-] + [\equiv FeH_3SiO_4] + [\equiv FeH_2SiO_4^-] \qquad (2)$$

$$Q = \{\equiv FeOH_2^+\} - \{\equiv FeO^-\} - \{\equiv FeH_2SiO_4^-\} \qquad [\text{mol g}^{-1}] \qquad (3)$$

One obtains after rearrangement:

$$Q' = a \cdot Q = [\equiv FeOH]\left(\frac{[H^+]}{Ka_1^s} - \frac{Ka_2^s}{[H^+]} - K_2^s\frac{[H_4SiO_4]}{[H^+]}\right)[\text{mol l}^{-1}] \qquad (4)$$

$$[H_4SiO_4]_T - [H_4SiO_4] - [H_3SiO_4^-] = [\equiv FeOH]\,(K_1^s[H_4SiO_4] + K_2^s[H_4SiO_4] \cdot [H^+]^{-1}) \qquad (5)$$

$$[\equiv FeOH] = ([FeOH]_T - [\equiv FeH_3SiO_4] - [\equiv FeH_2SiO_4^-])\left(\frac{[H^+]}{Ka_1^s} + 1 + \frac{Ka_2^s}{[H^+]}\right)^{-1} \qquad (6)$$

It is evident from this relation that the isoelectric point $pH_{iep}$ for which $\sigma_0 = 0$, is shifted by the adsorption of anions (cf. [20]). The surface charge $\sigma_0$ is compensated by ions of opposite charge in the Stern and diffuse layer. The specifically adsorbable species are typically present in a much smaller concentration than the inert electrolyte ions, so that only a negligible part of them is located in the diffuse layer.

Equilibrium constants for the surface interactions may depend on the surface charge because of the electrostatic influence of the charged surface groups in the interaction with ions. In the presence of an excess of inert electrolyte, a linear relationship between log $K$ and $\sigma_0$ is typically found:

$$\log K^s = \log K^s\,(\text{intr.}) \pm b\,\sigma_0 \qquad (9)$$

where $b$ is the slope.
By extrapolating to $\sigma_0 = 0$, an intrinsic equilibrium constant $K^s$ (intr.) is obtained. The linear regression (eqn. (9)) implies that the capacitance, $C$, which gives the proportionality between surface potential $\psi_0$ and surface charge, $C = \sigma_0/\psi_0$, is constant. Equation (10) can also be written as

$$\log K^s = \log K^s\,(\text{intr.}) + \frac{zF\psi_0}{2.3\,RT} \qquad (10)$$

## RESULTS

### *Acid—base properties of α-FeOOH*

Figure 1 gives the surface charge as a function of pH. It is calculated from the alkalimetric titration curve as

$$\sigma_0 = (\{\equiv MeOH_2^+\} - \{\equiv MeO^-\})\frac{F}{S} = (C_A - C_B - [H^+] + [OH^-])\frac{F}{a \cdot S} \qquad (11)$$

where $C_A$ and $C_B$ are the concentrations of strong acid and base (mol dm$^{-3}$) added, respectively, and $a$ is the concentration of FeOOH in the suspension (g dm$^{-3}$).

The dependence of p$K$ values on the charge is given by*:

$$pK^s_{a1} = 6.40 - 7.2\,\sigma_0 \qquad (12)$$

$$pK^s_{a2} = 9.25 - 4.4\,\sigma_0 \qquad (13)$$

The pH at zero point of charge and the values of the acidity constants are slightly dependent on the method by which goethite was prepared. Most

---

*Only the difference between positive and negative groups is measurable; it is not possible to distinguish between them. For the calculation of acidity constants it is assumed that only $\equiv MeOH_2^+$ is present in the acid part of the titration curve and only $\equiv MeO^-$ in the alkaline part. This assumption is justified if the difference $\Delta pK = pK^s_{a1} - pK^s_{a2}$ is large enough.

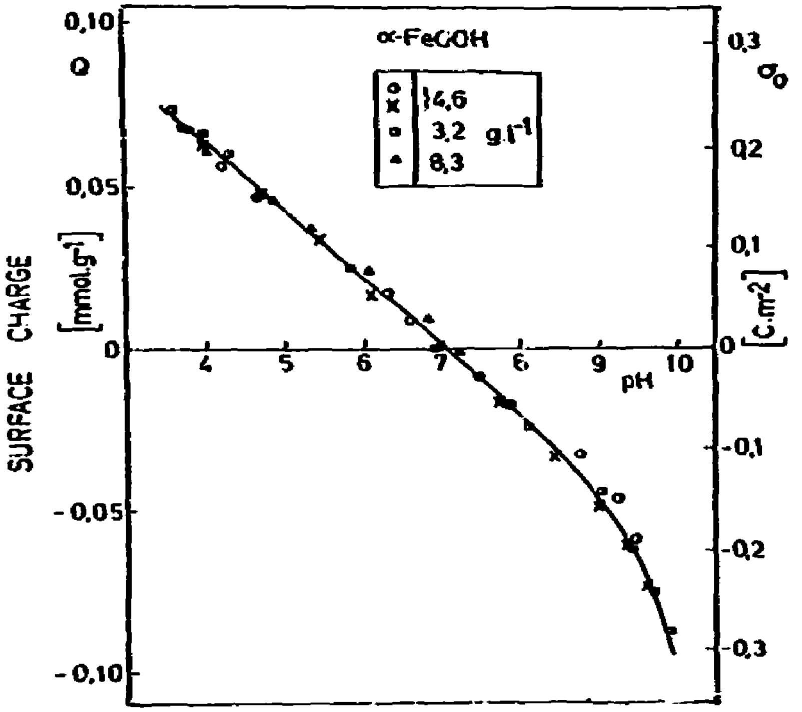

Fig. 1. Surface charge as a function of pH. The surface charge is calculated from alkalimetric and acidimetric titration curves (eqns (7), (8)).
The supporting electrolyte is 0.1 M $NaClO_4$.

likely several kinds of OH-groups may exist on the goethite surface (e.g., on edges or faces); the measured titration curves reflect an average over these OH-groups. The preparation of the goethite sample may affect the repartition of these OH-groups and thus the acidity constants.

### *Fluoride*

The shift in the titration curve (Fig. 2) caused by the surface coordination of $F^-$ ($\equiv FeOH + F^- \rightleftarrows \equiv FeF + OH^-$) is related to the quantity of $F^-$ bound as shown in Table 2.

The plot of the function $\Delta C/(1 + \alpha_2 - \alpha_0)$ vs. $[F^-]$ bound to the surface gives the number of $OH^-$ released per bound $F^-$ (Fig. 3b). The slope of 1 indicates that $F^-$ is stoichiometrically exchanged for $OH^-$ and that only monodentate surface complexes are formed. In Fig. 3a experimental data on $F^-$ binding are compared with curves calculated with the experimentally determined equilibrium constants (eqn (3), Table 1).

### *Sulfate*

Titration of α-FeOOH in the presence of sulfate results in a similar shift as

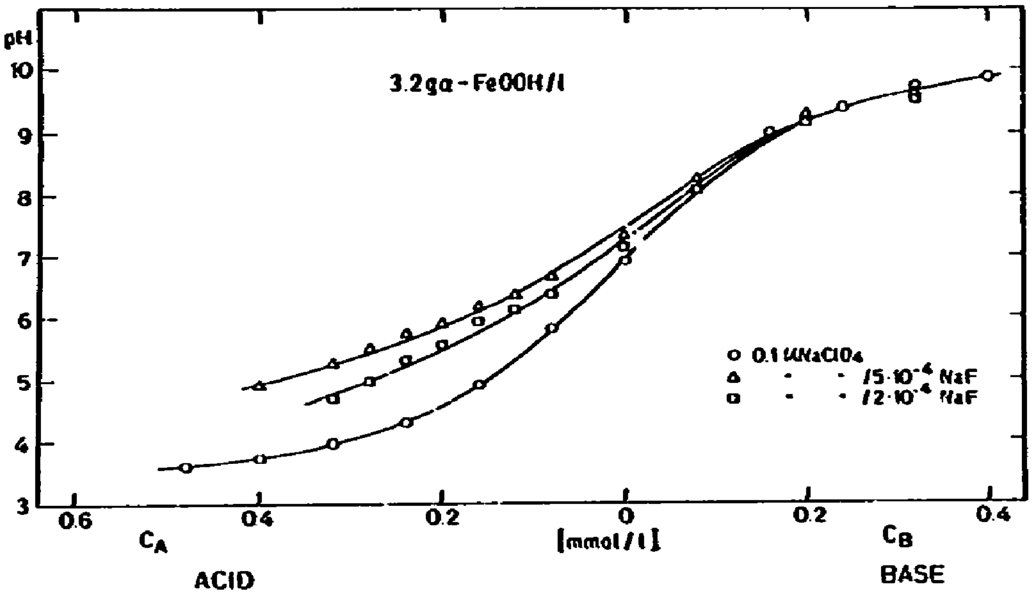

Fig. 2. The specific adsorption (surface coordination) of $F^-$ causes a displacement of the titration curve for α-FeOOH from which the extent of adsorption and the resulting surface charge can be calculated.

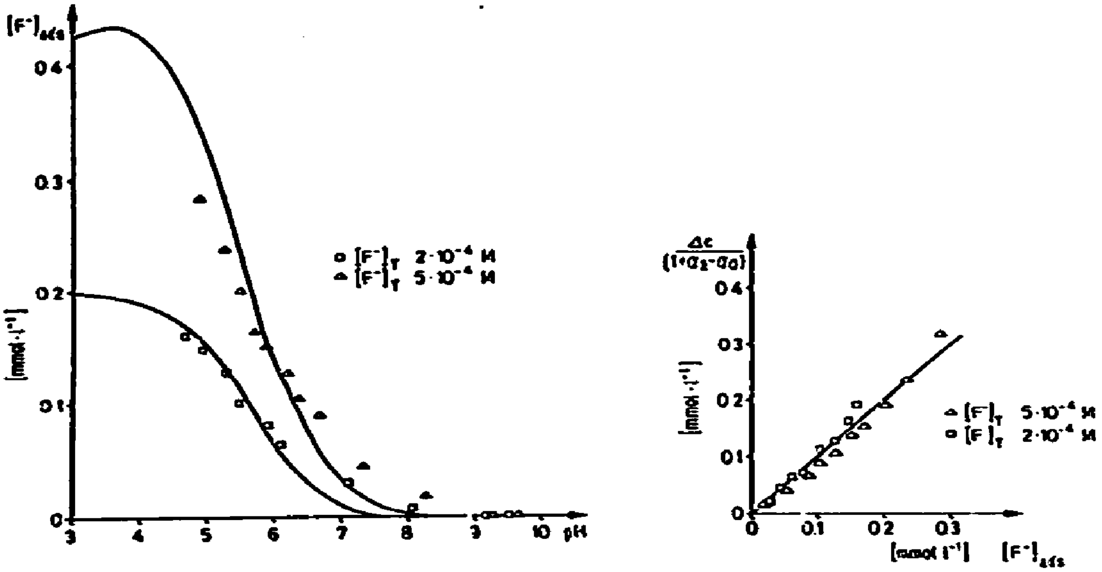

Fig. 3. (a). Extent of specific adsorption of $F^-$ on α-FeOOH. Curves were calculated from the experimentally determined equilibrium constant (eqn (3), Table 1). Points are experimental.

(b). Plot of the displacement of the titration curve (corrected for protolysis) versus the concentration of $F^-$ adsorbed (cf. eqn (5), Table 2). The slope of 1 indicates that monodentate surface complexes only are formed.

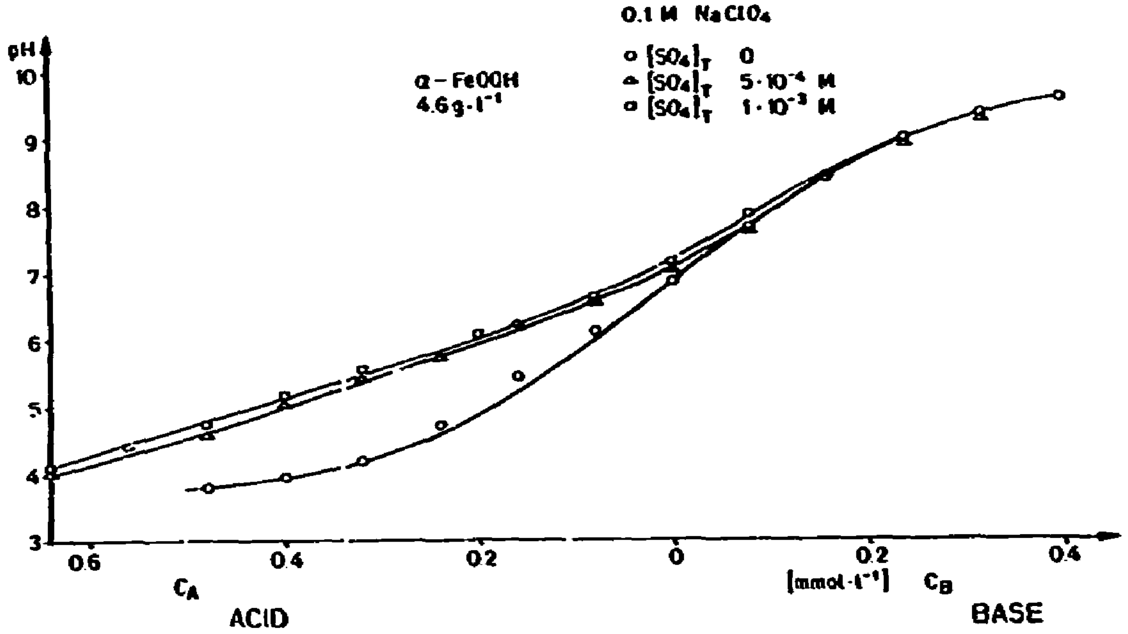

Fig. 4. The displacement of the titration curve of α-FeOOH caused by the specific adsorption of $SO_4^{2-}$.

in the presence of fluoride (Fig. 4). Two reactions are likely:

$$\equiv FeOH + SO_4^{2-} \rightleftarrows \equiv FeSO_4^- + OH^-; \qquad K_1^s$$

$$2\equiv FeOH + SO_4^{2-} \rightleftarrows \equiv Fe_2SO_4 + 2OH^-; \qquad \beta_2^s$$

The displacement of the titration curve (cf. Table 2) allows the calculation of [$\equiv FeSO_4^-$] and [$\equiv Fe_2SO_4$] and of the constants $K_1^s$ and $\beta_2^s$ (Table 1).

Constants calculated with these very simplified assumptions have a strong dependence on surface coverage; adsorption as calculated from these constants shows a not very good agreement with the experimental data (Fig. 5).

*Silicate*

$H_4SiO_4$ is considered as a diprotic acid in the pH range of the experiments. The titrations of α-FeOOH in the presence of silicate are shifted to lower pH-values, indicating a release of $H^+$ due to partial deprotonation of the adsorbed species (Fig. 6). The formation of $\equiv FeH_3SiO_4$ and $\equiv FeH_2SiO_4^-$ is taken into account [(7,8) in Table 1].

Table 3 illustrates how the equilibrium constants — as given in Table 1 — were calculated from the experimental data. $H_4SiO_4$ is adsorbed over a wide pH range (Fig. 7), with a maximum near pH 9.

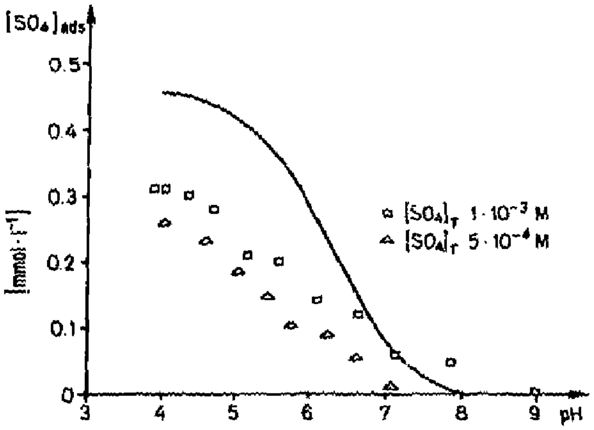

Fig. 5. Extent of adsorption of $SO_4^{2-}$ on $\alpha$-FeOOH. The curve is calculated from equilibrium constants for $[SO_4]_T = 5 \times 10^{-4}$ M (eqns (4), (5), Table 1). Points are experimental. The bad fit at low pH values may be caused by the difficulties involved in assessing the effects of $SO_4^{2-}$ modified surface charge.

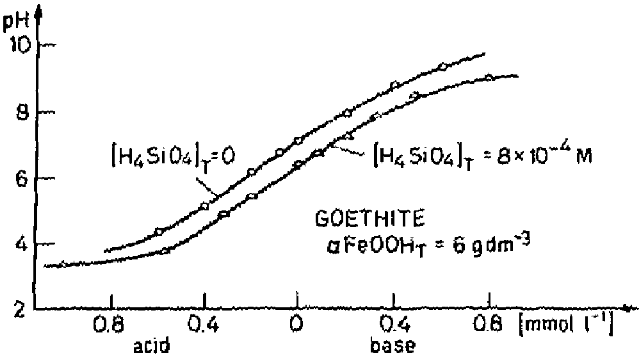

Fig. 6. The presence of $H_4SiO_4$ shifts the alkalimetric titration curve to lower pH values.

### *Phosphate*

For the interaction of phosphate with goethite various reactions (9--13 in Table 1) have to be taken into account. A similar scheme has been proposed by Gupta [12]. The best set of constants describing the experimental data was sought with the computer. The curves drawn and the distribution of the species as a function of pH obtained with the equilibrium constants (Table 1) are represented in Fig. 8.

## DISCUSSION

With the help of the experimentally determined equilibrium constants, the extent of adsorption and the surface charge of the hydrous oxide can be predicted adequately as a function of pH and other solution variables. The

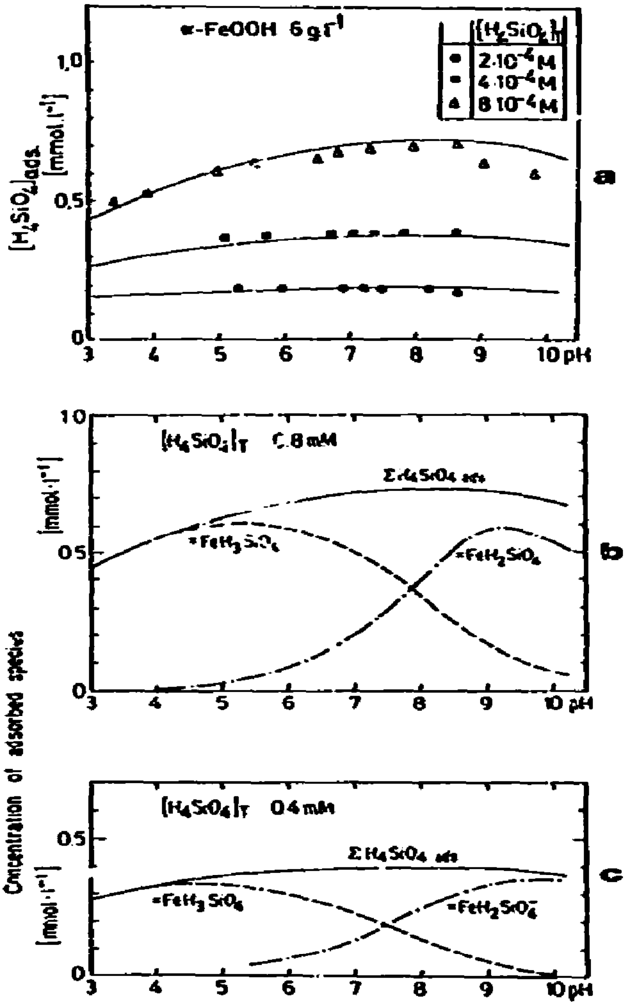

Fig. 7. $H_4SiO_4$ is adsorbed specifically over a wide pH range because two surface species $\equiv FeH_3SiO_4$ and $\equiv FeH_2SiO_4^-$ are formed. (Lines calculated with equilibrium constants.) (eqns (7), (6), Table 1). Points are experimental.

extent of adsorption and its pH-dependence can be explained by considering the affinity of the surface sites for the ligands and the acid—base properties of the surface sites and those of the ligands. The adsorption (binding) of simple weak acids or their anions is largest around the value of pH = $pK_a$.

As is shown by the equilibrium relationship

$$[\equiv MeA] = K_1^s\,[\equiv MeOH]\,[HA], \qquad (14)$$

the quantity adsorbed ($[\equiv MeA]$) will be highest when the product $[\equiv MeOH]$ $[HA]$ is at a maximum. This will often be around the $pK$ value of the acid as

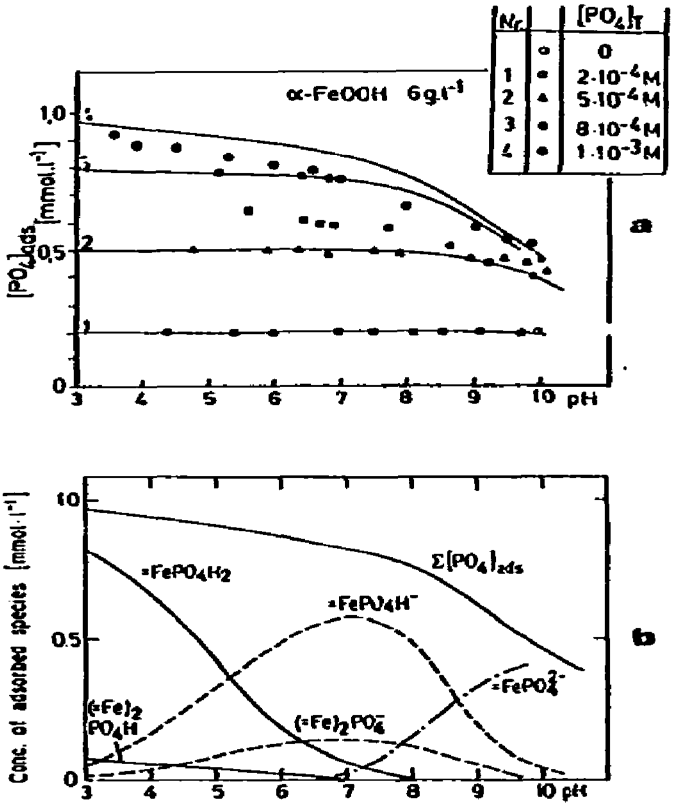

Fig. 8. (a). Phosphate adsorption on α-FeOOH. Lines computed with the help of equilibrium constants (eqns (9)—(13), Table 1).
(b). Distribution of phosphate surface species as a function of pH.

has been found by many authors [4, 5, 18, 19]. Because ≡MeOH is a dominant species over a broad pH range, the adsorption will extend over a wide pH range. Weak acids with several protons adsorb over a wider pH range.

The specific binding of ligands to the goethite surface is accompanied by a change in the proton balance at the surface. In the case of $F^-$ and $SO_4^{2-}$ a simple stoichiometric relationship between $OH^-$ released and ligand bound exists; this relationship is more complicated for the specific adsorption of weak acids because these bound ligands can become at least partly deprotonated. Information gained from the proton balance at the surface (binding of $H^+$ or its complexes minus binding of $OH^-$) obtained from alkalimetric or acidimetric titration and from the analytical determination of the extent of ligand adsorption permits to estimate whether in a given pH range protonated or deprotonated ligands are adsorbed.

Two kinds of observations in this study indicate the formation of inner sphere complexes at the α-FeOOH surface:

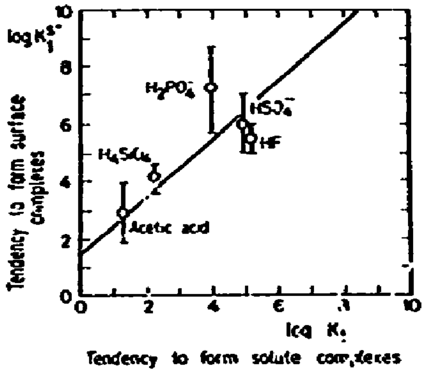

Fig. 9. Comparison of the *tendency to form surface complexes* ($K_1^{s*}$, eqn (16)) with that to form solute complexes ($K_1$, eqn. (15)).

1. The surface complex formation constants show the same trend in stability as the corresponding solute complex formation. In Fig. 9 the complex formation constants in solution

$$K_1 = [FeA]_{aq}/([FeOH_2^+]_{aq}\ [HA]) \tag{15}$$

are compared with the ligand exchange equilibrium constant for the surface reaction

$$K_1^{s*} = [\equiv FeA]/([\equiv FeOH]\ [HA]) \tag{16}$$

Despite the relatively large error range for the surface constants, it is obvious that the complexing tendency is similar at the surface and in solution. The same relationship between log $K_1$ and log $K_1^{s*}$ has been found by Kummert for the binding of aromatic acids on $\gamma$-$Al_2O_3$ [20]. The relationship between the coordination in solution and at oxide surfaces can be utilized to estimate surface coordination equilibrium constants (eqns (15), (16)) from the corresponding complex formation constants in solution. Thus, for example, $Cl^-$ is found not to adsorb specifically [5] at the surface of $\alpha$-FeOOH; this is in accord with the relatively weak (e.g. in comparison with $F^-$) tendency of $Cl^-$ to form chloro-Fe(III) complexes in solution.

2. The coordinating surface, i.e., its metal Lewis acid enhances the deprotonation of the surface species. If the adsorbed species were separated from the metal ion by one or two water molecules, the surface could not exert such a significant lowering of the acidity constant of the adsorbed species. Table 4 compares the acidity constants of the surface species with those in solution where such a comparison is possible.

The complex $FeH_2SiO_4^+$ (aq) does not exist in solution, so that the acidity constant $K_{a3}^s$ is compared with the $Mg^{2+}$ and $Ca^{2+}$ complexes.

The value of the acidity constant found from $\equiv FePO_4H_2$ is situated between the one for $H_2PO_4^-$ (aq) and the p$K_a$ of $FeH_2PO_4^{2+}$. This seems reasonable, as the binding of $H_2PO_4^-$ to a $\equiv Fe^+$ belonging to the surface must

TABLE 4

Comparison of acidity constants of surface complexes and solute complexes

Constants for solute complexes are from [13].

| | | | |
|---|---|---|---|
| $=FePO_4H_2$ | $\rightleftarrows$ | $=FePO_4H^- + H^+$ | − 4,4 |
| $=FePO_4H^-$ | $\rightleftarrows$ | $=FePO_4^{2-} + H^+$ | − 6,6 |
| $=Fe_2PO_4H$ | $\rightleftarrows$ | $=Fe_2PO_4^- + H^+$ | − 4,0 |
| $Fe(III)H_2PO_4^{2+}(aq)$ | $\rightleftarrows$ | $FeHPO_4^+ (aq) + H^+$ | − 2,4 |
| $MgH_2PO_4^+ (aq)$ | $\rightleftarrows$ | $MgHPO_4^0 (aq) + H^+$ | − 5,96 |
| $Fe(II)H_2PO_4^+(aq)$ | $\rightleftarrows$ | $FeHPO_4^0 (aq) + H^+$ | − 6,3 |
| $=FeSiO_4H_3$ | $\rightleftarrows$ | $=FeSiO_4H_2^- + H^+$ | − 7,4 |
| $MgH_3SiO_4^+(aq)$ | $\rightleftarrows$ | $MgH_2SiO_4^0(aq) + H^+$ | − 9,17 |
| $CaH_3SiO_4^+(aq)$ | $\rightleftarrows$ | $CaH_2SiO_4^0(aq) + H^+$ | −10,0 |

favor the proton dissociation; on the other hand ≡Fe has less influence than $Fe^{3+}$, as its charge is partly compensated by the binding in the crystal structure. $pK_{a3}^s$ may be compared with $pK_{a2}$ of the silicic acid; $Mg^{2+}$ and $Ca^{2+}$ have a weaker effect than ≡Fe, but one can suppose that $Fe^{3+}$ would influence more strongly the $pK_a$ of $H_3SiO_4^-$. Kummert [20] found similar relationships for organic acids at the aluminium oxide surface.

Direct (inner sphere) binding of ligands to the surface has been postulated from infrared absorption measurements on dried oxide surfaces treated with sulfate, phosphate and other ligands [21], but no method allowing the reliable measurement of IR spectra in aqueous media is known.

With regard to inner sphere complexation of $SO_4^{2-}$, our findings may appear to be at variance with those of Yates and Healy [14] who hypothesize on the basis of comparing the extent and rate of adsorption on goethite and α-chromia that $SO_4^{2-}$ is not significantly involved in direct exchange with ≡FeOH groups. Because of the difficulties we experienced in fitting the $SO_4^{2-}$ adsorption data in terms of a surface complexation equilibrium (Fig. 5), our experimental evidence is not sufficient to contradict this hypothesis.*

## IMPLICATIONS FOR NATURAL WATERS

A set of surface equilibrium constants permits the estimation of the *surface speciation* of an oxide in a natural water of a given composition. Table 5 gives the calculated surface speciation and surface charge for goethite equilibrated

---

*Initial adsorption of $SO_4^{2-}$ at small $SO_4^{2-}$ concentrations ($< 10^{-3}$ M) causes — as noted by us and by Yates and Healy [14] and (for the adsorption of $SO_4^{2-}$ on hematite) by Breeuwsma and Lyklema [22] — a small increase in the pH of zero point of charge (zero proton balance at the surface); but upon further increase in $[SO_4^{2-}]$ $pH_{zpc}$ is no longer shifted. Possibly, the initial $SO_4^{2-}$ adsorption is specific (e.g., at the edges of the goethite surface). Subsequently, at higher concentrations, $SO_4^{2-}$ behaves like an indifferent electrolyte.

TABLE 5

Speciation of the goethite surface in a natural lake water (approximated calculation)

$[\equiv FeOH]_T = 1 \cdot 10^{-6}$ mol l$^{-1}$ ($= 1 \cdot 10^{-3}$ g l$^{-1}$ with $\{\equiv FeOH\}_T = 1 \cdot 10^{-3}$ mol g$^{-1}$).

pH = 7.5.
$Q \approx -2.5 \cdot 10^{-7}$ mol l$^{-1}$ $\approx -5 \cdot 10^{-5}$ mol g$^{-1}$.
The constants for $HCO_3^-$, $Ca^{2+}$ and $Pb^{2+}$ are estimated.

| X | $C_T$ [mol l$^{-1}$] | Surface species | log $K_{intr.}$ | [≡FeX] (mol l$^{-1}$) | % [≡FeOOH]$_T$ |
|---|---|---|---|---|---|
| — | — | ≡FeOH | — | $2.5 \cdot 10^{-7}$ | 25 |
| $H^+$ | $3.2 \cdot 10^{-8}$ | $\equiv FeOH_2^+$ | −6.4 | $1.6 \cdot 10^{-7}$ | 16 |
| $OH^-$ | $4.9 \cdot 10^{-7}$ | $\equiv FeO^-$ | −9.25 | $5.5 \cdot 10^{-10}$ | 0.05 |
| $SO_4^{2-}$ | $1 \cdot 10^{-4}$ | $\equiv FeSO_4^-$ | −5.6 | $1.0 \cdot 10^{-11}$ | $1 \cdot 10^{-3}$ |
| $H_2PO_4^-$ | $1 \cdot 10^{-6}$ | $\equiv FeHPO_4^-$ | 7.2 | $3.5 \cdot 10^{-7}$ | 35 |
| $H_4SiO_4$ | $5 \cdot 10^{-5}$ | $\equiv FeH_3SiO_4$ | 4.1 | $1.5 \cdot 10^{-7}$ | 15 |
| | | $\equiv FeH_2SiO_4^-$ | −3.3 | $2.4 \cdot 10^{-8}$ | 2.4 |
| $HCO_3^-$ | $5 \cdot 10^{-3}$ | $\equiv FeCO_3^+$ | 2.5 | $4.9 \cdot 10^{-8}$ | 4.9 |
| $Mg^{2+}$ | $2 \cdot 10^{-4}$ | $\equiv FeOMg^+$ | −6.2 | $7.8 \cdot 10^{-9}$ | 0.8 |
| $Ca^{2+}$ | $1 \cdot 10^{-3}$ | $\equiv FeOCa^+$ | −8 | $4.9 \cdot 10^{-10}$ | 0.05 |
| $Pb^{2+}$ | $1 \cdot 10^{-8}$ | $\equiv FeOPb^+$ | −3 | $4.9 \cdot 10^{-10}$ | 0.05 |

with the inorganic components of a fresh water lake. The simultaneous equilibria have been resolved with an iterative computer program that considers the charge dependence of the equilibrium constants. Table 5 shows that the surface sites of α FeOOH will be preponderantly occupied by phosphate and silicate although these species are present in very small concentrations in the water. These species will also to a large extent determine the negative surface charge of α-FeOOH at the pH of the natural water. A more realistic model of a natural water has also to consider the adsorption of organic matter [23] and might have to take into account the formation of ternary surface complexes [24, 25]. On the basis of the equilibrium constants given by Kummert for organic acids on $\gamma$-$Al_2O_3$, we estimate that, in the concentration range of organic acids of 1—3 × $10^{-5}$ M, ca. 10% of the surface sites may be occupied by bound organic acids. This fraction may, however, be higher in nature because soluble polar organic substances are present in polymeric form (fulvic acid). The results of the calculations illustrate that oxides or oxide hydroxides of Fe(III) are an important sink and regulating factor for phosphate and silicate [26].

## ACKNOWLEDGEMENTS

Valuable advice given by Herbert Hohl, Paul Schindler, Walter Schneider and John Westall and the financial support by the Swiss National Foundation are acknowledged.

## REFERENCES

1 W. Stumm, C.P. Huang and S.R. Jenkins, Croat. Chem. acta 42, 223 (1970).
2 H. Hohl, W. Stumm, J. Colloid Interface Sci., 55 (1976) 281.
3 P.W. Schindler, B. Fürst, R. Dick and P. Wolf, J. Colloid Interface Sci., 55 (1976) 469.
4 F.J. Hingston, A.M. Posner and J.P. Quirk, Adv. Chem. Ser., 79 (1968) 82.
5 F.J. Hingston, A.M. Posner and J.P. Quirk, J. Soil. Sci., 23 (1972) 177.
6 J.W. Bowden, M.D.A. Bolland, A.M. Posner and J.P. Quirk, Nature, 245 (1973) 81.
7 F.J. Hingston, R.J. Atkinson, A.M. Posner and J.P. Quirk, Nature, 215 (1967) 1459.
8 R.J. Atkinson, A.M. Posner and J.P. Quirk, J. Phys. Chem., 71 (1967) 550.
9 M.A. Anderson, J.F. Ferguson and J. Gavis, J. Colloid Interface Sci., 54 (1976) 391.
10 C.P. Huang, J. Colloid Interface Sci., 53 (1975) 178.
11 R.O. James and T.W. Healey, J. Colloid Interface Sci., 40 (1972) 42, 40 (1972) 53.
12 S.K. Gupta, Dissertation, Univ. Bern, 1976.
13 R.M. Smith and A.E. Martell, Critical Stability Constants, Vol. 4, Plenum Press, New York, 1976.
14 D.E. Yates and T.W. Healy, J. Colloid Interface Sci., 52 (1975) 222.
15 L. Sigg, Ph.D. Thesis, ETH, Zürich, 1979.
16 D.E. Yates, Ph.D. Thesis, University of Melbourne, 1975.
17 A. Lazrus, E. Lorange and J.P. Lodge, Adv. Chem. Ser., 73 (1967) 164.
18 Y.R. Sims and F.T. Bingham, Soil Sci. Soc. Am. Proc., 32 (1968) 364.
19 W.W. Choi and K.Y. Chen, Environ. Sci. Technol., 13 (1979) 189.
20 R. Kummert, Ph.D. Thesis, ETH, Zürich, 1979.
21 (a) R.L. Parfitt and R. St. C. Smart, J.C.S. Faraday I, 73 (1977) 796.
(b) R.L. Parfitt and J.D. Russell, Soil Sci., 28 (1977) 297.
22 A. Breeuwsma and J. Lyklema, J. Colloid Interface Sci., 43 (1973) 437.
23 J. Davis and G. Sigg, in R.A. Baker (Ed.), ACS Symposium Series, in press.
24 J.A. Davis, R.O. James and J.O. Leckie, J. Colloid Interface Sci., 63 (1978) 480.
25 A.C.M. Bourg and P.W. Schindler, Chimia 32, 166 (1978).
26 B.F. Jones and C.J. Bowser, in Lakes, A. Lerman, ed., Wiley-Interscience, New York 1979.