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Acid–Base Properties of the Surface of Hydrous Ferric Phosphate in Aqueous Solutions

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ABSTRACT: The adsorption of hydrogen ions on precipitated hydrous $FePO_4(am)$ (HFP) was studied. The experiments were carried out in 0.3 $mol \cdot dm^{-3}$ KNO_3 solutions and $NaClO_4$ solutions at ionic strengths of (0.002, 0.010, 0.030, 0.1, 0.3, and 1.0) $mol \cdot dm^{-3}$. The acidity of surface ferrihydrols, >FeOH, and phosphohydrols, >POH, groups was evaluated from potentiometric acid–base titration curves. The pH values ranged from 2.5 to 5.5. The adsorption equilibria were found to be slow but showed good reversibility. Effects by medium ions were studied using two amorphous hydrated solids obtained with different procedures: (a) precipitation and washed by dialysis (HFP(dialyzed)); (b) precipitation in situ in the presence of the ionic medium in question HFP (in situ). On the exchange of protons at the interface HFP solution, a charged surface results with positively, $>FeOH_2^+$, and negatively, $>PO^-$, charged sites. The charge is a function of the solution acidity and is regulated by the acid–base equilibria:

$$> FeOH_2^+ \rightleftarrows\ > FeOH + H^+ \qquad \log^{Fe} K_{a1} = -4.66 \pm 0.05$$

$$> POH \rightleftarrows\ > PO^- + H^+ \qquad \log^{P} K_{a2} = -1.4 \pm 0.1$$

The zero charge point (ZCP = 3.04 ± 0.05) and the number of sites were determined.

INTRODUCTION

Phosphates are present in several natural systems.[1] Pollution (eutrophism) originating from the large use of phosphates in domestic and industrial activities makes the need for a strategy of removal from wastes urgent. The precipitation of iron(III) and aluminum(III) phosphates has been suggested.[2] Freshly precipitated iron and aluminum phosphates are colloids with large surface areas so that adsorption of metals may be conspicuous. The aim of this project is the study of the surface phenomena at the interface of hydrous ferric phosphate, HFP.

In this paper we report the investigation of the proton exchange at the solid–solution interface by acid–base titrations. The knowledge of the acid–base reaction on the surface is of paramount importance in the understanding of the metal ion adsorption on the solid surface.

In the initial stage of the work the amorphous hydrated solid was obtained by precipitation and then washed by decantation and dialysis to remove foreign ions and minimize changes in surface properties during the acid–base titration. The suspension was allowed to age for at least a year. The hydrous amorphous $FePO_4$ is designated as HFP(dialyzed). No specific effects of medium ions, Na^+ and/or ClO_4^-, could be noticed for ionic strengths inferior to 0.1 $mol \cdot dm^{-3}$. However, the effects observed at higher ionic strengths were irreproducible even under apparently identical conditions.

To throw some light on the nature of the specific effects by medium ions, a series of experiments was carried out with freshly, more active preparations, HFP(in situ). These resulted from precipitation in situ in the presence of the ionic medium in question. Hence, no washings were involved, and the suspension could be investigated soon after its preparation.

PROPERTIES OF HYDROUS FERRIC PHOSPHATE

The adsorption of hydrogen ions was studied using two amorphous hydrated solids obtained with different procedures: (a) precipitation and washed by dialysis (HFP(dialyzed)); (b) precipitation in situ in the presence of the ionic medium in question HFP(in situ).

Solubility of $FePO_4$(am). The dissolution of $FePO_4$ introduces in solution protolytes (Fe^{3+} and PO_4^{3-} ions) that cause important effects on the measurements. These effects should be evaluated exactly for a correct interpretation of the surface phenomena. According to the most recent acquaintances on the solution chemistry of iron(III) phosphate solutions, the equilibria regulating the solubility in the (H^+) range 10^{-2} to 10^{-4} $mol \cdot dm^{-3}$ is shown in eq 1

$$FePO_4(am) \rightleftarrows FePO_4(aq) \qquad -3 \geq \log K \geq -5.4 \tag{1}$$

while equilibrium 2

$$FePO_4(am) + 2H_2O \rightleftarrows FeOOH(am) + H_3PO_4$$
$$\log K = -6.5 \tag{2}$$

becomes important at $(H^+) < 10^{-4}$ $mol \cdot dm^{-3}$. Reaction 1, on the contrary of reaction 2, is independent of (H^+); therefore it has no effect on the measurement of the surface exchange of protons. A series of solubility determinations was then planned

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Table 1. Solubility Determinations on HFP(in situ)

$NaClO_4$	solubility, 10^5		
$mol\cdot dm^{-3}$	$mol\cdot dm^{-3}$	method	observations
0.002	5.71	gravimetric[a]	pH ≈ 2.8
0.010	5.99	gravimetric[a]	pH ≈ 2.7
0.010	5.58	spectrophotometric[b]	mother liquids of the preparation, pH ≈ 3
0.010	8.13	spectrophotometric[b]	suspension kept for 2 h at pH 5
0.10	6.2	spectrophotometric[b]	suspension kept for 2 h at pH 5
1.00	6.25	spectrophotometric[b]	suspension kept at pH = 6.43 for 2 days

[a] From the difference in the suspension concentration assuming all Fe(III) precipitated and the concentration resulting by the gravimetric determination as oxinate.[4] [b] The phosphate concentration in the clear solution kept in contact with HFP particles was analyzed by the molybdate test.[4]

to establish the extent in which reaction 2 occurs at $(H^+) < 10^{-4}\ mol\cdot dm^{-3}$.

In Table 1 the results of a few determinations with $FePO_4$-(in situ) are given. The solubility data refer to a not strictly controlled temperature. The samples were kept at room temperature which, in the period the measurements were carried out, was between (22 and 30) °C.

Practically a constant solubility $(6.3 \pm 2)\cdot 10^{-5}\ mol\cdot dm^{-3}$ is recorded in the pH range 2.7 to 6.4. This result can be interpreted with the predominance in solution of the species $FePO_4(aq)$ whose concentration is independent of pH.

The most important conclusion of these experiments is that the heterogeneous equilibrium 2 results to be sufficiently slow to produce unappreciable quantities of phosphoric acid even after months. Additional evidence comes from the following experiment. A sample of 5 mg of $FePO_4$, corresponding to 33 μmol, was suspended in 1 dm^3 of distilled water. If reaction 2 occurs, the concentration of H_3PO_4 would increase to reach a value of $10^{-6.5}\ mol\cdot dm^{-3}$, that is, the equilibrium constant of 2 at infinite dilution. The total concentration of phosphate would then be about $10^{-4.5}\ mol\cdot dm^{-3}$, the pH ≈ 4.5 and electrical conductance ≈20 $\mu S\cdot cm^{-1}$. The system observed for more than 4 months did not show any increase of electrical conductance from 3 $\mu S\cdot cm^{-1}$, whereas the pH was about 5, as that of the water equilibrated with laboratory atmosphere. We have then concluded that reaction 2 is very slow and does not introduce uncertainties in acid−base titrations carried out to pH values up to 6.

Density and Surface Area. The density of HFP samples, dried at 600 °C, was determined with a CCl_4-pycnometer. The resulting density was $2.55 \pm 0.02\ g\cdot cm^{-3}$, which, as expected, is lower than that of strengite, that is, $2.74\ g\cdot cm^{-3}$

Measurements by Brunauer−Emmett−Teller (BET) method[3] provide for HFP(*dialyzed*) values of around $(162 \pm 10)\cdot 10^3\ m^2\cdot kg^{-1}$. HFP(in situ) resulted in a slightly higher value, $(190 \pm 10)\cdot 10^3\ m^2\cdot kg^{-1}$. These estimates must be considered as a lower bound to the actual value since the reproducibility of the procedure is not good for porous solids as we think HFP is. Then the results depend on the outgassing procedure. During drying necessary for the determination, surface decomposition occurs and leads to significant underestimates of surface area.

An attempt is made theoretically to estimate the surface area assuming various particle sizes, which on the other hand should be measured directly by optical instruments.

A spherical particle of diameter δ has a surface $\varsigma = \pi\delta^2$ and a volume $\nu = (\pi/6)\delta^3$. A sample of 1 kg of solid with density $d\ (kg\cdot dm^{-3})$ contains N particles valuable from

$$N = 6\cdot 10^{-3}\pi^{-1}d^{-1}\delta^{-3}\ \text{particles/kg}$$

and has a specific area

$$s = N\varsigma = 6\cdot 10^{-3}\pi^{-1}d^{-1}\delta^{-3}\pi\delta^2 = 6\cdot 10^{-3}d^{-1}\delta^{-1} \qquad (3)$$

Table 2. Some Estimates of Surface Area of Particles with Different Diameters (Density of HFP = 2.55 $kg\cdot dm^{-3}$)

$\delta\cdot 10^9$	$\varsigma\cdot 10^{20}$	$\nu\cdot 10^{29}$	N	s
m	m^2	m^3	$particles\cdot kg^{-1}$	$m^2\cdot kg^{-1}$
2	1.257	0.419	$9.4\cdot 10^{22}$	$1.2\cdot 10^6$
5	7.854	6.544	$6.0\cdot 10^{21}$	$4.8\cdot 10^5$
10	31.41	52.35	$6.35\cdot 10^{20}$	$2.0\cdot 10^5$
20	125.7	418.9	$9.3\cdot 10^{19}$	$1.2\cdot 10^5$

The results of calculation, given in Table 2, indicate an average size of particles in the range 10 to 20 nm for specific areas found by BET. It would be interesting to compare these estimates with directly measured particles size.

Site Densities. Acid−base titrations to be described below indicate that a maximum of 3 mol of H^+ can be adsorbed per kilogram of HFP. Assuming a specific area of $1.7\cdot 10^5\ m^2\cdot kg^{-1}$, we evaluate a site density of $3\cdot 6.021\cdot 10^{23}$ sites/kg = $18\cdot 10^{23}$ sites/kg = $18\cdot 10^{23}/1.7\cdot 10^3 \approx 10\ sites\cdot nm^2$.

Sites of adsorptions of $[H^+]$ are indicated as *ferrihydrols*, >FeOH, and *phosphohydrols*, >POH. Sites >FeOH are equal in number sites >POH, but their chemical behavior is different. On exchange of protons at the HFP−solution interface a charged surface results with positively $>FeOH_2^+$ and $>POH_2^+$ and negatively $>FeO^-$ and $>PO^-$ charged sites. The charge is a function of the solution acidity and is regulated by the acid−base equilibria

$$>FeOH_2^+ \rightleftarrows\ >FeOH + H^+$$
$$^{Fe}K_{a1} = \{>FeOH\}(H^+)\{>FeOH_2^+\}^{-1} \qquad (4)$$

$$>FeOH \rightleftarrows\ >FeO^- + H^+$$
$$^{Fe}K_{a2} = \{>FeO^-\}(H^+)\{>FeOH\}^{-1} \qquad (5)$$

$$\mathrm{POH_2^+} \rightleftarrows \mathrm{>POH} + \mathrm{H^+}$$

$$^{P}K_{\mathrm{a1}} = \{\mathrm{>POH}\}(\mathrm{H^+})\{\mathrm{>POH_2^+}\}^{-1} \qquad (6)$$

$$\mathrm{>POH} \rightleftarrows \mathrm{>PO^-} + \mathrm{H^+}$$

$$^{P}K_{\mathrm{a2}} = \{\mathrm{>PO^-}\}(\mathrm{H^+})\{\mathrm{>POH}\}^{-1} \qquad (7)$$

where {} stands for surface concentration in $\mathrm{mol \cdot kg^{-1}}$ and the various K_{a} are apparent constants. The corresponding intrinsic constants $K_{\mathrm{a(intr)}}$ are found by correcting for the Coulombic energy according to eq 8

$$K_{\mathrm{a}} = K_{\mathrm{a(intr)}} \exp(\psi F/RT) \qquad (8)$$

where ψ is the surface potential.

The surface charge, Q in $\mathrm{mol \cdot kg^{-1}}$, is given by

$$Q = \{\mathrm{>FeOH_2^+}\} + \{\mathrm{>POH_2^+}\} - \{\mathrm{>FeO^-}\} - \{\mathrm{>PO^-}\} \qquad (9)$$

Indicating with T_{Fe} and T_{P}, respectively, the total number of sites ($\mathrm{mol \cdot kg^{-1}}$) of ferrihydrols and phosphohydrols the mass balance yields

$$T_{\mathrm{Fe}} = \{\mathrm{>FeOH}\} + \{\mathrm{>FeOH_2^+}\} + \{\mathrm{>FeO^-}\} \qquad (10)$$

$$T_{\mathrm{P}} = \{\mathrm{>POH}\} + \{\mathrm{>POH_2^+}\} + \{\mathrm{>PO^-}\} \qquad (11)$$

Finally, using mass balances and equilibrium conditions, we obtain

$$\begin{aligned} Q = {} & T_{\mathrm{Fe}}((\mathrm{H^+})/{}^{Fe}K_{\mathrm{a1}} - {}^{Fe}K_{\mathrm{a2}}(\mathrm{H^+})^{-1}) \\ & /(1 + (\mathrm{H^+})/{}^{Fe}K_{\mathrm{a1}} + {}^{Fe}K_{\mathrm{a2}}(\mathrm{H^+})^{-1}) \\ & + T_{\mathrm{P}}((\mathrm{H^+})/{}^{P}K_{\mathrm{a1}} - {}^{P}K_{\mathrm{a}}(\mathrm{H^+})^{-1}) \\ & /(1 + (\mathrm{H^+})/{}^{P}K_{\mathrm{a1}} + {}^{P}K_{\mathrm{a2}}(\mathrm{H^+})^{-1}) \end{aligned} \qquad (12)$$

Equation 12 forms the basis of the evaluation of T and K_{a}.

■ EXPERIMENTAL METHODS

Reagents. $\mathrm{Fe(NO_3)_3 \cdot 9H_2O}$ was obtained from Aldrich (p.a.) and $\mathrm{H_3PO_4}$ conc. was purchased from Merck Chemicals and used as supplied. Iron(III) perchlorate stock solutions were prepared by $\mathrm{Fe(ClO_4)_3 \cdot \mathit{x}H_2O}$ (Aldrich, p.a.) which was purified by crystallization from 1:1 $\mathrm{HClO_4}$. In the violet crystals no $\mathrm{Cl^-}$ ion and heavy metals could be detected. In the stock solutions, the iron(III) concentration was determined gravimetrically as oxinate[4] as well as iodometrically, that is, by amperometric titration with standard $\mathrm{Na_2S_2O_3}$ of the iodine formed on reducing Fe(III) with NaI in excess. The results agreed to within 0.1 %.

$\mathrm{HClO_4}$ stock solutions were prepared by diluting a 72 % Merck p.a. product and analyzed by titration with $\mathrm{KHCO_3}$, $\mathrm{Tl_2CO_3}$, with a reproducibility of 0.1 % or better.

NaOH and KOH solutions were prepared by generating $\mathrm{OH^-}$ ion at the cathode of the electrolysis cell, described elsewhere.[5] Sodium perchlorate (Merck p.a., as $\mathrm{NaClO_4 \cdot H_2O}$) stock solutions[6] were standardized gravimetrically after the evaporation of aliquots of the stock solutions and drying at 120 °C. Silver perchlorate[6] was prepared from $\mathrm{Ag_2O}$ (Aldrich p.a.) and $\mathrm{HClO_4}$. The silver concentration in the stock solution was determined by potentiometric titrations with NaCl. Sodium chloride, potassium chloride, and potassium nitrate were dried at 110 °C.

In Situ Hydrous Ferric Phosphate (HFP(in situ)). The suspension of HFP in a given medium, $I = (\mathrm{ClO_4^-})$, was prepared by mixing a sample of $\mathrm{Fe(ClO_4)_3}$, of exactly known iron(III), hydrogen ion, and perchlorate ion content, with the stoichiometric quantity of (standardized) $\mathrm{H_3PO_4}$. The precipitation of ferric phosphate was completed by neutralizing precisely the total acidity ($\mathrm{H_3PO_4} + \mathrm{HClO_4}$) with $\mathrm{Na_2CO_3}$. The suspension was then diluted to the desired $\mathrm{ClO_4^-}$ ion concentration. The starting materials were delivered in quantities such that the final suspension had a concentration of (10 to 20) g HFP(in situ)$\cdot \mathrm{dm^{-3}}$.

Suspensions in dilute inert electrolyte, say $\mathrm{NaClO_4}$ inferior to 0.1 $\mathrm{mol \cdot dm^{-3}}$, were prepared in volumes of 10 $\mathrm{dm^3}$. After the solid settled, the clear liquid excess was decanted to the desired suspension concentration.

To check the quantity of amorphous solid per unit volume, samples were collected in a porcelain dish, washed several times with small portions of water, ignited at 600 °C, and weighed. The gravimetric results were to be found inferior to the expected values, and the differences were ascribed to losses for the small but not null solubility of amorphous $\mathrm{FePO_4}$ (see below).

X-ray diffraction patterns indicate amorphous phases, even after a year from the precipitation.

Dialyzed Hydrous Ferric Phosphate (HFP(dialyzed)). A clear solution of 0.1 mol of $\mathrm{Fe(NO_3)_3 \cdot 9H_2O}$, Aldrich (p.a.), and 0.1 mol $\mathrm{H_3PO_4}$, Baker (p.a.), in 200 $\mathrm{cm^3}$ was diluted to 10 $\mathrm{dm^3}$, and the precipitation of ferric phosphate was completed by neutralizing the total acidity ($\mathrm{HNO_3}$) with $\mathrm{Na_2CO_3}$. Foreign ions, mostly $\mathrm{H^+}$, $\mathrm{Na^+}$, and $\mathrm{NO_3^-}$, were removed by repeated washings with water by decantation and dialysis. The progress in purification was monitored by the electrical conductance and the pH of the mother liquids. Washings were interrupted when the mother liquids had an electric conductance of about 3 $\mu\mathrm{S \cdot cm^{-1}}$ and a pH of about 5. During storage the electrical conductance was periodically controlled to verify that no appreciable transformation of $\mathrm{FePO_4}$(aged) in FeOOH(am) + $\mathrm{H_3PO_4}$ (see equilibrium 1) occurs. No significant increase in the concentration of $\mathrm{H_3PO_4}$ could be detected after more than 4 months. The amount of solid per unit volume was determined as for HFP(in situ).

Apparatus. During the EMF measurements the cell assembly, automatic buret, and gas washing bottles were placed in an air thermostat kept at 25.00 ± 0.02 °C. Glass electrodes manufactured by Metrohm Ltd. (Switzerland) were employed. Bridge solutions and reference electrodes were lodged in Wilhelm type bridges.[7] Silver electrodes were prepared according to Brown.[8]

Potentiometric titrations were carried out with a programmable computer controlled data acquisition unit 34970A, supplied by Agilent Technologies (Santa Clara, CA).

The hydrogen ion concentration of suspensions was measured as a function of ($C_{\mathrm{A}} - C_{\mathrm{B}}$) with cells (A), for $I \geq 0.1$ $\mathrm{mol \cdot dm^{-3}}$ $\mathrm{NaClO_4}$, and (B) for $I < 0.1$ $\mathrm{mol \cdot dm^{-3}}$ $\mathrm{NaClO_4}$. Measurements[9] performed in 0.3 $\mathrm{mol \cdot dm^{-3}}$ $\mathrm{KNO_3}$ were carried out with cell (C):

$$\mathrm{Ag/AgCl/(Na^+)} = (I - 0.01),\ (\mathrm{Ag^+}) = 0.01,$$

$$(\mathrm{ClO_4^-}) = I/I\ \mathrm{mol \cdot dm^{-3}}\ \mathrm{NaClO_4/TS1/GE}\ (I \geq 0.1) \qquad (\mathrm{A})$$

$$\mathrm{Ag/AgCl/3\ mol \cdot dm^{-3}\ KCl/3\ mol \cdot dm^{-3}\ NaCl/TS1/GE}\ (I < 0.1) \qquad (\mathrm{B})$$

$$\mathrm{Ag/AgCl/3\ mol\cdot dm^{-3}\ KCl/TS2/GE} \qquad \mathrm{(C)}$$

where GE stands for glass electrode.

The electromotive force (emf) of cells A, B, and C can be written as

$$E_A = E_{0A} + 59.16\log(\mathrm{H^+}) + E_{jA} \qquad (13)$$

$$E_B = E_{0B} + 59.16\log(\mathrm{H^+}) + E_{jB} \qquad (14)$$

$$E_C = E_{0C} + 59.16\log(\mathrm{H^+}) + E_{jC} \qquad (15)$$

in which E_0 terms are constants in each run and E_j is the liquid junction potential at the boundary salt bridge/TS.

At a given I, E_j is practically a function only of $(\mathrm{H^+})$. The dependence on $(\mathrm{H^+})$ was determined by acid–base titrations. The results are summarized as follows:

$$\begin{aligned} E_{jA}(I = 1.0) &= -59.16\log(1 + 2.45(\mathrm{H^+})) \\ &\approx -63(\mathrm{H^+})\ \mathrm{mV\cdot dm^3\cdot mol^{-1}} \end{aligned}$$

$$E_{jA}(I = 0.3) = -59.16\log(1 + 7.01(\mathrm{H^+}))\ \mathrm{mV\cdot dm^3\cdot mol^{-1}}$$

$$E_{jA}(I = 0.1) = -59.16\log(1 + 26.7(\mathrm{H^+}))\ \mathrm{mV\cdot dm^3\cdot mol^{-1}}$$

$$\begin{aligned} E_{jB}(I = 0.03) &\approx -30(\mathrm{H^+})\ \mathrm{mV\cdot dm^3\cdot mol^{-1}}, \\ &\text{for } (\mathrm{H^+}) \le 0.003\ \mathrm{mol\cdot dm^{-3}} \end{aligned}$$

$$\begin{aligned} E_{jB}(I = 0.01) &\approx -170(\mathrm{H^+})\ \mathrm{mV\cdot dm^3\cdot mol^{-1}}, \\ &\text{for } (\mathrm{H^+}) \le 0.003\ \mathrm{mol\cdot dm^{-3}} \end{aligned}$$

$$E_{jB}(I = 0.002) \approx 0, \text{ for } (\mathrm{H^+}) \le 0.002\ \mathrm{mol\cdot dm^{-3}}$$

$$E_{jC} \approx -170(\mathrm{H^+})$$

E_0 was checked in each titration in the absence of HFP from measurements in the range $(5 \text{ to } 2)\cdot 10^{-3} \ge (\mathrm{H^+})(= C_A - C_B) \ge 1\cdot 10^{-4}\ \mathrm{mol\cdot dm^{-3}}$. Values constant within ± 0.10 mV or better were calculated.

The potentials were read with a precision of $1\cdot 10^{-5}$ V. The emf of cells was read with a Keithley 642 type digital electrometer. Test solutions were purged of oxygen by bubbling purified and presaturated nitrogen gas. In solutions of pH < 3 emf values constant within 0.1 mV were recorded in less than 30 min after the addition of reagents and kept constant for several hours. In less acidic solutions the proton exchange becomes slower, and only after 6 h the potential drifts become less than $0.6\ \mathrm{mV\cdot h^{-1}}$ which was considered an acceptable criterion for stable readings. The X-ray powder patterns were obtained with an automatic Philips diffractometer using Cu Kα radiation (λ = 1.544 nm, Ni-filtered) and setting of 40 kV and 20 mA.

POTENTIOMETRIC ACID–BASE TITRATIONS

The function Q(pH) at 25 °C in different $\mathrm{NaClO_4}$ media was settled by potentiometric acid–base titrations. In a given medium of constant ionic strength, $I\ \mathrm{mol\cdot dm^{-3}}$, the equilibrium suspension had the general composition

$$\begin{aligned} \mathrm{TS1} = {} & C_A\ \mathrm{mol\cdot dm^{-3}\ HClO_4},\ C_B\ \mathrm{mol\cdot dm^{-3}\ NaOH}, \\ & (I - C_A)\ \mathrm{mol\cdot dm^{-3}\ NaClO_4},\ a\ \mathrm{g\cdot dm^{-3}\ HFP} \end{aligned}$$

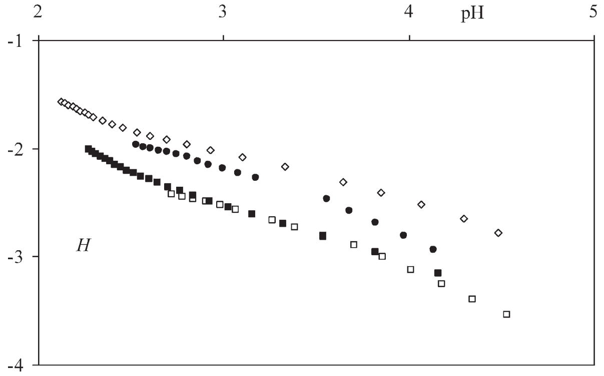


Figure 1. Titrations at 1.0 $\mathrm{mol\cdot dm^{-3}}$ (Na)$\mathrm{ClO_4}$ with differently aged HFP(in situ) preparations: 10 days (diamonds), 1 month (filled diamonds), 4 months (squares), reverse titration (filled squares).

The ionic strength values were (0.002, 0.010, 0.030, 0.1, 0.3, and 1.0) $\mathrm{mol\cdot dm^{-3}}$. The equilibrium concentration of $\mathrm{H^+}$ ions was varied from 0.002 to 0.010, depending on the I value, to $10^{-6}\ \mathrm{mol\cdot dm^{-3}}$. Higher and lower acidity values are limited by the slow dissolution of $\mathrm{FePO_4}$ which renders much longer the time of equilibration. The a values ranged from (1.3 to 3) $\mathrm{g/\cdot dm^{-3}}$.

A special series of measurements was performed in 0.3 $\mathrm{mol\cdot dm^{-3}\ KNO_3}$. Then, the equilibrium suspension had the composition

$$\begin{aligned} \mathrm{TS2} = {} & C_A\ \mathrm{mol\cdot dm^{-3}\ HNO_3},\ C_B\ \mathrm{mol\cdot dm^{-3}\ KOH}, \\ & (I - C_A)\ \mathrm{mol\cdot dm^{-3}\ KNO_3},\ a\ \mathrm{g\cdot dm^{-3}\ HFP} \end{aligned}$$

The hydrogen ion concentration of TS1 was measured as a function of $(C_A - C_B)$. From the primary data $(C_A, C_B, (\mathrm{H^+}), a)$ the proton excess in $\mathrm{mol\cdot kg^{-1}}$ was calculated

$$H = (C_A - C_B + K_w/(\mathrm{H^+}) - (\mathrm{H^+}))/a \qquad (16)$$

in which K_w the ion product of water at the various I was assumed after Baes and Mesmer.[10]

CALCULATION AND RESULTS

Measurements with HFP(in situ). The most noticeable features of the H(pH) curves, illustrated in the graph of Figure 1 relevant experiments at $I = 1.0\ \mathrm{mol\cdot dm^{-3}}$, can be summarized by the points:

(i) In the entire experimental range investigated the H values are always negative.

(ii) Each $H(\mathrm{pH})_I$ curve shows an inflection point, H_{ip}, at pH = 3.0 ± 0.1.

(iii) The H_{ip} values are dependent on both I and aging of the suspension, showing initially a rapid increase, then becoming less pronounced. In fact, the magnitude of H_{ip} depends on the replacement of $\mathrm{Na^+}$ with $\mathrm{H^+}$ on the surface (which increases with I and with the aging period).

The curves recorded in different aging periods all have an inflection point at about pH = 3, whereas the value of H_{ip} decreases to reach a stationary value after 2 months, a value that keeps approximately unchanged for 4 months. Typical results are given in Table 3. Probably, the slow process involves a specific interaction with sodium ions. In the following we assume that this slow process has no effect during a titration; in other words

Table 3. Data for HFP(in situ) in Various Media and H_{ip} Values Recorded at Different Times

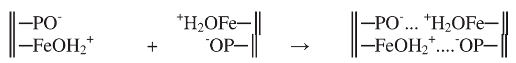
I				$-H_{ip}$
$mol \cdot dm^{-3}$	prepared	titrated	pH_{ip}	$mol \cdot kg^{-1}$
0.002	26/4/10	24/5/10	3.11 ± 0.05	≈0
0.010	26/4/10	30/5/10	3.05 ± 0.05	0.17 ± 0.03
0.030	4/6/10	13/6/10	3.02 ± 0.05	0.50 ± 0.03
0.030	4/6/10	10/9/10	3.02 ± 0.05	0.47 ± 0.04
0.10	2/4/10	16/4/10	3.02 ± 0.03	1.88 ± 0.03
0.10	3/4/10	2/5/10	3.09 ± 0.03	2.10 ± 0.04
0.10	3/4/10	5/9/10	3.04 ± 0.03	2.08 ± 0.04
0.30	4/9/10	2/10/10	2.99 ± 0.03	2.42 ± 0.05
1.00	9/3/10	19/3/10	3.01 ± 0.03	2.05 ± 0.05
1.00	9/3/10	11/4/10	3.05 ± 0.03	2.22 ± 0.02
1.00	9/3/10	20/6/10	3.06 ± 0.03	2.49 ± 0.02
1.00	9/3/10	24/9/10	2.91 ± 0.03	2.50 ± 0.02

surface changes do not occur in the period in which a titration is accomplished. We have attempted to clarify this point by performing reverse titrations. If the hypothesis is true, data H(pH) of reverse titration must coincide with those from forward titration. Generally, if the forward titration was extended to pH values of 6 and the most alkaline solution was kept in prolonged contact with the suspension, the points of the reverse titration fall on a different curve displayed versus more negative H values. However, the shape of the reverse titration was very similar to that of the forward titration. The only appreciable difference rests on the magnitude of H_{ip}. On the other hand, if the titration was stopped at pH ≤ 5 and the back-titration was started as soon as possible, points of the forward and back-titrations coincided within the limits of experimental accuracy.

The interpretation of the data is based on the hypothesis that HFP has a finite cation exchange capacity. Immersing a HFP suspension in an electrolyte solution results in partial ionization of the positive counterion (e.g., Na^+) and partial replacement of sodium with hydrogen. The extent of ionization (the magnitude of H_{ip}) depends on the (Na^+) and (H^+). Increasing (H^+) at constant (Na^+) results in further replacement of Na^+ with H^+ and ionization of fewer H^+ sites. At high (Na^+) or ionic strength, the exchange Na^+-H^+ is reduced and H_{ip} is less pH sensitive. Since, however, at the same ionic strength H_{ip} slowly changes with time we assume that the exchange Na^+-H^+ is independent of pH in the period a titration is accomplished.

To achieve zero total charge, when $H_{ip} \neq 0$, H must be increased toward the acid side of the H_{ip} until $H = -H_{ip}$.

One may ask which kind of structure is responsible of the exchange capacity with Na^+ ions. Suppose there were freshly precipitated HFP particles, shaped approximately spherical and nanometer sized. On aging HFP coagulates, and the resulting aggregates are porous to form a swollen gel. The surface of nanoparticles contains positive $>FeOH_2^+$ and negative $>PO^-$ sites and aggregation originates from electrostatic interactions (hydrogen bonds) as in the scheme



$$\left\Vert\begin{array}{l}-PO^- \\ -FeOH_2^+\end{array}\right. + \left.\begin{array}{r}{}^+H_2OFe- \\ {}^-OP-\end{array}\right\Vert \rightarrow \left\Vert\begin{array}{l}-PO^- \ldots {}^+H_2OFe- \\ -FeOH_2^+ \ldots {}^-OP-\end{array}\right\Vert$$

In the inside of the disordered structure of a porous aggregate, comprising a large number of nanoparticles, channels are present which allow the passage of ions and molecules through the surface of the structure. When the HFP is precipitated in the presence of sodium ions part of the hydrogen ions involved in the bond $>FeOH_2^+ \cdots {}^-OP<$ in the channels is replaced by Na^+. The exchange, as the experiments described above indicate, is rather slow so that the exchange equilibrium does not affect appreciably, during the span of a potentiometric acid–base titration, the phenomena occurring at the surface of the aggregate.

Evaluation of H_{ip} and pH_{ip}. Data H(pH) in the vicinity of the inflection point, say within the range 2.7 ≤ pH ≤ 3.3, were fitted with the polynomial $H = H_{ip} + p(H^+) + q(H^+)^{-1}$. The best parameters ($H_{ip}$, p, and q) were calculated by least-squares procedures. The most probable H_{ip} and pH_{ip} evaluated in different titrations are reported in Table 3.

Evaluation of T_{Fe} (= T_P). It seems very unlikely that, in the pH range investigated, 2 to 6, each of the four terms in eq 9 will attain significant levels. It seems more reasonable to explain data of the present accuracy with only two exchange equilibria. At this point it is important to know which of the four sites might be responsible of the proton exchange in the available acidity range.

We may imagine, according to Parks,[11] the iron(III) phosphate to be a complex oxide, that is, a mixture of Fe_2O_3 and P_2O_5, whose surface contains OH groups of different types. As a first approximation, these may be considered independent, and the isoelectric point of each type of site, $IEP_{(s)}$, will be that of the pure oxide or hydroxide. The net surface charge at a pH between the two $IEP_{(s)}$'s is the algebraic sum of the negative charge on the more acid sites and the positive charge on the more basic sites.

The zero charge point, ZCP, lies between the two $IEP_{(s)}$ of the end members of a binary system. Parks[11] proposes for hydrous Fe_2O_3 $IEP_{(s)} = 9.3$ and for the hypothetical hydrous P_2O_5 $IEP_{(s)} = -3.4$. This rule yields 2.95 for the ZCP of $FePO_4$, a value indeed not very far to the inflection points indicated by the present data. In other words, the sites of the Fe_2O_3 in the vicinity of ZCP are present mostly as charged $>FeOH_2^+$, while $>PO^-$ sites prevail on the surface of the phosphorus oxide. On the whole at the ZCP the net surface charge is null or $\{>FeOH_2^+\} = \{>PO^-\}$. The expression of H then becomes

$$\begin{aligned} Q &= H - H_{ip} = \{>FeOH_2^+\} - \{>PO^-\} \\ &= T_{Fe}((H^+)/({}^{Fe}K_{a1} + (H^+)) - {}^{P}K_{a2}/({}^{P}K_{a2} + (H^+))) \end{aligned} \tag{17}$$

which is the basis of the calculation of T_{Fe}.

The most favorable conditions for the evaluation of T_{Fe} are met at high electrolyte concentrations. Then, the data are satisfactorily explained with a high capacitance model. Within the scope of this model apparent acidic constants are related to intrinsic ones by:[12]

$$\log K_a = \log K_{a(intr)} + \psi F/(2.303RT) = \log K_a + \alpha Q \tag{18}$$

where α is constant at a constant I. At high I, α is small so that $K_a \cong K_{a(intr)}$.

To assess T_{Fe} we consider data at $I = 1.0\ mol \cdot dm^{-3}$ and pH > 3. In the basic side of the inflection point ${}^{P}K_{a2}/({}^{P}K_{a2} + (H^+)) \cong 1 - (H^+)/{}^{P}K_{a2}$ and, since $\log({}^{P}K_{a2}{}^{Fe}K_{a1}) \cong -6.0$, we may approximate $\{>PO^-\} = T_{Fe}(1 - 10^{-6.0}(H^+)/{}^{Fe}K_{a1})$. Taking into account 18 and putting

$$\xi = (H^+)10^{(-\alpha Q)} \tag{19}$$

eq 17 is transformed into 20

$$Q = T_{Fe}(H^+)/((H^+) + {}^{Fe}K_{a1}) + T_{Fe}(1 - 10^{-6.0}(H^+)/{}^{Fe}K_{a1})$$
$$= T_{Fe}\xi/(\xi + {}^{Fe}K_{a1(intr)}) + T_{Fe}(1 - 10^{-6.0}\xi/{}^{Fe}K_{a1(intr)}) \quad (20)$$

The most probable T_{Fe}, α, and ${}^{Fe}K_{a1(intr)}$ values are found by least-squares procedures. From data at 1 mol·dm^{-3} we calculate

$$\alpha = 0.20 \pm 0.05, \quad T_{Fe} = 1.53 \pm 0.05, \quad \text{and}$$
$$\log {}^{Fe}K_{a1(intr)} = -4.0 \pm 0.1$$

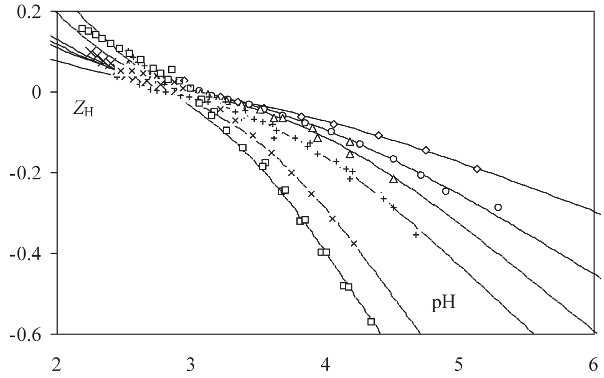


Figure 2. Titrations with HFP(in situ). Z_H, eq 21 as a function of pH at different (Na)ClO$_4$ concentrations (mol·dm^{-3}): ◊, 0.002; ○, 0.01; △, 0.030; +, 0.10; ×, 0.30; □, 1.00. Curves calculated with the parameters in Table 4.

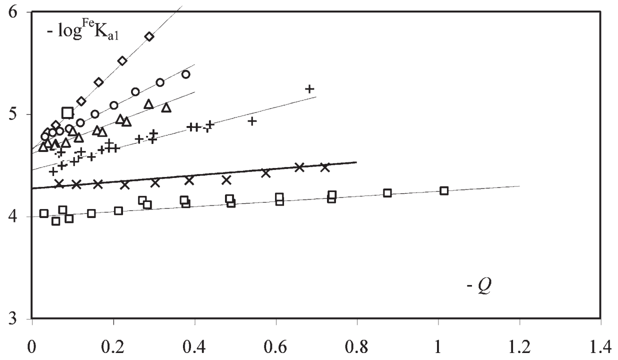


Figure 3. The log ${}^{Fe}K_{a1}$ as a function of Q. Symbols as in Figure 2. The straight lines represent the best fit assuming ${}^{Fe}K_{a1(intr)}$ and α values in Table 4.

Acidic Surface Constants. The calculation of the apparent constants at each I level is based on expression 21:

$$Z_H = Q/T_{Fe} = ((H^+)/({}^{Fe}K_{a1} + (H^+)) - {}^{P}K_{a2}/({}^{P}K_{a2} + (H^+)) \quad (21)$$

which was deduced assuming T_{Fe} from the previous section. Z_H is the relative surface charge. The Z_H(pH) data are visualized in the graph of Figure 2.

Reliable ${}^{Fe}K_{a1}$ values are obtained from data at pH > 3, when ${}^{P}K_{a2}/({}^{P}K_{a2} + (H^+))$ in 21 is well approximated by $1 - (H^+)/{}^{P}K_{a2} = 1 - (H^+)\,{}^{P}K_{a1}10^{6.0}$. Equation 21 then yields

$$({}^{Fe}K_{a1})^2 + {}^{Fe}K_{a1}\{(H^+)^2 - (1 + Z_H)10^{-6.0}\}(H^+)^{-1} - Z_H)10^{-6.0} = 0 \quad (22)$$

At pH < 3, $((H^+)/({}^{Fe}K_{a1} + (H^+)) \cong 1 - 10^{-6.0}/({}^{P}K_{a2}(H^+))$ and ${}^{P}K_{a2}$ is calculated with 23

$$({}^{P}K_{a2P})^2 + {}^{P}K_{a2}\{10^{-6.0} - (1 - Z_H))(H^+)^2\}(Z_H)(H^+))^{-1} + 10^{-6.0}Z_H)^{-1} = 0 \quad (23)$$

The plots log K_a versus Q for data at pH > 3 are visualized in Figure 3. The points fall on straight lines as expected by the constant capacitance model, $\log {}^{Fe}K_{a1} = \log {}^{Fe}K_{a1(intr)} + \alpha Q$. The most probable values of intrinsic constants and α are given in Table 4. The calculation of ${}^{P}K_{a2P}$ from data at pH < 3, due to the limited pH range available, is less accurate. The variation of ${}^{P}K_{a2}$ with Q is too uncertain to allow an estimate of α. The values proposed in Table 4 are average values rather than extrapolated ones. Within the large limits of error the sum $\log {}^{Fe}K_{a1} + \log {}^{P}K_{a2}$ is always coincident with the expected value of $-6.0 = -2\text{pH}_{ip}$. The differences between constants at low I and those at I > 0.1 and 0.3 are in part explained with changes in the activity coefficient of HClO$_4$ in NaClO$_4$ media. Evaluations by SIT lead to insufficient corrections (see Table 4). The marked increase of ${}^{Fe}K_{a1}$ at increasing electrolyte concentration can be explained by specific interactions of medium ions with the surface.

Measurements Relative to HFP(dialyzed). The data were collected in pH and a ranges similar to those employed for HFP(in situ). The H(pH) curves show features similar to those found with HFP(in situ), shown in Table 5. The points fall on curves with an inflection point at pH = 3. However, the ordinate at the inflection point, H_{ip}, is significantly smaller and becomes different from zero only at I > 0.1 mol·dm^{-3}. At any rate the specific interactions of medium ions is much reduced. To establish whether the exchange ability of HFP versus Na$^+$ and/or ClO$_4^-$ ions is specific, a series of measurements was carried out in 0.3 mol·dm^{-3} KNO$_3$. As the results shown in Table 5

Table 4. Surface Acidic Constants and Values of α for HFP(in situ) ($y_\pm$, Molar Activity Coefficient (Trace) of HClO$_4$ in NaClO$_4$ Media)

I mol·dm^{-3}	$-\log {}^{Fe}K_{a1(intr)}$	$-\log {}^{P}K_{a2}$	α kg·mol^{-1}	$-\log y_\pm$	$-\log {}^{Fe}K_{a1(intr)}$ I = 0
0.002	4.66 ± 0.01	≈1.4	3.80 ± 0.12	0.02	4.68
0.01	4.67 ± 0.05	1.46 ± 0.05	2.05 ± 0.14	0.05	4.72
0.03	4.66 ± 0.05	1.3_8 ± 0.2	1.3 ± 0.3	0.07_5	4.73
0.1	4.46 ± 0.05	1.4 ± 0.2	1.0 ± 0.2	0.10	4.56
0.3	4.24 ± 0.05	≈1.5	0.3_2 ± 0.2	0.12	4.36
1.0	4.05 ± 0.10	1.6_5 ± 0.2	0.2 ± 0.05	0.10	4.15

Table 5. Survey of Results on HFP(dialysed)

$NaClO_4$	H_{ip}		α			
$mol\cdot dm^{-3}$	$mol\cdot kg^{-1}$	$-\log {}^{Fe}K_{a1(intr)}$	$kg\cdot mol^{-1}$	$-\log {}^{P}K_{a2(intr)}$	$-\log y_{\pm}$	$-\log {}^{Fe}K_{a1}$ $I = 0$
0.002	0.00	4.8 ± 0.1	3.0 ± 0.3	~1.5	0.02	4.82
0.010	0.00	4.7 ± 0.1	2.4 ± 0.2	~1.5	0.05	4.75
0.030	0.0133	4.69 ± 0.05	1.9 ± 0.2	1.4 ± 0.1	0.075	4.76
0.10	0.00	4.67 ± 0.05	1.2 ± 0.1	1.3_5 ± 0.1	0.10	4.77
0.10[a]	0.0133	4.67 ± 0.05	1.1 ± 0.1		0.10	4.77
0.10	0.0553	4.64 ± 0.05	1.3 ± 0.1		0.10	4.74
0.30	0.094	4.52 ± 0.05	0.6_8 ± 0.1	1.5 ± 0.1	0.12	4.67
0.30	0.100	4.45 ± 0.05	0.8_1 ± 0.1	1.55 ± 0.05	0.12	4.57
1.00	0.133	4.41 ± 0.05	0.45 ± 0.05	1.6 ± 0.1	0.10	4.51
1.00	0.133	4.42 ± 0.05	0.41 ± 0.05	1.5 ± 0.2	0.10	4.52
			KNO_3 $mol\cdot dm^{-3}$			
0.30	0.165	4.26 ± 0.05	0.4_6 ± 0.1	1.7_5 ± 0.1	0.17	4.43
0.30[a]	0.500	4.24 ± 0.05	0.6_2 ± 0.1		0.17	4.41

[a] Reverse titration.

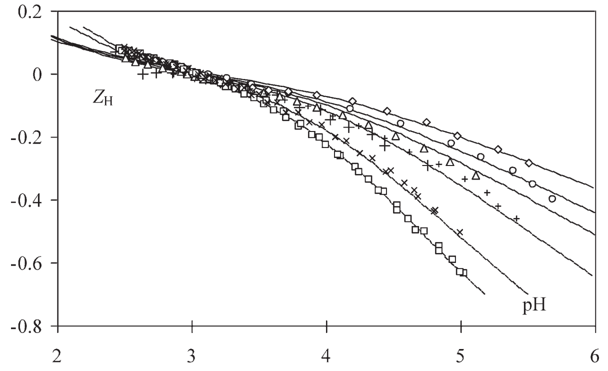


Figure 4. Titrations with HFP(dialyzed). Z_H as a function of pH. Symbols as in Figure 2. Curves are calculated with the parameters given in Table 5.

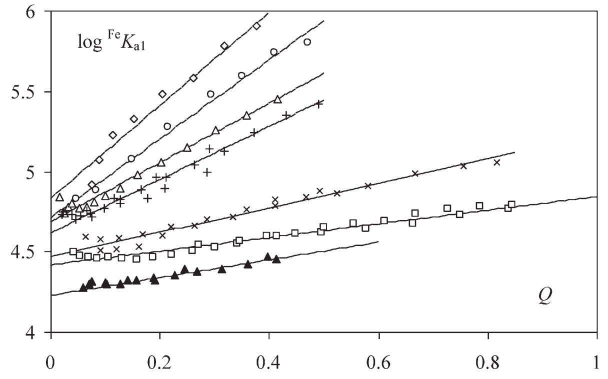


Figure 5. $\log {}^{Fe}K_{a1}$ as a function of Q. Symbols as in Figure 2. Filled triangles represent data at 0.3 $mol\cdot dm^{-3}$ KNO_3. Straight lines are calculated with the parameters in Table 5.

indicate, there is no appreciable difference between the two media. Notice that the reverse titration in 0.3 $mol\cdot dm^{-3}$ KNO_3 was performed after the test solution was left for a night at pH = 5.5 before reacidification, thus in conditions favorable to the exchange of K^+ with H^+ ions. This explains the abnormal drop of H_{ip}. However, the K_a values determined from data of this series coincide within the limits of experimental accuracy with constants evaluated in parallel titrations at $I = 0.3$ $mol\cdot dm^{-3}$.

The data treatment is similar to the one described above for HFP(in situ). First, the number of sites per kg of $FePO_4$, $T_{Fe} = T_P$, was obtained from data at 1 $mol\cdot dm^{-3}$ $NaClO_4$ and 0.3 $mol\cdot dm^{-3}$ KNO_3. It was concluded that $T_{Fe} = 1.33 \pm 0.03$ $mol\cdot kg^{-1}$, hence lower than 1.53 relative to HFP(in situ). This is probably on account of a lower specific surface area.

The function $Z_H = Q/T_{Fe}$, illustrated in Figure 4, was analyzed as above for data relevant HFP(in situ) to yield $^{Fe}K_{a1(intr)}$, $^{P}K_{a2(intr)}$, and α. In Figure 5 are shown the graphs $\log {}^{Fe}K_{a1}$ versus Q. The results of calculations are given in Table 5. The last column of Table 5 reports intrinsic constants corrected for the activity coefficient of $HClO_4$ and HNO_3. The constants calculated for $I \leq 0.3$ $mol\cdot dm^{-3}$ agree satisfactorily. The small but systematic deviations at higher I as ascribable to specific effects different from those arising from the displacement of the inflection point.

■ DISCUSSION

During the last few decades reactions at the solid−liquid interface have been interpreted by a number of equilibrium models. All of these are founded on the law of mass action and may assume corrections for electrostatic effects at the liquid−solid interface. The most commonly used models are the following three.

(i) The nonelectrostatic model in which electrostatic effects are neglected. The most serious limitation of this model is the great number of sites with different constants needed to explain the data.

(ii) The constant capacitance model based on a linear relationship between the charge at the inner Helmholtz plan, which represents specifically adsorbed ions, and the surface potential.

(iii) The Langmuir−Freundlich model which is a useful alternative to models i and ii. This model invokes a continuous distribution of acidity constants about a modal value in the context of a Gaussian distribution.

The models are equivalent in fitting experimental data though the intrinsic equilibrium constants may differ considerably. Consequently the choice of an electrostatic model is not obvious. The guiding criterion for using the constant capacitance model is the simplicity of calculations.

The specific capacitance κ, $CV^{-1}\cdot m^{-2}$, = σ/ψ, according to Stumm and Morgan[12] is related to the parameter α in 18 by

$$\alpha = z^2F^2/(2.303RTs\kappa) \tag{24}$$

where F, R, and T have the usual meanings, z is the charge of the exchanged ion and s is the specific area. Taking $s = 162.4\cdot 10^3\ m^2\cdot kg^{-1}$, as resulted from BET, we estimate for κ a value of $10\ \alpha^{-1}$, which means for high ionic strengths a very high capacitance, thus a low ψ value to justify the assumption of a nonelectrostatic model. It must be added that these estimates are based on specific areas from BET which might be underestimated for a porous solid.

The density of proton binding at the HFP surface was evaluated as $6.02\cdot 10^{23}\ T_{Fe}s^{-1}$. We calculate for HFP(dialyzed) 5 ferrihydrols/nm^2. The surface contains an equal number of phosphohydrols. These figures compare well with proton densities reported for hydrous silica and iron(III) hydroxide. However, in consideration of the underestimated specific areas by BET the proton densities must be understood as high bounds.

■ SYMBOLS

a, suspension concentration in $g\cdot dm^{-3}$
H, surface proton excess in $mol\cdot kg^{-1}$, eq 16
H_{ip}, the value of H at the inflection point
HFP(in situ), hydrous $FePO_4$ precipitated from solution in the presence of a given ionic medium
HFP(dialyzed), hydrous $FePO_4$ precipitated and washed by decantation and dialysis
I, ionic strength in $mol\cdot dm^{-3}$ adjusted with $(Na)ClO_4$
${}^{Fe}K_{a1}$, apparent constant of equilibrium 14
${}^{Fe}K_{a2}$, apparent constant of equilibrium 15
${}^{P}K_{a1}$, apparent constant of equilibrium 16
${}^{P}K_{a2}$, apparent constant of equilibrium 17
$K_{a(intr)}$, intrinsic constant, eq 18
Q, surface charge in $mol\cdot kg^{-1}$, eqs 9 and 17
s, specific area in $m^2\cdot kg^{-1}$
T_{Fe}, total number of ferrihydrols, $mol\cdot kg^{-1}$, eq 10
T_P, total number of phosphohydrols, $mol\cdot kg^{-1}$, eq 11
Z_H, relative surface charge, eq 21
α, slope of the plots $\log K_a$ versus Q
κ, specific capacitance in $CV^{-1}\cdot m^{-2}$
σ, surface charge in Cm^{-2}
ψ, surface potential in V
$\{\}$, surface concentration in $mol\cdot kg^{-1}$

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