Determination of Diffuse Double Layer protonation constants for hydrous ferric oxide (HFO): supporting evidence for the Dzombak and Morel compilation

Patrius Julius Pretorius[1]* and Peter William Linder[2]

[1]*Division of Water, Forestry and Environmental Technology, CSIR, PO Box 320, Stellenbosch 7599, South Africa*

[2]*Department of Chemistry, University of Cape Town, Rondebosch 7700, South Africa*

ABSTRACT

The acid-base properties of hydrous ferric oxide were studied by glass electrode potentiometry. From the potentiometric data, surface protonation constants were derived according to the Diffuse Double Layer convention. Chemical equilibrium modelling of the experimental system suggests that titration points below pH 4 should not be used for the determination of protonation constants because of potential HFO dissolution. Surface protonation constant, PZC and binding site estimates agree excellently with currently available best estimates.

Keywords: Surface complexation, diffuse double layer, adsorption, hydrous ferric oxide, surface protonation

INTRODUCTION

The fate and transport of trace metals in natural systems are to a large extent influenced by adsorption onto particulate phases, such as the oxides of iron, manganese and aluminium as well particulate organic matter. Amongst the information required for predicting the fate, transport and effects of trace metals in natural systems are data describing adsorption of trace metals by particulate material. The surface properties of colloidal particles play an important role in determining their trace metal adsorption capacities. Fundamental to this are the acid–base properties of these materials (Smith and Jenne, 1991). Dzombak and Morel (1990) compiled a comprehensive and valuable collection of Diffuse Double Layer surface complexation constants for HFO. These constants were determined by reworking the results of critically selected adsorption studies published in the open literature. Notwithstanding the reliability of the Dzombak and Morel database, there is justification for continually re-investigating the systems considered because of inevitable residual uncertainties in the adsorption constants listed. These are related to uncertainties regarding the exact experimental conditions employed in the studies selected by them, the fact that data from a limited number of different laboratories were used and the nature of the iron solids employed by the different laboratories. Also, the presence of carbonates has been said to have an effect on surface parameters determined for the oxides of iron (Lumsdon and Evans, 1994).

In this paper, we report Diffuse Double Layer surface complexation constants for HFO which were determined under experimental conditions closely following the data selection criteria employed by Dzombak and Morel (1990). CO_2 was scrupulously excluded in the experiments. Furthermore, a rigorous electrode calibration procedure was employed to ensure that the glass electrode was calibrated accurately in terms of hydrogen ion concentration, instead of activity. Poor, or inappropriate electrode calibration procedures are frequently the prime source of poorly determined equilibrium constants (Martell *et al.*, 1988).

MATERIALS AND METHODS

Preparation of HFO

Preparation of HFO took place in a glass titration vessel under purified N_2 atmosphere. The gas was bubbled through a 50% KOH solution to remove CO_2 and Fiesser's solution (Vogel, 1985) to remove O_2. The gas was pre-wetted by bubbling through a 0.3 M $NaNO_3$ solution. 40.4 g $Fe(NO_3)_3.9H_2O$ (Merck pro analysi) was weighed into a 1000cm^3 volumetric flask. To this, 7.65 g $NaNO_3$ (Merck GR) was added. In a N_2 purged glove box, using boiled-out deionized glass distilled water, the solution was made up to the mark. This resulted in a 0.1 M $Fe(NO_3)_3$ solution with an ionic strength of

0.69 M. 20.00 cm^3 of this solution was added to a N_2 flushed, thermostatted glass titration vessel using a Metrohm Dosimat 665 automatic burette. After the attainment of temperature equilibration (25°C), 6.00 cm^3 1 M NaOH was slowly added to the solution using a Metrohm Dosimat 665 burette. The solution was constantly stirred using a Teflon coated stirrer bar and a magnetic stirrer. HFO started precipitating immediately upon addition of NaOH. The precipitate was aged for four hours under constant stirring and inert atmosphere.

Measuring [H^+]

Hydrogen ion concentration was measured using a glass electrode and a calomel reference electrode (Metrohm). A common deficiency in reported equilibrium constant determination studies is the improper calibration of the pH meter (May *et al.*, 1982; Martell *et al.*, 1988). The electrode system was calibrated in terms of hydrogen ion concentration, [H^+], instead of hydrogen ion activity. Hydrogen ion concentration is calculated from EMF readings using the Nernst equation:

$$E = E^{const} - s\,log[H^+]$$

where E^{const} and s are the electrode intercept and slope respectively. The parameter E^{const} incorporates electrode potentials, liquid junction potential effects and activity coefficients. In order to measure [H^+] accurately, a thorough electrode calibration regime should be followed to obtain values for E^{const} and electrode slope s. The calibration procedure followed in this work consisted of two steps. First, the Nernstian behaviour of the glass electrode was checked using three buffer solutions (Radiometer buffers 4.01, 7.00 and 9.18). EMF was plotted against buffer pH. A deviation of less than 5% from the theoretical Nernstian value was deemed to be acceptable. Second, a known amount of glycine was weighed out into a titration vessel and dissolved in 20.0 cm^3 0.3 M $NaNO_3$. The solution was titrated with a standardized 0.1 M KOH solution containing 0.3 M $NaNO_3$. Titration data, which consisted of volume of titrant (cm^3) and EMF readings (millivolt) were used as input into ESTA (May *et al.*, 1985; 1988), a programme which allows the simultaneous determination of equilibrium constants and electrode parameters. From the titration data collected, glycine protonation constants and electrode intercept, E^{const}, were determined. The theoretical Nernstian slope of 59.16 mV/pH was used. The agreement between glycine protonation constants determined here and those published in the literature (NIST, 1993) were taken as a measure to assess the quality of the electrode parameters. For all calibration titrations, discrepancies less than 0.05 log units for $\log\beta$s were obtained. Titrations were carried out in duplicate or until the difference in E^{const} calculated from the different titrations was less than 0.2 mV.

Owing to the fact that this calibration procedure is time consuming, a single point calibration was also performed at the time of electrode calibration. This consisted of measuring the EMF of a 0.1 M HNO_3 solution at 25°C and an ionic strength of 0.3 M $NaNO_3$. This single point calibration point is denoted as E_{acid}^{cal}. This exercise was repeated before each subsequent titration to obtain E_{acid}^{exp} which was then used to adjust E_{cal}^{const} to yield E_{exp}^{const}. Implicitly the assumption is made here that the electrode response to change in [H^+] (*i.e.* the slope) remains constant.

Assessing the influence of the suspension effect

The suspension effect refers to the difference in pH observed between a suspension and its supernatant (Jenny *et al.*, 1950; Bates, 1964). This effect implies that accurate [H^+] determination is not possible in a suspension. The presence of this effect was assessed using the method used by Jenny to illustrate it. EMF was measured with the electrodes in the suspension under constant stirring. Stirring was discontinued and the suspension allowed to settle out. The electrodes were lifted so that they were in contact only with the supernatant. A drop in EMF of approximately 0.4 mV was observed. However, this drop corresponds well with the 0.6 mV drop observed in an 0.1 M HNO_3 solution upon discontinuation of stirring. The same result was obtained after the addition of 1 cm^3 0.1 M NaOH to the suspension, indicating that the effect is also not observable at high pH. It may thus be concluded that no evidence of the suspension effect was found.

Acidimetric titrations

After the freshly prepared solid was aged for four hours, an additional amount of 0.20 cm^3 NaOH was added to the suspension. The suspension was titrated with 0.1004 M HNO_3 with an ionic strength of 0.3 M $NaNO_3$. Titrations were carried out using a computer controlled Metrohm ABU 80 automatic burette. EMF was monitored using a glass electrode and calomel reference electrode (both Metrohm). Acid additions were made once EMF drift was less than 0.2 mV/300 seconds, or, alternatively, after 300 seconds had elapsed.

Adsorption constant determination

Protonation constants were determined using the non-linear optimization programme FITEQL version 3.1 (Herbelin and Westall, 1994). FITEQL is an iterative optimization programme which allows the optimization of a number of specified parameters. The Goodness of Fit of a given model is given by, WSOS/DF, which is the weighted sum of squares divided by the degrees of freedom of the problem. WSOS/DF values between 0.1 and 20 are indicative of good agreement between model and experiment. Input data consisted of (a) total hydrogen ion concentration (T_H) in mol dm^{-3}, (b) the logarithm of free hydrogen ion concentration, log[H^+], (c) dilution factors and (d) mass of solid in g dm^{-3}. Parameters to be optimized were adsorption constants and surface site concentration. In order to select the best model, constants and binding site concentrations were determined on a titration by titration basis. Once the best model was selected, best estimates for adsorption constants and binding site concentrations were determined by pooling all titration data in one input file. Error estimates for experimental data used in the FITEQL calculations were similar to those used by Dzombak and Morel.

Following Dzombak and Morel (1990), titration data were modelled assuming a homogeneous surface (*i.e.*, all sites ≡XOH are equivalent) and the following surface species:

$$\equiv XOH + H^+ \rightleftharpoons \equiv XOH_2^+ \quad \log K_1$$
$$\equiv XOH \rightleftharpoons \equiv XO^- + H^+ \quad \log K_2$$

The parameters which were optimized are log K_1, log K_2 and total site concentration [≡XOH]. The HFO surface area was assumed to be 600 m^2 g^{-1}, instead of the observed N_2-BET surface area of 327 m^2 g^{-1}. This corresponds to the approach followed by Dzombak and Morel. They justify the use of 600 m^2 g^{-1} by noting that the conditions employed in determining N_2 -BET surface areas may lead to surface decomposition and result in an underestimation of the true surface area. The observed N_2-BET surface area corresponds well with values listed in Table 5.1 of Dzombak and Morel.

RESULTS AND DISCUSSION

Figure 1 shows pH vs T_H results for three titrations. pH values were calculated from EMF readings using the Nernst equation and electrode parameters (E_{Cell}, s) determined during electrode calibration. Good reproducibility was obtained. The curves are quite featureless, with a slight levelling off at high and low pH.

Figure 2 compares experimental and calculated T_H values over a pH range of 3 to 10.7. A total of 53 data points were used in this calculation. A summary of the results obtained from this calculation is given in Table 1.

Goodness of Fit parameters determined for the respective titrations are just outside the range regarded as indicating an acceptable fit. Inspection of Figure 2 shows that the fit at low pH is not very good. A possible reason may be that, at low pH, dissolution of HFO takes place. Because of this, aqueous phase Fe(III) concentration may become significant, leading to reactions not accounted for in the FITEQL model used to obtain the calculated values shown in Table 1. This was investigated by simulating the experimental system, using MINTEQA2 (Allison *et al.*, 1991). Simulations were carried out over a pH range of 2 to 7 and a different iron solid was allowed to precipitate in each simulation. The equilibrium constants used in these simulations were those contained in the MINTEQA2 database. The constants were compared with those listed in JESS (May and Murray, 1991a,b) and NIST (1993). Good agreement amongst the various databases were found.

Simulation results are shown in Figure 3. The iron solids which were allowed to precipitate are Ferrihydrite (curve a), Lepidocrocite (curve b), Maghemite (curve c), Goethite (curve d) and Hematite (curve e). It is clear from Figure 3 that Fe^{3+} concentrations ranging from 10^{-2} M to 10^{-10} M may be expected at pH 3, depending on the

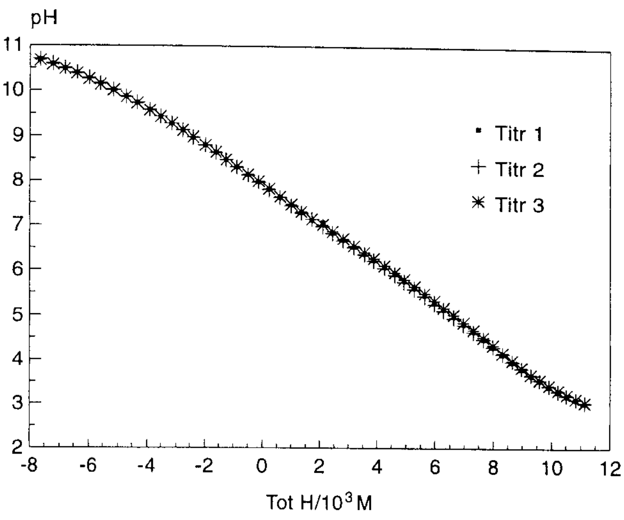

Figure 1 *pH vs Total H (mol dm⁻³) data for three HFO titrations recorded at T = 25°C and I = 0.3.*

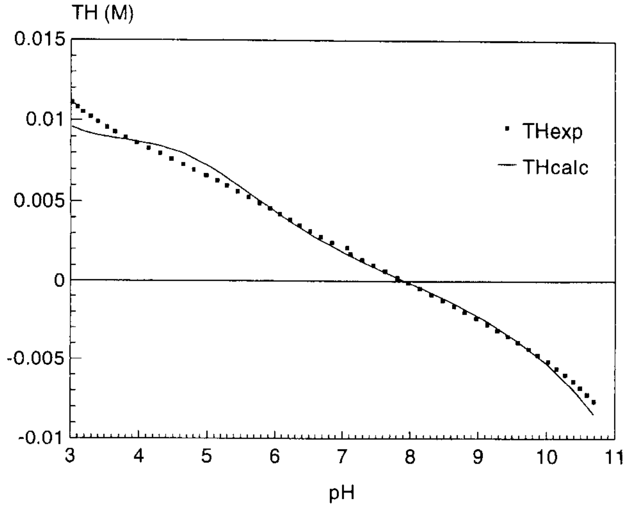

Figure 2 *Experimental and calculated (FITEQL) Total H vs pH curves using data recorded at T = 25°C, I = 0.3 and pH 3 to 10.7.*

Table 1 Summary of hydrous ferric oxide protonation results obtained using 53 data points

Parameter	Titration 1 Ionic strength (mol dm^{-3})		Titration 2 Ionic strength (mol dm^{-3})		Titration 3 Ionic strength (mol dm^{-3})	
	0.3	0.0	0.3	0.0	0.3	0.0
Log K_1	6.95	7.08	6.92	7.05	6.97	7.10
Log K_2	–8.87	–9.00	–8.88	–9.01	–8.87	–9.00
Site concentration (M)	1.05 × 10^{-2}		1.08 × 10^{-2}		1.08 × 10^{-2}	
WSOS/DF	25.0		24.9		23.6	
pH range	3.02–10.7		3.03–10.7		3.03–10.7	

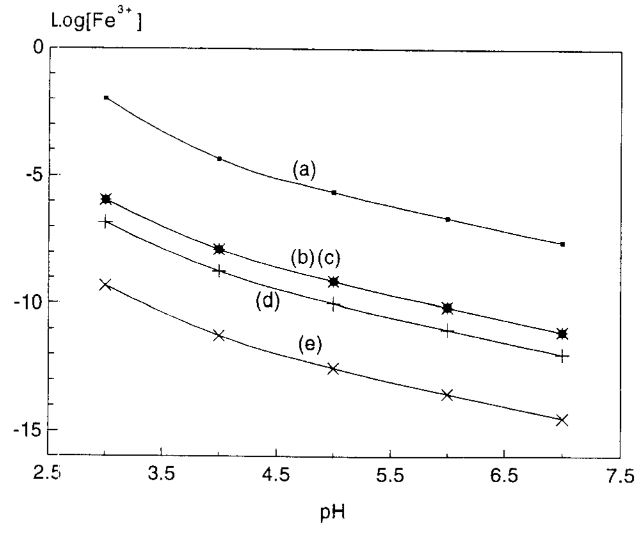

Figure 3 *Log[Fe^{3+}] as a function of pH and mineral allowed to form as calculated by MINTEQA2. (a = ferrihydrite, b = lepidocrocite, c = maghemite, d = goethite, e = hematite).*

Table 2 Summary of hydrous ferric oxide protonation results obtained using 42 data points.

Parameter	Titration 1 Ionic strength (mol dm^{-3})		Titration 2 Ionic strength (mol dm^{-3})		Titration 3 Ionic strength (mol dm^{-3})	
	0.3	0.0	0.3	0.0	0.3	0.0
Log K_1	7.20	7.33	7.18	7.31	7.22	7.35
Log K_2	–8.67	–8.80	–8.67	–8.80	–8.66	–8.79
Site concentration (M)	8.74×10^{-3}		8.73×10^{-3}		8.79×10^{-3}	
WSOS/DF	4.4		4.2		3.5	
pH range	4.47–10.7		4.47–10.7		4.50–10.7	

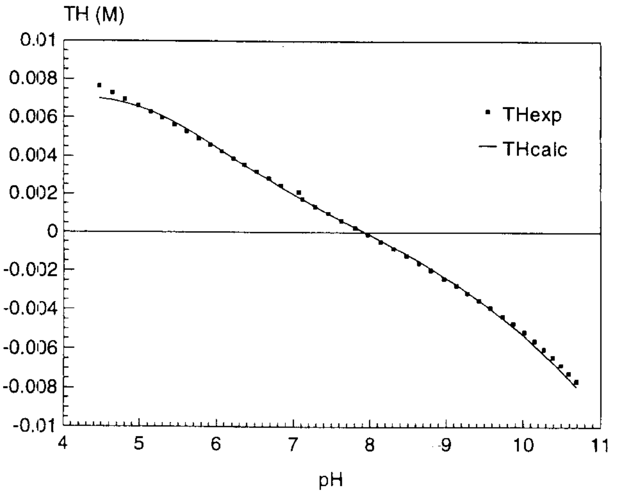

Figure 4 *Experimental and calculated (FITEQL) TH vs pH curves using data recorded at T = 25°C, I = 0.3 over a pH range of 4.47 to 10.7.*

iron solid allowed to precipitate. Figure 3 thus suggests that data collected below pH 4 should be disregarded because of possible dissolution of the solid being studied.

A typical result obtained using a smaller data set is shown in Figure 4. A summary of the optimized parameters obtained from using smaller data sets is shown in Table 2. Rewriting the adsorption reactions as acid dissociation constants, we obtain best estimates by calculating average log K's:

$$\equiv XOH_2^+ \rightleftharpoons \equiv XOH + H^+ \quad \log K_1 = -7.33 \pm 0.02$$

$$\equiv XOH \rightleftharpoons \equiv XO^- + H^+ \quad \log K_2 = -8.80 \pm 0.004$$

This compares well with the values of –7.29 and –8.93 obtained by Dzombak and Morel for the corresponding reactions. From the relationship

$$PZC = 0.5(pK^{int}_1 + pK^{int}_2)$$

we obtain PZC = 8.07, which is in close agreement with values listed by Dzombak and Morel.

Average binding site concentration calculated from the data in Table 2 is 8.75×10^{-3}mol.dm^{-3}. This is equivalent to 0.108 mol sites/mol HFO, assuming 89g HFO per mol Fe. This value is lower than the 0.2 mol sites/mol HFO used by Dzombak and Morel, but is within the range observed by others (Table 5.3 in Dzombak and Morel).

It may thus be concluded that the agreement between protonation constants determined in this work and those tabulated by Dzombak and Morel is good, thus providing confirmation of the reliability of the latter.

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