



PII S0016-7037(00)00948-1

Limitations of the potentiometric titration technique in determining the proton active site density of goethite surfaces

JOHANNES LÜTZENKIRCHEN,¹ JEAN-FRANÇOIS BOILY,² LARS LÖVGREN,^{3,*} and STAFFAN SJÖBERG³¹Forschungszentrum Karlsruhe GmbH, Institut für Nukleare Entsorgung, Postfach 3640, D-76021 Karlsruhe, Germany²Geochemistry Group, Institut für Mineralogie und Petrographie, Sonneggstrasse 5, ETH-Zürich, CH-8092 Zürich, Switzerland³Department of Inorganic Chemistry, Umeå University, SE-901 87, Umeå, Sweden

(Received July 5, 2001; accepted in revised form April 29, 2002)

Abstract—Density of proton active surface sites at mineral surfaces is a property of fundamental importance in equilibrium modeling of surface complexation reactions. In this article, methods for an experimental determination of these sites at the surface of α -FeOOH (goethite) are explored. It is shown that previously obtained saturation data of goethite with respect to protons do not yield a site density that can be considered as an intrinsic sorbent property: the results are below crystallographically expected values and values for different ionic media in terms of composition and concentration yield different numbers—for example, chloride would yield higher values than nitrate at the same concentration, and higher electrolyte concentration would favor higher apparent maxima. Although site saturation might be explained by electrostatic repulsion, which is more efficient at high electrolyte concentration or for certain ions, further independent experimental results show that no saturation occurs on goethite down to $\text{pH} \equiv -\log[\text{H}^+] = 2.2$ and possibly to $\text{pH} = 1.0$ in 0.6 M NaCl. For those very low pH values, the experimental charging curve was obtained by coulometric back titration (using the Gran plot) or titrations with tris (hydroxymethyl)-aminomethane of the supernatant of acidified goethite suspension. These experimental data are to our knowledge the first high quality data at such low pHs. However, small errors in the determination of proton concentrations (1%) are shown to strongly affect the shape of the charging curve for $\text{pH} < 2$. Furthermore, goethite dissolution (proton consumption and iron reduction in coulometric titrations) and liquid junction effects interfere at low pH, hampering the straightforward application of coulometric Gran titrations over the whole pH range. From these experiments, it can nonetheless be ascertained that a minimum of 2.5 protons/nm² can be adsorbed at the goethite surface from the point of zero charge (pH 9.4) to pH 0.9. Although these studies are restricted to goethite, those studies in which titrations with excess acid and base have been used for the determination of proton active site concentrations of sorbents should be reconsidered. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

The site density (SD) of mineral surfaces is a fundamental property from different points of view:

- (1) Mineral surfaces as scavengers for toxic solutes may exhibit maximum adsorption densities that are strongly related to the SD when adsorption occurs via surface complexation (SC). Sorption beyond the threshold imposed by a SD is controlled by other mechanisms.
- (2) Values of SD are required in surface complexation models (SCMs) where all other modeling parameters are in principle related to it.

Unfortunately, literature values of SD for a given mineral phase are commonly spread over a wide range.

Major discrepancies between different schools of thought mainly stem from their different “historical” backgrounds. This is readily observed for the case of the determination of SD in the past three decades:

- (1) Solution or coordination chemists, such as Schindler and Stumm (1987), have developed the mainframe of SC theory as it is still applied today by coupling mass law equations with theories of the electrical double layer. This accounts for the observed charge dependence of the SC equilibria. Their treatment of the SD parameter was

to estimate the number of proton active sites by titrating particles with excess acid or base. From these experiments a saturation level of proton or hydroxyl adsorption has been reported (e.g., Schindler and Kamber, 1968; Lövgren et al., 1990; Hoins, 1991; Hoins et al., 1993; Marmier et al., 1993; Pivovarov, 1998).

- (2) Colloid scientists (e.g., Yates, 1975) are traditionally interested in particle charge with the objective of quantifying particle stability. Their approach to the SD of particles has been to either estimate it from crystallographic considerations or from experimental tritium exchange data. Both values are usually in good agreement but this treatment typically disregards probable differences in chemical reactivity among the different surface groups expected on a certain solid. This point is improved by the work of a group in Wageningen (Hiemstra et al., 1989) by explicitly distinguishing between different sites, such as singly, doubly, and triply coordinated surface oxygens, and their respective reactivities.
- (3) Another possibility would be to use the SD parameter as an adjustable one and to fit it to experimental data, which is not uncommon (e.g., Johnson, 1990; Boily and Fein, 1996; Daughney and Fein, 1998); the problems associated to this approach have been discussed in Venema (1997) and Lützenkirchen (1999a, b).

* Author to whom correspondence should be addressed (lars.lovgren@chem.umu.se).

(4) Measured maximum adsorption densities have been summarized (Dzombak and Morel, 1990) and averaged.

Usually one of the available options is “chosen” and then applied to multicomponent systems (e.g., Dzombak and Morel, 1990; Sahai and Sverjensky, 1997; Sverjensky and Sahai, 1998). Unfortunately, the numbers obtained by the different approaches can differ by more than one order of magnitude. Most unfortunate is that all the different options typically result in models that are capable of describing adsorption data in simple binary and ternary systems. This leaves anyone involved in SC modeling in a very unfortunate situation, not only because the parameters are interrelated, and thus stability constants for surface complexes will depend on the chosen SD, but also because there is at present no rule how to obtain SD's.

A survey of the literature of SC modeling reveals that this fundamental problem has received not more than speculative attention. Koretsky et al. (1998) have made a careful review of much of the available literature. Experimentalists rely on the low values they find by saturating the surface with some probe (most frequently by protons, resulting in the proton-active site density, or PASD), whereas others, who believe in, for example, crystallographic values, speculate about the experimental problems involved in such saturation experiments. Maximum proton adsorption at levels far below the crystallographically expected maximum charge might be explained by the electrostatic repulsion that may occur under high surface charge conditions. Better shielding of positive surface charge by changing either the nature of the anion in the background salt at constant ionic strength (from nitrate to chloride) or increasing the ionic strength should then result in increasing saturation values. As a consequence the PASD parameter (as determined in this way) would not be an intrinsic particle or sorbent property. Surface complexation parameters based on such PASDs would have very limited applicability because of the existing parameter interdependencies. On the basis of this survey of the current treatment of SDs it seems necessary to attempt a clarification of the results obtained with the so far applied experimental approaches. This must concern the methods themselves and details in the treatment of raw data. In this article, we discuss the titration method, which we have adopted in our laboratory. For goethite, this approach had been thought to be corroborated by several observations. The equilibration time in the postulated saturation pH region is usually very short, typically within 15 min at pH below 3, whereas equilibration times may be much longer at higher pH (Lövgren et al., 1990). Also, anion adsorption maxima of strongly bound anions (e.g., phosphate, arsenate) are often found at ratios of ~ 0.5 or 1.0 with respect to the obtained site concentrations (e.g., Nilsson, 1995; Laiti, 1996).

Other aspects have indicated that the presence of a saturation level might be a feature that deserves detailed attention. Nilsson (1995) reported that proton uptake on goethite in the presence of phosphate was higher than expected from the previously determined PASD. Gunneriusson (1993) found that PASD was $\sim 10\%$ higher in 0.1 mol/L NaCl than in 0.1 mol/L NaNO_3 .

The determination of PASDs with excess titrant involves work under extreme pH conditions: either very acidic (e.g., for goethite at $\text{pH} < 3$) or very alkaline (e.g., for silica at $\text{pH} > 11$). At low pH, the amount of adsorbed protons can be a very small fraction of the total concentration of protons in the

system; one therefore runs into the problem of subtracting large numbers. At high pH, not only does the same hold for the base additions, but also glass electrodes usually reach their limit. In addition, depending on the time scale of the experiment, dissolution of the suspended particles can perturb the proton balance. Back titrations of supernatants of acidified goethite suspensions, as a means to determine the free proton concentration, will then be a better option than in situ potentiometric titrations.

On the basis of the fundamental importance of SD and the existing uncertainty on how to determine this property, the research reported in this article was intended to check the proton saturation level by carrying out saturation experiments at different ionic strengths, to test the electrostatic repulsion hypothesis, and to corroborate the existence of the adsorption maximum by back-titrating the supernatant of acidified goethite suspensions. Although this is only done for goethite we hope that our new experimental results help toward a more unified approach in PASD determinations for metal (hydr)oxides in general.

2. EXPERIMENTAL

2.1. Materials and Methods

All solutions and goethite suspensions were made from deionized and boiled water at total ionic strengths of 0.05 , 0.1 , 0.6 , and 2.0 mol/L NaCl (Merck, p.a., dried at 453 K) and NaNO_3 (Merck p.a., dried at 353 K). Stock solutions of HCl (Merck, p.a.) and HNO_3 (Merck, p.a.), standardized against tris (hydroxymethyl)-aminomethane (Trizma base), were used to prepare all titrants in the eight different ionic media at acid concentrations not exceeding 10% of the total ionic strength. We define ph as $-\log [\text{H}^+]$, where $\text{h} = [\text{H}^+]$, well noting that we are working in a proton concentration scale.

In this study, three different batches of goethite (G) were used. G-I was prepared and aged as described in detail earlier (Lövgren et al., 1990). Another batch, G-II, was prepared by using the procedure by Hiemstra and van Riemsdijk (1996). The third sample, G-III, was supplied in dried form by Alexander Robertsson (Department of Civil Engineering, Stanford University), and had been synthesized according to Van Geen et al. (1994). The surface area of the different goethite batches is ~ 25 to 40 m^2/g for G-I and G-III and ~ 90 m^2/g for G-II.

Two types of experiments were carried out: (1) potentiometric titrations of goethite suspensions in different ionic media in terms of composition and salt concentration; and (2) Gran (Gran, 1952) titrations of supernatant samples obtained from centrifuging/filtering suspension samples or after settling of particles after equilibration of the suspension. Experiments carried out at high ionic strengths on concentrated suspensions of particles of large surface area were especially of value to study proton uptake at low ph as the concentration of protons consumed by the surface is larger, thereby reducing errors caused by subtracting large values of total and free proton concentrations.

2.1.1. Potentiometric titrations

The experimental setup has been described in detail elsewhere (e.g., Sjöberg and Lövgren, 1993). Continuous potentiometric titrations of goethite suspensions in NaCl and NaNO_3 were carried out as described in Lövgren et al. (1990). Gran titrations of the supernatants of acidified goethite suspensions were carried out by coulometrically generated hydroxide ions. This approach turned out to be an important step to acquire high-quality data because preliminary attempts that used dilute standardized NaOH yielded larger errors.

2.1.2. Preparation of samples for Gran titrations

Three options were chosen to obtain experimental data on supernatant samples, which could be analyzed by Gran plots:

(1) Samples from several continuous titrations were taken at differ-

ent volumes of acid added in the assumed region of maximum proton adsorption according to Lövgren et al. (1990) and Gunnarsson (1993). The pH of the samples was determined by Gran titrations of the supernatant with a standardized base or a coulometer. The volumes of the supernatant samples varied from 5 to 20 mL. Therefore, to obtain the necessary volume in the titration vessel (so that the electrode, salt bridges and platinum net of the coulometer would be immersed), known volumes of an electrolyte solution of known proton concentration were added. The sample dilution could cause an undesired uncertainty.

- (2) A suspension was prepared and taken to a desired pH. The suspension was allowed to equilibrate for at least 24 h and then allowed to settle. A sample from the clear supernatant was titrated coulometrically. Sample volumes were usually 40 or 50 mL. Reversibility of the overall charging curve was tested in these systems and it was concluded that proton adsorption even at the very high proton concentrations was reversible within expected experimental errors. With this method, data over the whole range of pH were obtained to ensure that the experimental procedures would give data in agreement with continuous titrations for $\text{pH} > 3$.
- (3) The suspensions were prepared as in the last method except that the samples were centrifuged after some minutes of equilibration. Those in the range $0.9 < \text{pH} < 1.6$ were centrifuged after 2 to 4 min, whereas those at $1.6 < \text{pH} < 3.0$ were centrifuged after 15 min. Samples (30 mL) in the pH range 1.6 to 3.0 were analyzed by coulometric Gran titrations. Those in the pH range 0.9 – 1.6 were analyzed by titrating large volumes of tris (hydroxymethyl)-aminomethane solutions with a manual burette with methyl red as an end point indicator.

Option 1 was carried out with samples from 0.1, 0.6 and 2.0 mol/L NaCl suspensions of different goethite preparations. Options 2 and 3 were carried out only on the high surface area goethite in 0.6 mol/L NaCl. Concentrations of dissolved Fe(III) were determined by vis spectrophotometry (Shimadzu UV-2100) at 480 nm with the thiocyanate method (Vogel, 1978).

2.1.3. Data treatment

Data treatment of the raw titration data was performed with MAJO, a program developed in our laboratory (Magnus Karlsson and Johan Lindgren, personal communication). The basic equation for the treatment of the experimental raw data is the following:

$$E = E_0 + g \cdot \log h + E_j \quad (1)$$

E is the measured potential (mV), E_0 is the standard e.m.f. of the cell, and h is the free proton concentration, implying that all results reported here were obtained on the concentration scale. In Eqn. 1, g is the slope of the electrode, and E_j (mV) is the liquid junction potential (see below). The value of g is here taken as the theoretical Nernstian one (59.16 mV), which has been checked for the setup by comparing the glass electrode with the hydrogen gas electrode. Thus, for every titration, experiment E_0 remains to be determined. This can be done by titrating solutions of known concentration of acid with standardized NaOH solutions or coulometrically generated hydroxide ions or by titrating suspensions with excess acid — that is, under conditions where any reaction except those between hydroxyls, water, and protons can be excluded, which is a valid assumption where saturation of particles with protons occurs. A complication in the use of Eqn. 1 arises through the liquid junction potential, E_j , which in acidic solutions is linearly related to the concentration of protons by

$$E_j = J_{ac} \cdot h \quad (2)$$

It is therefore necessary to solve Eqn. 1 numerically at low pH. The parameter J_{ac} is ionic strength dependent and has been determined by Sjöberg et al. (1983) for a range of NaCl concentrations. These parameters are applied in this study. For higher ionic strengths, the absolute values of J_{ac} are smaller ($J_{ac} = -49.7/I$ mV), and the influence of the liquid junction potential on extracted pH is shifted to more acidic situations. As will be seen, besides the increased proton uptake, this is an advantage of experiments at high ionic strength.

All raw data were preliminarily treated with respect to pH_{susp} — that

is, the pH of a suspension for a given solid concentration and electrolyte concentration and composition. The pH_{susp} was usually found to be around 8.5. A solid titration with sample G-III indicated an increase of pH_{susp} with increasing solid concentration. The resulting site concentrations in the preliminary treatment have been assumed to correspond to the proton uptake between pH_{susp} and the expected onset of the maximum uptake ($\text{pH} = 3$) based on Lövgren et al. (1990). Data can then be normalized by applying Eqn. 3:

$$\Delta Z = (H - h + [\text{OH}^-])/[\equiv\text{FeOH}]_{\text{tot}} \quad (3)$$

where H is the total concentration of protons in the systems (mol/L), relative to the pH of suspension, h is the free proton concentration, and $[\equiv\text{FeOH}]_{\text{tot}}$ is the proton active site concentration (mol/L) determined by the forced plateau at $2.7 < \text{pH} < 3.0$. In this fashion, $\Delta Z = 0$ at $\text{pH}_{\text{susp}} = 8.5$; note that this is not the point of zero charge. Alternatively, we may use the point of zero charge of goethite at $\text{pH} = -\log a_{\text{H}^+} = 9.4$ (Boily et al., 2001) to plot the absolute surface charge density (σ) in terms of C/m^2 .

Gran titrations can also be treated directly by the MAJO program. In the Gran plots from option 2a, substantial number of data points were obtained (>50 data points per Gran titration). These curves were strictly linear until the equivalence point. For very low pH values, they were nonlinear as a result of liquid junction potential, reduction of ferric ions from the proton-promoted dissolution of goethite in the coulometric titrations, or both. For each Fe(III) ion found in the supernatant solution, three protons were assumed to have been consumed, and one electron added in the coulometric titrations was assumed not to have been generating hydroxide. Liquid junction parameters estimated from some of these curves or on blank titrations (to check titrant concentration coulometrically) agreed very well with those published by Sjöberg et al. (1983).

Finally, all speciation calculations were performed with a modified version of FITEQL 2.1 (Westall, 1982) elaborated in our laboratory.

3. RESULTS AND DISCUSSION

It has been indicated in the previous section that E_0 can be obtained by assuming that only water is reactive. In other words, every addition of protons to a titration vessel will cause the corresponding response in free proton concentration. For goethite, this would allow an in situ calibration of the system, if a saturation of PASD occurred. This was suggested and practiced by Lövgren et al. (1990) on the basis of (1) previous work by others indicating such maximum uptake and (2) the observation that equilibrium was reached rapidly at $\text{pH} < 3$.

To minimize effects of liquid junction at low pH, we have included both 0.6 and 2.0 mol/L media. In all the data sets, it was possible to find a plateau, irrespective of ionic strength using the method of Lövgren et al. (1990). Figure 1 shows the site concentrations obtained in this way for the range of ionic media tested with different goethite samples. The site concentration is larger for larger ionic strengths and is larger in NaCl than in NaNO_3 . Renormalization to the true pzc does not affect the tendencies. From these results, which are in agreement with an electrostatic effect on site saturation, it can be concluded that a PASD of goethite, which is obtained by titration with excess acid, is not an intrinsic sorbent property. It must rather be considered as a conditional parameter that depends on medium concentration and composition. This is a very important result, as it invalidates the physical relevance of related parameters, such as capacitances and stability constants, in these SCMs.

With respect to the liquid junction potentials we have to add that, as indicated by Sjöberg and Lövgren (1993), the tips of the salt bridges used with suspensions in our laboratory have a shape that differs from those used by Sjöberg et al. (1983). This

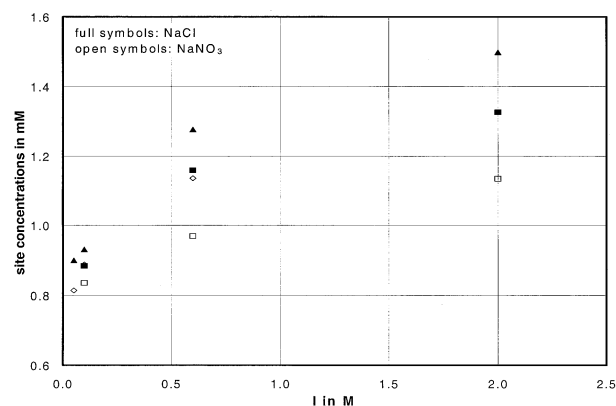


Fig. 1. Concentrations of proton uptake between $\text{pH}_{\text{zpc}} - \text{pH}_3$ for goethite obtained from titration with excess acid after treatment of the raw data as described in the text as a function of ionic strength and medium composition. Results are from three different batches of G-I (different symbols used for the respective batches) at total initial solid concentrations of 10.8 g/L; specific surface area is between 25 and 40 m^2/g .

might cause a small change in J_{ac} . However, the high ionic strength results should be free of liquid junction interference. The “apparent” saturation in 2 mol/L NaCl should extend from $\text{pH} = 3$ down to $\text{pH} = 2.2$ without interference of liquid junction, on the basis of the parameters from Sjöberg et al. (1983). However, a plateau over the whole range of pH could not be obtained. In this respect, the onset of the saturation can only be assumed to occur in 2.0 mol/L at the same pH as in 0.1 mol/L. The data in 2.0 mol/L did not indicate a plateau at $\text{pH} > 3.0$. Below this value, a cooptimization of E_0 and site concentration with the MAJO program yielded parameter sets that depend on the range of experimental data used. Assuming that the onset of the plateau always occurred at $\text{pH} < 3.0$, one would obtain even larger ionic strength effects than what is shown in Figure 1.

Because liquid junction effects are of minor importance at high ionic strengths, it is clear that the pH range used for an optimization of E_0 influences both the cooptimized proton active site concentration and E_0 . Sensitivity analyses indicated that the existence of a plateau cannot be verified by this kind of data treatment. For the lowest pH values ($2.2 < \text{pH} < 2.5$), small variations of E_0 can transform a plateau into a charging curve of increasing or even decreasing surface charge with decreasing pH . Although in the absence of goethite dissolution, the measured potentials in suspensions at $\text{pH} < 3.0$ are stable within 10 min on hundredths of a millivolt, we do not claim that E_0 can be determined with that precision. Comparison of external calibration (in a homogeneous solution—i.e., ex situ) and internal electrode calibration (in suspension—i.e., in situ) shows variations in $E_0 \leq 0.6$ mV, corresponding to 0.01 pH units. From the results in 2 mol/L NaCl, the effects of E_0 would be expected to hold at even higher pH , so that the experimental method, and the subsequent data treatment, clearly reach their limits with suspensions at low pH . However, it is important to add at this point that, except in 0.05 mol/L, variations in E_0 of ± 0.6 mV do not affect data at $\text{pH} > 3.0$ in all cases tested (~ 100 data sets).

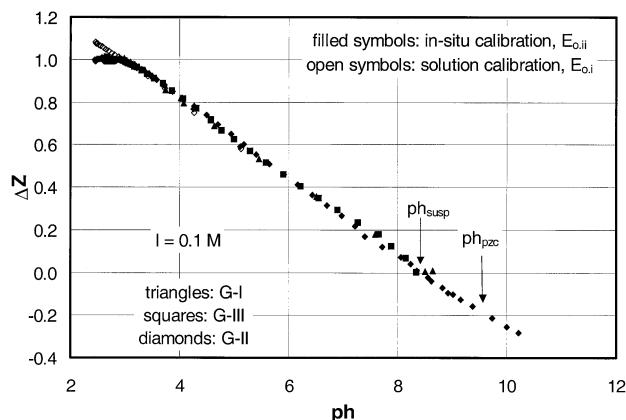


Fig. 2. Proton consumption function as a function of pH for different goethite preparations and effect of the calibration procedure (see text for details). ΔZ , defined by Eqn. 3, is equal to 0 at the pH of suspension (pH_{susp}) of the washed goethite preparation, which is not the point of zero charge (pH_{zpc}). Goethite G-I was prepared and treated as in Lövgren et al. (1990) G-II was prepared as described by Hiemstra and van Riemsdijk (1996). G-III was prepared as goethite G-I but freeze-dried (courtesy Dr. Bargar).

The experimental insight gained by the reported results is supported by recent Monte Carlo simulations of titration curves of humics, where it is shown that the errors at the extreme ends of the titrations became larger (Smith et al., 1999) for the respective conditions.

It is now clear that the treatment of the titration data causes a saturation that is entirely based on the assumption that, besides the autoprotolysis of water, no other reactions are taking place, and that E_0 is close but not equal to the externally determined value. This was verified by a determination of E_0 in two ways but on one titration data set. The experiment was started by a titration allowing an ex situ calibration in the absence of particles (yielding $E_{0,i}$). Then the goethite suspension was added and a titration was carried out to low pH , so that a calibration in the presence of particles could also be performed (yielding $E_{0,ii}$). The use of these two values the charging curve could result in different situations. (1) By applying $E_{0,i}$ to the goethite data, we generally did not observe a saturation with protons at $I = 0.1$ mol/L for $2.6 < \text{pH} < 3$ (cf. Fig. 2). (2) $E_{0,ii}$ results in a plateau because the assumption is that no proton uptake occurs (cf. Fig. 2).

With the whole series of experiments, it was found that $E_{0,ii}$ differed from $E_{0,i}$ by ± 0.6 mV. The lower the pH , the more sensitive is the existence of a plateau to the value of E_0 . Therefore, with the problems related to the calibration in mind, the existence of a plateau with purely chemical significance can be questioned.

The coincidence of the ΔZ plots for the different goethite samples does not indicate that the surface charge of these samples are identical. On the contrary on the surface charge density vs. pH plot G-II has a lower charge. The normalization by the ΔZ notation results in overlapping curves because the relative surface charge curves are straight lines that are normalized by the value at $\text{pH} = 3$. Figure 2 therefore provides the information that the drift criterion used with our setup gives straight lines for all goethite samples at $I = 0.1$ mol/L, whereas,

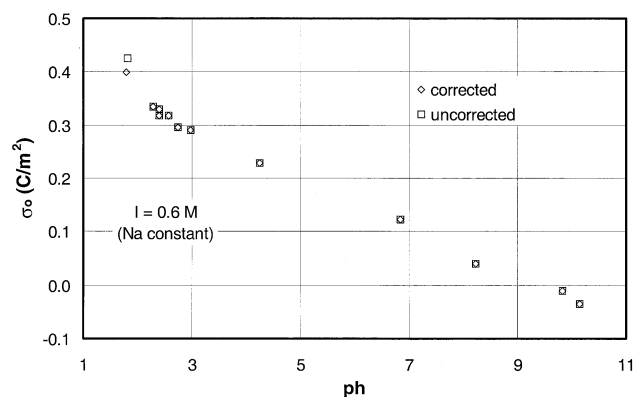


Fig. 3. Absolute surface charge density obtained by titrating supernatant samples (long equilibration times, settling of particles). Titrations were either performed coulometrically ($\text{pH} < 6$) or with acid ($\text{pH} > 6$). All titrations were performed on one sample of goethite. G-II uncorrected data indicate that dissolved iron (III) is not taken into account; corrected data indicate that dissolved iron (III) is accounted for as described in the text.

for example, Venema (1996) reports some curvature for G-II around the PZC with the less severe drift criteria and setup used.

It should also be noted that the results presented up to this point cannot be taken as proof of the absence of a proton adsorption maximum that is less than crystallographic values. We have therefore investigated this possibility by attempting to obtain proton saturation at lower pHs by using a different approach. To obtain the most favorable experimental conditions, a high-surface-area goethite (G-II) was used. Realizing that the data at low pH have to be obtained with high precision to allow an assessment of saturation values, the experiments conducted with respect to the saturation phenomenon consisted in back titrations of supernatant samples collected at low pH. The raw data can be treated in a simple Gran plot (in the absence of particles), which provides very accurate free proton concentrations. Experiments performed on small samples via the coulometric approach (option 1) always resulted in proton uptake higher than the “apparent” plateau. Therefore, a series of experiments was carried out using favorable conditions of high ionic strength (0.6 mol/L NaCl), high specific surface area goethite, and high solid concentration. Coulometric titrations and titrations with tris (hydroxymethyl)-aminomethane of supernatant samples of such suspensions revealed an ongoing proton uptake in the range $2.2 < \text{pH} < 0.9$ without a clear sign of saturation, as is shown in Figures 3 and 4, respectively.

To our knowledge, these are the first data obtained with the mentioned precautions for such acidic conditions. The data corroborate that the previously discussed plateau was “forced” on the data in the treatment and that the experimental window using the continuous titrations should be closed for $\text{pH} < 3$ for these suspensions. Values at $\text{pH} < 2.2$ (shown in Fig. 3) should, however, be considered with care as Fe(III) was found in solution. Proton uptake experiments at low pH are likely to be in dynamic equilibration, whereby the kinetics of proton adsorption are significantly faster than those of goethite dissolution. The concentrations of dissolved Fe(III) were all near or below the detection limit of the analytical method—that is, near

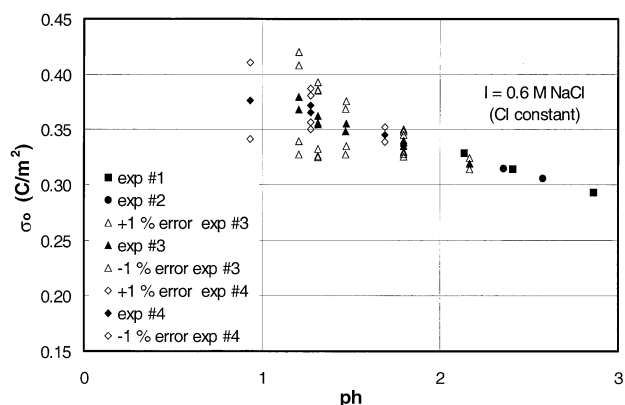


Fig. 4. Absolute surface charge density obtained by titrating supernatant samples (short equilibration times, filtration of particles). Titrations were either performed coulometrically ($\text{pH} > 1.5$) or with Tris ($\text{pH} < 1.5$). Titrations were performed on individual samples of G-II and when errors are given in triplicate.

the micromolar concentrations—and thus all well below the maximum solubility concentrations. The proton balance, corrected for the concentration of dissolved Fe(III) through goethite dissolution and the reduction of Fe(III) to Fe(II) in the coulometric titrations, was not significantly affected from those results (Fig. 4). Figure 4 also shows errors of 1% in free proton concentration to have a strong effect on the calculated proton consumption at $\text{pH} < 1.5$. The mean values nonetheless indicate the uptake of protons to continue down to $\text{pH} = 1.5$. More uncertain is the data down at $\text{pH} = 0.9$ where dissolved Fe(III) has some additional influence on the outcome of the results without, however, providing contradictory evidence to continuous protonation of the goethite surface.

At very low pH, the ionic strength deviates from 0.6 mol/L. At $\text{pH} 0.9$ the ionic strength is 0.72 mol/L. This implies that the activity coefficients also deviates from those valid for 0.6 mol/L. According to the Extended Debye-Hückel equation with the parameters of Helgeson, Kirkham, and Flowers (1982) the activity coefficients differ by 0.003 resulting in a difference in charge density at $\text{pH} 0.9$ of 0.011 C/m^2 .

The experimental results strongly suggest that estimations of the PASD parameter for well-crystallized goethite, at this stage, are best made from crystallographic information. Imaging of well-crystallized particles and/or tritium exchange experiments allow an estimation of the total density of surface hydroxyls (i.e., the sum of singly, doubly, and triply coordinated surface oxygens with respect to bulk goethite Fe(III); cf. Fig. 5). It should, however, be noted that the MUSIC framework suggests that not all of these hydroxyls are proton active (Fig. 6). Because SDs of individual sites should be difficult to find experimentally we are faced with a problematic situation, namely a necessary assumption concerning the value of SD. Recall that this parameter is fundamental and its treatment should be as unified as possible.

Transmission electron microscopic images show the goethite particles to be elongated needles with an aspect ratio of roughly 10:1 (Boily et al., 2001). However, given the range of sizes of the particles, this can only be seen as a rough average. The terminations of the needles were thus evaluated to represent

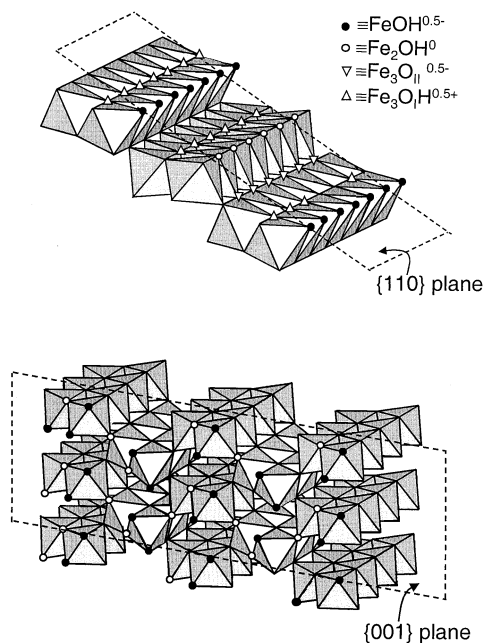


Fig. 5. Schematic representation of the {110} and {001} plane of the goethite surface, along with the distribution and density of singly ($\equiv\text{FeOH}^{0.5-}$), doubly ($\equiv\text{Fe}_2\text{OH}^0$), and triply ($\equiv\text{Fe}_3\text{O}_{\text{II}}\text{H}^{0.5+}$ and $\equiv\text{Fe}_3\text{O}_{\text{II}}^{0.5-}$) coordinated surface oxygens with respect to underlying Fe(III) atoms. The protonation states of these four surface sites was primordial chosen from the surface protonation model of Hiemstra et al. (1996), at pH_{pzc} , for illustrative purposes only.

10% of the total surface area—that is, more or less the upper limit of our estimations and the value adopted by Hiemstra and van Riemsdijk (1996). We also choose the {001} plane as being representative of these terminations bearing in mind that planes close to this, such as the {021} plane, are also likely to be present (Cornell and Schwertmann, 1996). Finally, the Transmission electron microscopic images show that the {110}

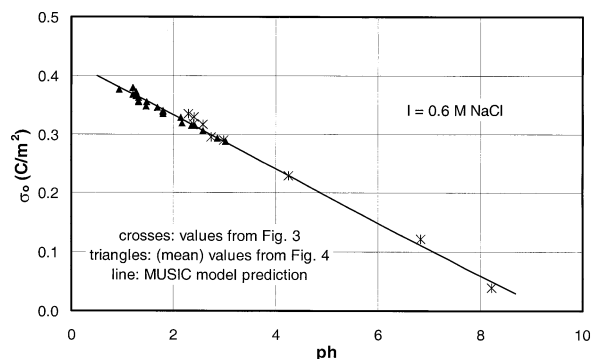


Fig. 6. Simplified MUSIC model prediction of proton uptake on goethite with singly coordinated sites (3.6 sites/nm^2 , $\text{pK} = 9.4$), triply coordinated sites (2.7 sites/nm^2 , $\text{pK} = 9.4$), symmetric electrolyte ion pair formation constants of $\log(K_{\text{ip}}) = -0.5$, and Stern Layer capacitance of 0.78 F/m^2 (Boily et al., 2001). Calculations were carried out with a modified version of FITEQL 2.1 (Westall, 1982) with the Stern Layer Model to account for surface electrostatics; no parameter adjustment was used.

Table 1. Surface site density on goethite.

Structure	{110} ^a	{001} ^a	Total ^b
$\equiv\text{FeOH}^{0.5-}$	3.0	9.1	3.61
$\equiv\text{Fe}_2\text{OH}^0$	3.0	9.1	3.61
$\equiv\text{Fe}_3\text{O}_{\text{II}}\text{H}^{0.5+}$	6.0	0.0	5.4
$\equiv\text{Fe}_3\text{O}_{\text{II}}^{0.5-}$	3.0	0.0	2.7

^a Sites/nm² on the crystal plane.

^b Site/nm² on a goethite particle whose surface area is represented by 90% of the {110} plane and 10% of the {001} plane.

plane dominates the surface area of the particles (P. Weidler, personal communication), an observation in agreement with Cornell and Schwertmann, 1996). At this point, it can then become useful to speculate on which site is proton active and which is not. The SD of singly, doubly, and triply coordinated surface oxygens on the {110} and {001} planes of goethite are reported in Table 1. The total SD of $\equiv\text{FeOH}^{0.5-}$ is determined by considering its density on the {110} and {001} plane: $3.0 \text{ sites/nm}^2 \times 90\% + 9.1 \text{ sites/nm}^2 \times 10\% = 3.6 \text{ sites/nm}^2$. The titration data indicate that 2.5 protons/nm^2 (i.e., 0.4 C/m^2) can be taken up by the goethite surface from pH_{pzc} to $\text{pH} = 0.9$. In a simplified $(1 - \text{pK})$ model, the singly coordinated sites have a maximum protonation constant of $1/\beta_1 = h_{\text{pzc}}$:



then only a maximum of half of the sum of singly coordinated sites—that is, $(2.7 + 0.9)/2 = 1.8 \text{ sites/nm}^2$ —can be protonated below the pzc. This would leave a minimum 0.7 sites/nm^2 unaccounted for, a value that could not be justified by surface roughness because the goethite surface was shown to be well crystallized (e.g., Cornell and Schwertmann, 1996). Previous data on such well-crystallized goethite did not go significantly beyond 0.2 C/m^2 (Venema, 1996), 0.22 C/m^2 (Boily et al., 2001) or 0.23 C/m^2 (Rietra et al., 2000), which could still be modeled by a one-site model. So the present data invalidate such a single-site approach.

In the complete MUSIC model (Venema et al., 1996a) $\log\beta_1$ is less than pH_{pzc} . According to this model, the singly coordinated sites are completely deprotonated at the pzc. This means that 3.6 protons/nm^2 can be adsorbed to this site, compared with the experimentally observed adsorption of 2.5 protons/nm^2 . Also, in this model, a second kind of site is required to satisfy the pzc condition. This condition is met with the charges of the triply coordinated sites, which, according to Venema et al. (1996a), do not exhibit pH-dependent charge in the pH range of interest for the {110} face of goethite. In contrast to Venema et al. (1996a), Rustad et al. (1996, 2000) proposed that triply coordinated sites and even doubly coordinated sites are proton active in the pH range of interest. Despite these contradictions, it can generally be concluded that these sites should not be neglected in surface protonation models, even if these may not be proton active. Models of this type are especially useful to model adsorption reactions at the molecular scale, where the explicit contributions of each of these sites in stabilizing a surface complex is taken into consideration. On the other hand, models making use of one generic site representing the sum of singly, doubly, and triply coordinated oxygens are likely to make use of best-fitting surface complexes that are not

necessarily representative of species at the molecular scale. A crystallographic value of SD coupled in a MUSIC-like framework, where the differences in reactivity of singly, doubly, and triply coordinated sites are taken into account, is thus likely to be a promising approach for SC studies at the molecular level (e.g., Venema et al., 1996b; Boily et al., 2000a–c). In this fashion, all options can be kept open, such that ions that are believed to interact with all types of surface functional groups can be distinguished from those that are believed to be more selective.

4. CONCLUSIONS

It has been shown that PASD at goethite surfaces will be underestimated by continuous titrations with strong acids. If PASD can be determined for some other solid in this way, it should be done by back-titrating supernatant samples with the highest precision possible; for acidic solutions a coulometer is recommended. Our results suggest that the effect of ionic strength on such PASD values should be considered. For goethite, treatment of raw data that was based on previous suggestions resulted in apparent PASD values that depend on electrolyte concentration and composition, making these parameters not very useful in the search for a comprehensive model.

In this study, we have furthermore established that the goethite surface sites do not saturate in 0.6 mol/L NaCl at pH > 2.2—and most probably not even until pH = 0.9. These results are in agreement with the MUSIC model and suggest that SDs calculated from crystallographic information might be a good estimate for modeling purposes. Furthermore, because there are several sites involved in the MUSIC model, their individual SDs cannot be experimentally corroborated for the time being.

At present, there are no specific rules in choosing a SCM for a given system. From our point of view, the objective of a model should constrain the available options. A model with the objective of including information on the molecular structure of surface complexes, for instance, should contain as much information as possible on the physicochemical aspects of the mineral surface. Our experimental results strongly suggest that such models should not make use of low site densities, especially considering that proton affinity constants, electrolyte adsorption constants, and capacitance values can all be correlated to this value. A crystallographic SD used in the MUSIC framework is therefore likely to be a more successful approach to predict molecular-scale adsorption on well-crystallized surfaces.

Acknowledgments—This work was supported by the Swedish Natural Science Research Council and by grants from EERO and the Foundation for Strategic Research to J.L. and a FCAR Ph.D. Scholarship to J.-F.B. We are also grateful for valuable comments and suggestions given by the associate editor, Prof. D. A. Sverjensky, and three anonymous reviewers.

Associate editor: D. A. Sverjensky

REFERENCES

- Boily J. F. and Fein J. B. (1996) Experimental study of cadmium–citrate co-adsorption onto α -Al₂O₃. *Geochim. Cosmochim. Acta* **60**, 2929–2938.
- Boily J. F., Persson P., and Sjöberg S. (2000a) Benzenecarboxylate surface complexation at the goethite (α -FeOOH)/water interface: III. The influence of particle surface area and the significance of modelling parameters. *J. Colloid Interface Sci.* **227**, 132–140.
- Boily J. F., Persson P., and Sjöberg S. (2000b) Benzenecarboxylate surface complexation at the goethite (α -FeOOH)/water interface: II. Linking IR spectroscopic observations to mechanistic surface complexation models for phthalate, trimellitate, and pyromellitate. *Geochim. Cosmochim. Acta* **64**, 3453–3470.
- Boily J. F., Persson P., and Sjöberg S. (2000c) Benzenecarboxylate surface complexation at the goethite (α -FeOOH)/water interface: I. A mechanistic description of pyromellitate surface complexes from the combined evidence of infrared spectroscopy, potentiometry, adsorption data, and surface complexation modeling. *Langmuir* **16**, 5719–5729.
- Boily J. F., Lützenkirchen J., Balmès O., Beattie J., and Sjöberg S. (2001) Modeling proton binding at the goethite (α -FeOOH)/water interface. *Coll. Surf. A* **179**, 11–27.
- Cornell R. M. and Schwertmann U. (1996) *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*. VCH.
- Daughney C. J. and Fein J. B. (1998) The effect of ionic strength on the adsorption of H⁺, Cd²⁺, Pb²⁺, Cu²⁺ by *Bacillus subtilis* and *Bacillus licheniformis*: A surface complexation model. *J. Colloid Interface Sci.* **198**, 53–77.
- Dzombak D. A. and Morel F. M. M. (1990) *Surface complexation modeling. Hydrous Ferric Oxide*. Wiley.
- Gran G. (1952) Determination of the equivalence point in potentiometric titrations, Part II. *Analyst* **77**, 661–671.
- Gunneriusson L. (1993) Aqueous speciation and surface complexation to goethite (α -FeOOH) of divalent mercury, lead and cadmium. Ph.D. thesis. Umeå University, Umeå, Sweden.
- Helgeson J. C., Kirkham D. H., and Flowers G. C. (1982) The theoretical prediction of the thermodynamic behaviour of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5KB. *Am. J. Sci.* **281**, 1249–1516.
- Hiemstra T., De Wit J. C. M., and van Riemsdijk W. H. (1989) Multisite proton modelling at the solid/solution interface: A new approach II. Application to various important (hydr)oxides. *J. Colloid Interface Sci.* **133**, 105–117.
- Hiemstra T. and van Riemsdijk W. H. (1996) A surface structural approach to ion adsorption: The charge distribution (CD) model. *J. Colloid Interface Sci.* **179**, 488–508.
- Hiemstra T., Venema P., and van Riemsdijk W. H. (1996) Intrinsic proton affinity of reactive surface groups of metal (hydr)oxides: The bond valence principle. *J. Colloid Interface Sci.* **184**, 680–692.
- Hoins U. (1991) Zur Schwermetall-Adsorption on oxidischen Oberflächen—Der Einfluss von Sulfat. Dissertation, ETH Zürich, Switzerland.
- Hoins U., Charlet L., and Sticher H. (1993) Ligand effect on the adsorption of heavy metals: The sulfate–cadmium–goethite case. *Air Water Soil Poll* **68**, 241–255.
- Johnson B. B. (1990) Effect of pH, temperature and concentration on the adsorption of cadmium on goethite. *Environ. Sci. Technol.* **24**, 112–118.
- Koretsky C. M., Sverjensky D. A., and Sahai N. (1998) A model of surface site types on oxide and silicate minerals based on crystal chemistry: Implications for site types and densities, multi-site adsorption, surface infrared spectroscopy, and dissolution kinetics. *Am. J. Sci.* **298**, 349–438.
- Laiti E. (1996) Interactions between phosphonate/phosphate ligands and hydrous alumina surfaces. Ph.D. thesis. Umeå University, Sweden.
- Lövgren L., Sjöberg S., and Schindler P. W. (1990) Acid/base reactions and Al(III) complexation at the surface of goethite. *Geochim. Cosmochim. Acta* **54**, 1301–1306.
- Lützenkirchen J. (1999a) Parameter estimation for the Constant Capacitance Surface Complexation Model: Analysis of parameter interdependencies. *J. Colloid Interface Sci.* **210**, 384–390.
- Lützenkirchen J. (1999b) The constant capacitance surface complexation model and variable ionic strength: An evaluation of applications and applicability. *J. Colloid Interface Sci.* **217**, 8–18.

- Marmier N., Dumonceau J., Chupeau J., and Fromage F. (1993) Comparative study of trivalent lanthanide ions sorption on hematite and goethite. *Comp. Rend. Acad. Sci., Ser. 2*, **317**, 1561–1567.
- Nilsson N. (1995) Inner/outer sphere complexation of phosphate and organic ligands at the goethite-water interface. Ph.D. thesis. Umeå University, Umeå, Sweden.
- Pivovarov S. (1998) Acid-base properties and heavy alkaline earth metal adsorption on the oxide-solution interface: Non-electrostatic model. *J. Colloid Interface Sci.* **206**, 122–130.
- Rietra R. P. J., Hiemstra T., and van Riemsdijk W. H. (2000) Electrolyte anion affinity and its effect on oxyanion adsorption on goethite. *J. Colloid Interface Sci.* **229**, 199–206.
- Rustad J. R., Felmy A. R., and Hay B. P. (1996) Molecular statics calculation of proton binding to goethite surfaces: A new approach to estimation of stability constants for multisite surface complexation models. *Geochim. Cosmochim. Acta* **60**, 1563–1576.
- Rustad J. R., Dixon D. A., and Felmy A. R. (2000) Intrinsic acidity of aluminium, chromium (III) and iron (III) μ_3 -hydroxo functional groups from ab initio electronic structure calculations. *Geochim. Cosmochim. Acta* **64**, 1675–1680.
- Sahai N. and Sverjensky D. A. (1997) Evaluation of internally consistent parameters for the triple-layer model by the systematic analysis of oxide surface titration data. *Geochim. Cosmochim. Acta* **61**, 2801–2826.
- Schindler P. W. and Kamber H. R. (1968) Die Acidität von Silanolgruppen. *Helv. Chim. Acta* **51**, 1781–1789.
- Schindler P. W. Stumm W. (1987) The surface chemistry of oxides, hydroxides and oxide minerals. In *Aquatic Surface Chemistry: Chemical Processes at the Particles-Water Interface* (ed. W. Stumm). pp. 83–110. Wiley.
- Sjöberg S., Hägglund Y., Nordin A., and Ingri N. (1983) Equilibrium and structural studies of silicon(IV) and aluminium (III) in aqueous solution. V. Acidity constants of silicic acid and the ionic product of water in the medium range 0.05–2.0 M Na(Cl) at 25 C. *Mar. Chem.* **13**, 35–44.
- Sjöberg S. and Lövgren L. (1993) The application of potentiometric techniques to study complexation reactions at the mineral/water interface. *Aquat. Sci.* **55**, 324–335.
- Smith D. S., Adams N. W. H., and Kramer J. R. (1999) Resolving uncertainty in chemical speciation determinations. *Geochim. Cosmochim. Acta* **63**, 3337–3347.
- Sverjensky D. A. and Sahai N. (1998) Theoretical prediction of single-site enthalpies of surface protonation for oxides and silicates in water. *Geochim. Cosmochim. Acta* **62**, 3703–3716.
- van Geen A., Robertson A. P., and Leckie J. O. (1994) Complexation of carbonate species at the goethite surface: Implications for adsorption of metal ions in natural waters. *Geochim. Cosmochim. Acta* **58**, 2073–86.
- Venema P. (1996) Charging and ion adsorption behaviour of different iron (hydr)oxides. Ph.D. thesis. Wageningen Agricultural University, Wageningen, The Netherlands.
- Venema P., Hiemstra T., Weidler P. G., and van Riemsdijk W. H. (1996a) Intrinsic proton affinity of reactive surface groups of metal (hydr)oxides: Application to iron (hydr)oxides. *J. Colloid Interface Sci.* **198**, 282–295.
- Venema P., Hiemstra, and van Riemsdijk W. H. (1996b) Multisite adsorption of cadmium on goethite. *J. Colloid Interface Sci.* **183**, 515–527.
- Vogel A. I. (1978) *Vogel's Textbook of Quantitative Inorganic Analysis* (eds. J. Bassett, R. C. Denney, G. H. Jeffery, and J. Mendham). 4th ed. pp. 741–742. Longman.
- Westall J. C. (1982) *FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants from Experimental Data*. Version 2.1 Report 82-02. Department of Chemistry, Oregon State University, Corvallis, OR.
- Yates D. A. (1975) The structure of the oxide/aqueous electrolyte interface. Ph.D. thesis. University of Melbourne, Australia.

Appendix A.. Absolute surface charge density determined by titrating individual supernatant samples of G- II at an ionic strength of 0.6 M NaCl.^a

log[H ⁺]	σ ($\mu\text{C cm}^{-2}$)
0.936	0.376
1.207	0.368
1.207	0.380
1.207	0.380
1.272	0.365
1.273	0.372
1.273	0.372
1.314	0.355
1.314	0.356
1.315	0.363
1.471	0.348
1.471	0.348
1.472	0.355
1.691	0.345
1.691	0.345
1.691	0.345
1.793	0.335
1.794	0.338
1.794	0.340
2.137	0.329
2.167	0.319
2.167	0.319
2.292	0.335
2.357	0.315
2.393	0.318
2.397	0.329
2.409	0.314
2.573	0.317
2.575	0.305
2.737	0.296
2.863	0.293
2.978	0.290
3.014	0.288
4.252	0.229
6.841	0.122
8.232	0.040
9.824	-0.011

^a Titrations were either performed coulometrically (pH > 1.5) or with Tris (pH < 1.5).