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Surface potential of hematite in aqueous electrolyte solution: Hysteresis and equilibration at the interface

Tajana Preočanin *, Ana Čop, Nikola Kallay

Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10001 Zagreb, Croatia

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Abstract

Electrostatic potential at the inner plane of the hematite aqueous interface, i.e., surface potential, was measured by means of a single-crystal hematite electrode. Acidic solutions were titrated with base and then back-titrated with acid. Surface potentials were evaluated from electrode potentials by setting the zero value at the isoelectric point. In the case of fast titrations the equilibration time was approximately 10 min, and significant hysteresis was obtained, more pronounced at higher electrolyte concentrations. Hysteresis disappeared in slow titration runs when the equilibration time was extended up to 120 min, and also when ultrasound was applied. Hysteresis was observed in the pH region close to neutrality, where the concentrations of potential-determining H^+ and OH^- ions are low. Equilibration was fast in acidic and basic regions. These results are explained on the basis of the kinetics of surface reactions, supported by the following rate of single-crystal electrode equilibration. It is concluded that the equilibration rate at the interface is specific for a given system and is not a general phenomenon. As several systems may undergo fast equilibration, such data may be regarded as equilibrium data and interpreted by the surface complexation model. In other cases, one should perform kinetic tests and apply extended equilibration times.

Keywords: Surface potential; Single-crystal electrode; Surface complexation model; Hysteresis; Hematite; Surface charge; Metal oxides; Electrical double layer

1. Introduction

Equilibrium within the Electrical Interfacial Layer (EIL) has been the subject of numerous investigations. Common measurements include potentiometric titration of the dispersion leading to the surface charge density [1,2], electrokinetic measurements [3], and measurements of the adsorption of counterions [4], as well as of other charged species [5]. Data interpretation and predictions of the behavior of the systems are based on the surface complexation model (SCM) [6,7] using certain assumptions on the EIL structure. There are several theoretical models in use, differing in some details, which cannot be distinguished on the basis of the available experimental results [8]. Some new techniques should therefore be introduced to elucidate this complex problem. Recently, measurements with single-crystal metal oxide electrodes (SCrE) enabled determination of the (inner) surface potential φ_0 of metal oxides in aqueous electrolyte solutions. This information is essential for obtaining activity coefficients of the charged species directly bound to the surface [9] and thus enabling critical examination of the theoretical models describing the interfacial equilibrium. Metal electrodes covered with colloidal metal oxide particles do not provide results on surface potentials, since, due to the porosity of the oxide layer, their potential is predominantly determined by the redox equilibrium and influenced by the solubility of the oxide [10–12]. The ion-sensitive field effect transistors (ISFET) technique seems to produce more reliable results [13,14]. The idea of constructing a single-crystal hematite electrode [15] was inspired by the results obtained with the ice electrode [16]. The hematite electrode showed that the dependency of the surface potential on pH does not obey the Nernst equation. The magnitude of the slope was found to be significantly lower, which confirms the applicability of SCM. However, poor reproducibility was obtained in the basic region [15,17,18], which was not explained.

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* Corresponding author. Fax: +385 1 46 06 131.
E-mail address: tajana@chem.pmf.hr (T. Preočanin).

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Hysteresis in measurements related to the interfacial charging process was noticed in measurements of the surface charge density [19] and electrokinetics [20], but also in calorimetry experiments [21]. Hysteresis was found in the region close to neutrality but disappeared in more acidic as well as in basic regions. This phenomenon was theoretically treated by Piasecki [22] by considering the kinetics of the surface reactions. The aim of this article is to examine hysteresis in the measurements of surface potentials. These data are the results of direct measurements and may thus be taken as being more reliable.

2. Materials and methods

All solutions were prepared using redistilled and decarbonated water: $NaNO_3$ (p.a., Fluka), HNO_3 (0.1 $mol\,dm^{-3}$, titrival, Fluka), NaOH (0.1 $mol\,dm^{-3}$, titrival, Fluka), and standard buffers (Fluka).

The electrode was made from a hematite single crystal (origin: Vesuvius, Italy) and was described earlier [15]. A reference Ag|AgCl|Cl^-(aq) electrode with a salt bridge (Metrohm, 6.0233.100) was used. The salt bridge was filled with $NaNO_3$ solution at the same concentration as in the measuring system. The pH was measured with a glass electrode (Metrohm, 6.0222.100) connected to the same reference electrode. Measurements of electromotivities [23] were performed with a pH meter (Metrohm, 713) and automatic potentiometric titrator (Metrohm, Titrino 736GP). The glass electrode was calibrated using five buffer solutions (pH 3, 5, 7, 8, and 10). The systems were thermostated at 25.0 °C and kept under argon. The ionic strength was controlled with $NaNO_3$ and was 10^{-2}, 10^{-1}, and 1 $mol\,dm^{-3}$, respectively.

So called "fast titrations" were performed in a standard manner; i.e., the equilibration time was taken as corresponding to the glass electrode. In practice, the readings of glass and hematite electrode potentials were taken approximately 10 min after addition of a titrant portion. To obtain the equilibrium values of the hematite electrode potentials, "slow titrations" were performed. In these titrations the equilibration time for each portion of the titrant was as long as 120 min. Since the application of ultrasound was found to promote equilibration [24], a separate titration experiment, with an immersed ultrasonic probe, was performed.

Evaluation of surface potentials from the measured electromotivity data was based on the isoelectric point of hematite found [15] at $pH_{iep} = 6.1$. It was assumed that in a very slow experimental run, in which hysteresis disappeared (Fig. 1), the point of zero potential, pH_{pzp}, at which $\varphi_0 = 0$ coincides with the isoelectric point, pH_{iep}. In the same experiment, the surface potential at pH 2 was evaluated as $\varphi_0 = 150$ mV. Since in all experiments good reversibility was obtained at pH 2, this point was taken as the common reference point.

3. Results

Figs. 2 and 3 show the hysteresis for two fast titrations performed at different ionic strengths. First, the acidic HNO_3 solution, containing a determined amount of $NaNO_3$, was titrated with NaOH, and then back titration of the basic solution with HNO_3 was performed. Hysteresis was found in the broad pH region, and was significantly more pronounced at higher ionic strengths. Equilibration was fast and the hysteresis disappeared in very acidic (pH ≈ 2) and in very basic (pH ≈ 12) solutions.

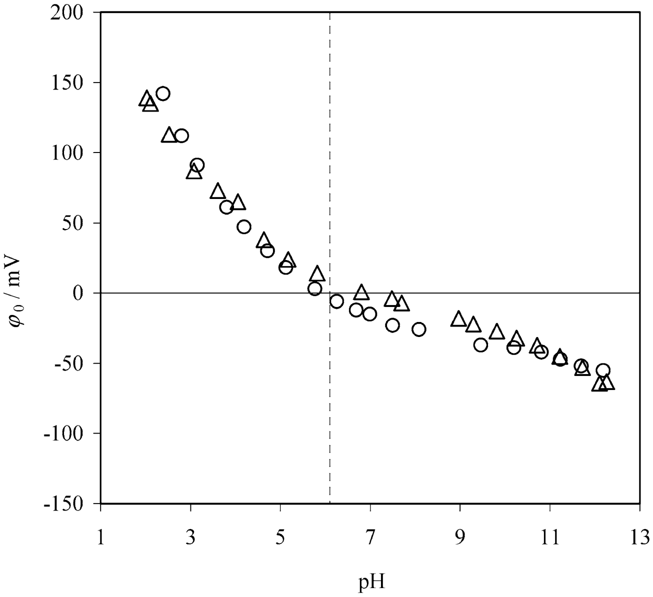

Fig. 1. Slow titration with single-crystal hematite electrode at moderate ionic strength. Surface potential at the hematite aqueous interface (φ_0) as a function of pH of the solution. Titration of acidic solution with NaOH (△), and back titration of basic solution with HNO_3 (○). $c(NaNO_3) = 10^{-2}$ $mol\,dm^{-3}$. Temperature: 25.0 °C. Equilibration time was variable: 20 min in acidic and basic regions (5 > pH > 9) and up to 120 min in the neutral region (5 < pH < 9).

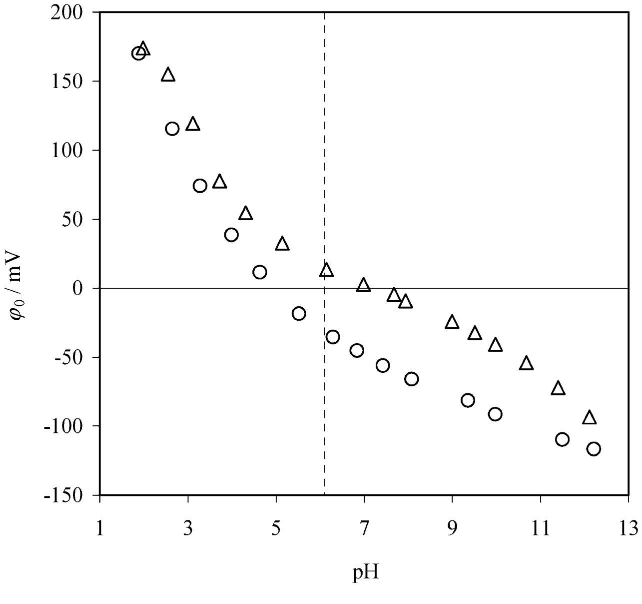

Fig. 2. Fast titration with single-crystal hematite electrode at moderate ionic strength. Surface potential at the hematite aqueous interface (φ_0) as a function of pH of the solution. Titration of acidic solution with NaOH (△), and back titration of basic solution with HNO_3 (○). $c(NaNO_3) = 10^{-2}$ $mol\,dm^{-3}$. Temperature: 25.0 °C. Equilibration time: ~10 min.

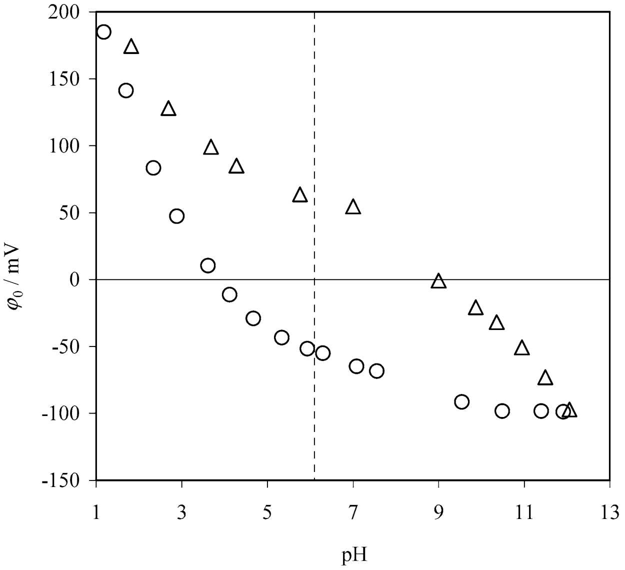

Fig. 3. Fast titration with single-crystal hematite electrode at high ionic strength. Surface potential at the hematite aqueous interface (φ_0) as a function of pH of the solution. Titration of acidic solution with NaOH (△), and back titration of basic solution with HNO_3 (○). $c(NaNO_3) = 1\ \mathrm{mol\,dm^{-3}}$. Temperature: 25.0 °C. Equilibration time: ~10 min.

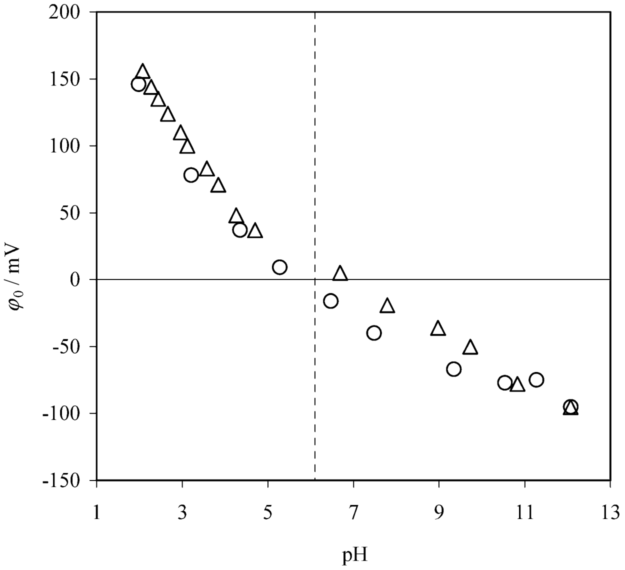

Fig. 4. Fast ultrasound titration with single-crystal hematite electrode at moderate ionic strength. Surface potential at the hematite aqueous interface (φ_0) as a function of pH of the solution. Titration of acidic solution with NaOH (△), and back titration of basic solution with HNO_3 (○). $c(NaNO_3) = 10^{-2}\ \mathrm{mol\,dm^{-3}}$. Temperature: 25.0 °C. Equilibration time: ~10 min. After addition of a portion of the titrant, the system was treated with ultrasound for ~1 min and left to equilibrate for ~4 min.

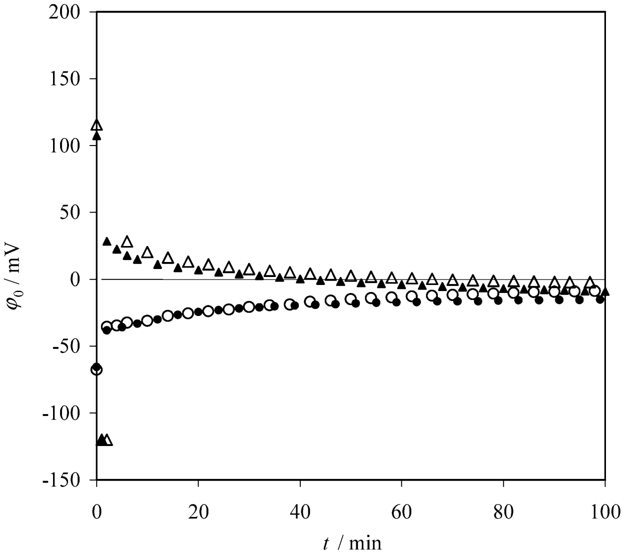

Fig. 5. Kinetics of equilibration at the hematite aqueous interface. Time dependency of surface potential φ_0. Single-crystal hematite electrode was equilibrated in HNO_3 solution (pH 2; △, ▲) and in basic solution (pH 12; ○, ●). After 30 min of equilibration, the hematite electrode was immersed into $NaNO_3$ solution (0.1 $\mathrm{mol\,dm^{-3}}$, pH 6.5; △, ○) and into sodium hydrogen phosphate buffer (0.1 $\mathrm{mol\,dm^{-3}}$, pH 6.5; ▲, ●). Temperature: 25.0 °C.

Fig. 1 displays the results of slow titration and of slow back-titration. Again, the acidic HNO_3 solution was titrated with NaOH and then back-titrated with HNO_3. Extended equilibration time practically resulted in disappearance of hysteresis, so these data may be considered as equilibrium results. In the acidic region, the slope of the φ_0 (pH) function was found to be −49 mV in 0.01 $\mathrm{mol\,dm^{-3}}$ $NaNO_3$.

Fig. 4 displays the results of fast ultrasound titration. No hysteresis was detected as in the case of slow titration. Application of the ultrasound probe did not damage the electrodes. It is worth noting that ultrasound also promoted equilibration of the glass electrode.

Equilibration kinetics at the interface was examined by measuring the time response of the hematite crystal electrode and is demonstrated in Fig. 5. Two experiments, each with two runs, were performed. The hematite electrode was first kept and equilibrated in acidic (pH ≈ 2, first run) or basic (pH ≈ 12, second run) solutions of 0.1 $\mathrm{mol\,dm^{-3}}$ $NaNO_3$.

In the first experiment, the hematite electrode, already equilibrated in acidic solution (pH ≈ 2), was rinsed and immersed into 0.1 $\mathrm{mol\,dm^{-3}}$ $NaNO_3$ aqueous solution of pH 6.5. The potential of the hematite electrode changed with time, approaching the final equilibrium value ($\varphi_0 = -5$ mV). In the second run, the hematite electrode was equilibrated in the basic solution (pH ≈ 12) and then rinsed and immersed into 0.1 $\mathrm{mol\,dm^{-3}}$ $NaNO_3$ aqueous solution of pH 6.5. Again, the potential changed, approaching the same equilibrium value of −5 mV.

The second experiment was similar. The only difference was that the hematite electrode was immersed into hydrogen phosphate buffer of the same ionic strength and pH 6.5. The equilibration time was found to be similar. The final equilibrium value of surface potential was somewhat lower ($\varphi_0 = -15$ mV), indicating specific adsorption of phosphate ions onto the hematite surface, which is in agreement with the literature [25].

The effect of ultrasound on the rate of equilibration is presented in Fig. 6. In this experiment the initial pH was lower than 2. The kinetic plot clearly shows that ultrasound markedly accelerates equilibration at the interface.

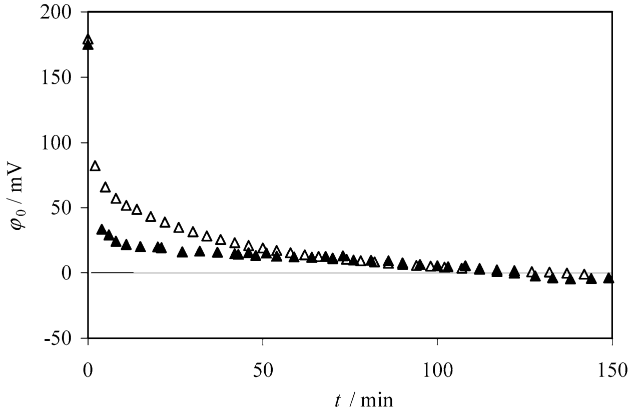

Fig. 6. Effect of ultrasound on the kinetics of equilibration at the hematite aqueous interface. Time dependency of surface potential φ_0. Hematite electrode was equilibrated in HNO_3 solution (pH < 2). After 30 min of equilibration, the hematite electrode was immersed into $NaNO_3$ solution (0.1 mol dm^{-3}, pH 6.5). The experiments were performed in the presence (▲) and in the absence (△) of ultrasound applied for 1 min every 10 min. Temperature: 25.0 °C.

4. Discussion

Measurements of the surface potential at solid–liquid interfaces, such as the metal oxide–aqueous interface, provide important information on the interfacial equilibrium. The equilibrium may be considered by the surface complexation model [6,7]. Several assumptions about the mechanism of surface charging were considered. For example, in the case of the $1 - \mathrm{p}K$ mechanism [26], if the partial charge number of the negative surface groups is $-1/2$, the following surface reaction equation holds,

$$\equiv \mathrm{MO}^{-1/2} + \mathrm{H}^+ \to \equiv \mathrm{MOH}^{+1/2},$$

$$K^\circ_{1/2} = \exp(F\varphi_0/RT) \cdot \frac{\{\mathrm{MOH}^{+1/2}\}}{\{\mathrm{MO}^{-1/2}\} \cdot a_{\mathrm{H}^+}}, \tag{1}$$

where $K^\circ_{1/2}$ is the thermodynamic equilibrium constant of the corresponding surface reaction, and φ_0 is the electrostatic surface potential affecting the state of charged surface groups $\equiv \mathrm{MO}^{-1/2}$ and $\equiv \mathrm{MOH}^{+1/2}$. Curly braces denote surface concentrations (amount of surface species per surface area) being proportional to the activities of interfacial species. Exponential term in Eq. (1) represents activity coefficients of charged surface species [9].

Inner surface potential φ_0 in the case of the $1 - \mathrm{p}K$ mechanism is, according to Eq. (1), given by

$$\varphi_0 = \frac{RT\ln 10}{F}\log K^\circ_{1/2} - \frac{RT\ln 10}{F}\log\left(\frac{\{\mathrm{MOH}^{+1/2}\}}{\{\mathrm{MO}^{-1/2}\}}\right) - \frac{RT\ln 10}{F}\mathrm{pH}. \tag{2}$$

According to the $2 - \mathrm{p}K$ mechanism [27], the interaction of amphotheric surface sites with potential determining ions is described by the two-step protonation

$$\equiv \mathrm{MO}^- + \mathrm{H}^+ \to \equiv \mathrm{MOH},$$

$$K^\circ_1 = \exp(F\varphi_0/RT) \cdot \frac{\{\mathrm{MOH}\}}{\{\mathrm{MO}^-\} \cdot a_{\mathrm{H}^+}}, \tag{3}$$

$$\equiv \mathrm{MOH} + \mathrm{H}^+ \to \equiv \mathrm{MOH}_2^+,$$

$$K^\circ_2 = \exp(F\varphi_0/RT) \cdot \frac{\{\mathrm{MOH}_2^+\}}{\{\mathrm{MOH}\} \cdot a_{\mathrm{H}^+}}, \tag{4}$$

where K°_1 and K°_2 are thermodynamic equilibrium constants of the corresponding surface reactions, and φ_0 is the electrostatic potential affecting the state of charged surface groups $\equiv \mathrm{MOH}_2^+$ and $\equiv \mathrm{MO}^-$.

Inner surface potential φ_0, in the case of the $2 - \mathrm{p}K$ mechanism, is, according to Eqs. (3) and (4) given by

$$\varphi_0 = \frac{RT\ln 10}{2F}\log\left(K^\circ_1 \cdot K^\circ_2\right) - \frac{RT\ln 10}{2F}\log\left(\frac{\{\mathrm{MOH}_2^+\}}{\{\mathrm{MO}^-\}}\right) - \frac{RT\ln 10}{F}\mathrm{pH}. \tag{5}$$

The last terms in Eqs. (2) and (5) suggest the Nernstian slope of the φ_0 (pH) function, but the second term, determined by the ratio of free positive and free negative surface groups, causes reduction of the slope of the φ_0 (pH) function.

The above equations represent the equilibrium state at the surface. If the surface is not completely equilibrated, Eqs. (2) and (5) are no longer representative. Change of the state of the system results in processes leading to a new equilibrium state. These processes could be fast, slow or even very slow. Let us consider equilibration at the metal oxide aqueous interface, represented by reaction (1) or by reactions (3) and (4). Decrease of pH will cause advancement of these reactions, while an increase in pH will result in advancement in the opposite direction. These processes are commonly followed by the pH measurements, and equilibration is assumed once a stable reading on the pH meter is achieved. In the acid–base titration, equilibration in the bulk of the system is fast, so the slowest process is the equilibration at the glass/electrolyte interface. However, in the case of the acid–base titration of a metal oxide dispersion, the equilibration at the interface might be slow and so the pH reading may appear "stable" despite the fact that the metal oxide interfacial layer is still far from equilibrium. It is obvious that the equilibration process is fast at first, and then its rate gradually decreases, slowly approaching the equilibrium state. For example (Fig. 5), the rate of increase of the surface potential after 20 min is about 0.3 mV min^{-1}, but the surface potential is still 20 mV below its equilibrium value.

Most of the reports published in the literature do not consider the possibility of slow equilibration at the solid/liquid interface. There are reports on the kinetics of ionic interactions within the Electrical Interfacial Layer [28–30], but most of the data on the equilibrium state do not consider possible problems due to incomplete equilibration. Hysteresis, however, was detected in some reports. If the pH of an originally acidic suspension was increased by addition of a base, different results were obtained with respect to the experimental run in the opposite direction. Such hysteresis was found in calorimetric titrations of titania suspension [21], electrokinetic ζ-potential of zirconia particles [20], and surface charge measurements with alumina [19].

The kinetics of interfacial reactions could be treated as consisting of two steps [31]. The first step is transport between the bulk of the solution and the interfacial layer. The second step is binding of the adsorbing species to the surface. The problem was theoretically treated by Piasecki [22]. It was shown that hysteresis disappears in very acidic and very basic systems and is significantly pronounced in the pH region around neutrality, which is in agreement with this report.

In previous reports [15,17] dealing with the surface potential measurements with single-crystal metal oxide electrodes, stable readings were obtained in the acidic region, while the readings were not stable in neutral and moderately basic systems. Measurements of surface potentials are reliable because these measurements are direct; the relative value of the surface potential is obtained directly from the instrument reading. Hysteresis was found to be more pronounced at higher electrolyte concentrations, as in the case of surface charge [19] and ζ-potential measurements [20]. This finding might be explained by the fact that the surface charge density is higher at higher electrolyte concentrations and so more time is required for equilibration. In very acidic and very basic solutions, the concentrations of potential determining ions are high causing fast interfacial processes.

It is clear that the rate of equilibration, and thereby possible hysteresis, is specific and depends on the nature of the surface. We believe that there are numerous systems that equilibrate rapidly, so reported data may be regarded as equilibrium data and theoretically treated by the surface complexation model. On the other hand, the scattering of the data on the isoelectric points of metal oxides [32] might be partially explained by hysteresis. A sample stored in acidic solution may show a higher isoelectric point than the same sample stored in a basic solution. Therefore, to obtain accurate equilibrium data, a test on hysteresis should be performed. The absence of hysteresis suggests that data correspond to the equilibrium. Equilibration may be promoted by the application of the high-intensity ultrasound field, but this method may produce other complications.

Measurements of surface potentials, enabled by the construction of single-crystal electrodes, provide important information on the surface equilibrium. First, the activity coefficients of charged surface species are determined directly by the surface potential. Then, according to Eqs. (2) and (5), surface potential measurements provide information on the ratio of surface concentrations of positively and negatively charged surface groups. This information, together with the surface charge density data, enables evaluation of surface concentrations of specific surface groups, since surface charge density is determined by the difference in their surface concentrations.

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