Measurement of the surface potential of individual crystal planes of hematite

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Abstract
A device for measuring surface potentials of individual crystal planes was constructed. The surface potentials of the (0 1 2), (1 0 −2), (1 1 3), and (1 1 −3) crystal planes of hematite were measured as a function of pH at different sodium nitrate concentrations. Results of measurement enabled differentiation between the planes, showing agreement with the surface potentials obtained with a single-crystal hematite electrode. At low ionic strength there was no significant difference in potential between the crystal planes, whereas at relatively high ionic strength the difference was noticeable. In the absence of counterion association, but also in the case of their symmetric association taking place, point of zero potential (pH_{pzp}) coincides with other zero points, i.e., with the isoelectric point (pH_{iep}) and the point of zero charge (pH_{pzc}). If the counterion affinities toward association are not equal, the pH_{pzp} is shifted in the same directions as the pH_{pzc}. The shift in the point of zero potential to the basic region was more pronounced for the (1 1 −3) plane than for the (1 0 −2) one, indicating a higher affinity of anions for association with oppositely charged surface groups compared to cations. It was demonstrated that measurements of surface potentials of individual crystal planes could help to better understand the equilibrium at solid/liquid interfaces.

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Keywords: Surface potential; Surface complexation model; Hematite; Crystal planes; Single-crystal electrodes

1. Introduction
Colloidal particles are often composed of aggregated nano-single crystals [1,2]. Their surface is thus heterogeneous as different crystal planes are exposed to the liquid medium. Apparently, different planes will exhibit different chemical characteristics; the density of active groups will depend on the type of planes, and on their affinity for ionization [3–5]; electrical capacitance of the plane will depend on the density of surface sites [3]. Consequently, the overall interfacial characteristics of colloidal particles will be average, depending on the features of individual planes and on their abundance [6]. The same is true of the colloidal single-crystalline particles which exhibit heterogeneity on a larger scale.

Due to experimental difficulties most of the data published in the literature relate to the colloidal systems and to their “average” properties: adsorption densities, surface charge densities, and electrokinetic potentials.

Use of single-crystals (both natural and synthetic samples) enabled measurements and characterizations of surface properties of individual planes. Among the techniques most frequently used for investigation of individual crystal-face-specific reactivity, i.e., direct information on the pH-charging properties are atomic force microscopy (AFM) [7,8], scanning force microscopy (SFM) [9], and scanning tunneling microscopy (STM) [10]. A diffraction study of hydrated surfaces was also carried out to interpret the reactivity of a model surface in an aqueous environment [11]. Zhang et al. [12] measured cation adsorption at the (1 1 0) rutile crystal face, applying the X-ray standing-wave technique. Electrokinetic properties, such as electroosmotic behavior [13] and streaming potential [14], of different crystal planes were also examined. Second-harmonic generation (SHG) spectroscopy together with acid–base potentiometric titration served to characterize the crystal surface and to determine the point of zero charge [15].

However, advanced theoretical studies take account of the characteristics of individual planes, and even predict the overall behavior of the system. The relationship among charge distribution, surface hydration, and structure of the metal hydroxide
interface was analyzed in detail by Hiemstra, Van Riemsdijk et al. [3,4,16]. Rustad et al. [17–19] used molecular statistics calculation to model and identify surface species. Zarzycki et al. applied Monte Carlo simulations to study the acid–base properties of the clays [20] and metal oxide [21,22]/electrolyte interface as well as the influence of surface heterogeneity to adsorption. Sverjensky [23] predicted the pristine point of zero charge from crystal chemistry and solvation theory. Structural properties of the bulk crystal and crystal surface were calculated by Lazzeri et al. [24].

The bulk of the hematite crystal is composed of alternating layers of iron cations and oxygen anions. The cations occupy two-thirds of the space between the oxygen layers. Each cation is bound to three oxygen atoms from the layer above and to two oxygen atoms from the layer below. The properties of the hematite–electrolyte solution interface were found to depend on the structure of the hematite surface and on surface hydroxyl configuration (SHC) [4]. Several possible faces of the hematite crystal were observed [4,5,17–19,25] having different densities of singly, doubly, and triply coordinated OH groups. Venema et al. [4] introduced the idea that singly and triply coordinated OH groups are reactive groups, whereas doubly coordinated OH groups are not reactive. They calculated proton affinities of individual surface groups of hematite (0 0 1) and (1 1 0) faces and found that those two faces have different point of zero charge [26]. In this article the surface potentials of the (0 1 2), (1 0 2), (1 1 3), and (1 1 3) crystal planes of hematite were observed.

Recently, measurement of the surface potential \( \Psi_0 \), i.e., of the electrostatic potential of the inner Helmholtz plane, has been introduced. For that purpose single-crystal electrodes (SCrE) have been developed [27,28]. The measured electrode potentials are converted to surface potentials using the isoelectric point (i.e.p.) as an approximation of the point of zero potential (p.z.p.). Such a procedure is correct in the neutral electrolyte medium at relatively low ionic strength. At higher ionic strengths the p.z.p. differs from the i.e.p. so all other potential differences in the measuring circuit need to be determined and subtracted from the measured SCrE values. For that purpose one needs to know the electroneutrality point (the pristine point of zero charge) and to measure the SCrE potential at the isoelectric point [29].

The aim of this work is to describe the construction of a device for measuring surface potentials of individual planes and to present the results obtained with a hematite single crystal.

2. Theoretical

The surface potential \( \Psi_0 \) is an important parameter characterizing interfacial properties [30]. According to the surface complexation model (SCM), the surface potential at metal oxide/aqueous interfaces is determined by the pH value. The following reactions may take place at the hematite surface [31]:

\[
\begin{align*}
\equiv \text{Fe}^{0} & \rightarrow \equiv \text{FeO}^{+} + \text{H}^{+} \rightarrow \equiv \text{FeOH}^{+}, \\
1-pK, & \text{single-step-protonation mechanism}, \\
\end{align*}
\]

\[
\begin{align*}
\equiv \text{FeOH}^{+} & \rightarrow \equiv \text{FeOH}^{2+}, \\
2-pK, & \text{second-step-protonation mechanism}. \\
\end{align*}
\]

\[
\begin{align*}
\equiv \text{FeO}^{-} & \rightarrow \equiv \text{FeOH}^{-}, \\
2-pK, & \text{first-step-protonation mechanism}. \\
\end{align*}
\]

According to the SCM, the surface potential \( \Psi_0 \) is given by

\[
\Psi_0 = \frac{RT \ln 10}{F} \left( \text{pH}_{\text{pzc}} - \text{pH} \right) - \frac{RT}{F} \ln \left( \frac{\text{[FeOH}^{+}]^{1/2}}{\text{[FeOH}^{-}]^{1/2}} \right),
\]

\[
1-pK, \\
\]

\[
\Psi_0 = \frac{RT \ln 10}{F} \left( \text{pH}_{\text{pzc}} - \text{pH} \right) - \frac{RT}{2F} \ln \left( \frac{\text{[FeOH}^{+}]^{1/2}}{\text{[FeOH}^{-}]^{1/2}} \right),
\]

\[
2-pK, \\
\]

where the curly braces denote surface concentrations of relevant species, while other symbols have their usual meaning. The first term in the r.h.s. of Eqs. (4) and (5) is Nemstian, suggesting the \( \Psi_0(\text{pH}) \) function slope of, e.g., \(-59.2\) mV at 25 °C. However, the second term indicates that the magnitude of the slope may be significantly lower. The mechanism of the surface charging reaction may be always questioned. However, Eqs. (1)–(5) clearly show that regardless of the assumed reaction mechanism the second term in the \( \Psi_0(\text{pH}) \) function, being responsible for the lowering of the slope, is determined by the ratio of the surface concentrations of (more) positive to the (more) negative surface groups. The slope will therefore be conditioned by the characteristics of the plane exposed to the liquid medium (charging mechanism, surface density of active sites, and respective thermodynamic protonation equilibrium constants), and also by the liquid medium composition (the type and concentration of electrolyte) owing to the association of counterions and the equilibrium in the diffuse part of the electrical interfacial layer (EIL) [32]. Accordingly, surface potential measurements may be used to distinguish between the physico-chemical properties of crystal planes.

3. Experimental

3.1. Chemicals

All solutions were prepared using distilled, deionized, and decarbonated water; NaNO₃ (p.a., Fluka), NaOH (0.1 mol dm⁻³, titrival, Fluka), HNO₃ (0.1 mol dm⁻³, titrival, Fluka).

A hematite single-crystal electrode was constructed using the natural \( \alpha-\text{Fe}_{2}\text{O}_{3} \) mineral from Elba (Italy). The crystal surface was cleaned by extensive rinsing with distilled water. Four planes were examined, two and two symmetrically equivalent ones (0 1 2) and (1 0 2), and (1 1 3) and (1 1 3). To characterize the clean sample surface, high-resolution specular X-ray reflectivity data were collected and integrated using CrysAlis (Oxford Diffraction (2003) Oxford Diffraction Ltd., Xcalibur CCD system, CrysAlis Software system, Version 1.170). Fig. 1 shows the structures of crystalline planes. According to Barron and Torrent [5] the (0 1 2) hematite crystal faces have singly and triply coordinated OH groups, whereas the (1 1 3) faces have singly, doubly, and triply coordinated OH groups. The (0 1 2)
Fig. 1. Structural models of the hematite crystal planes (0 1 2) (a) and (1 1 3) (b). Small spheres, Fe atoms; large spheres, O atoms. H atoms are not included because their positions could not be determined by X-ray scattering.

hematite surface structure was described in detail by Catalano et al. [33].

3.2. Apparatus

To measure the surface potential of an individual plane a special device was constructed (Fig. 2). A detail of construction is given in Fig. 3. A solution of predetermined composition was supplied from the beaker through a tube to the surface. The flow was regulated by the valve at the outlet. The contact of the solution with the selected crystal plane was made possible with the tip shown in Fig. 3. The sealing was ensured by pressing the tip with a thin rubber ring to the crystal surface. The contact area occupied only a part of the examined surface and was approximately 3 mm². The hematite crystal was mounted in the plastic gum and direct electric contact with the crystal was ensured by a copper wire. The reference electrode was immersed in the solution in the beaker. The salt bridge was filled with the NaNO₃ solution having the same concentration as the measuring system. The pH of the solution was measured by means of a glass electrode against the same reference electrode. Two pH meters were used. The pH was changed by addition of the acid to the base solution.

3.3. Procedure

Experiments were performed at low (10⁻³ mol dm⁻³) and at high (10⁻¹ mol dm⁻³) ionic strengths. The beaker was filled with 0.001 mol dm⁻³ NaOH solution. The system was kept under an argon atmosphere at 22°C. The potentials of the hematite and glass electrodes were measured independently. Constant readings (dE/dt < 0.1 mV min⁻¹) were observed after the equilibration time of 10 min. The accuracy of the readings was estimated as ±1 mV, except in the neutral region.
where, due to the slower equilibration, the accuracy was about ±5 mV. The pH was decreased by subsequent addition of portions of 0.1 mol dm\(^{-3}\) HNO\(_3\) solution. The ionic strength remained constant (10\(^{-3}\) mol dm\(^{-3}\)) until the equivalence point was reached, but increased up to 2 × 10\(^{-3}\) mol dm\(^{-3}\) at final pH ≈ 3. The only difference between the low ionic strength experiments and those performed at high ionic strength was that in the latter crystalline NaNO\(_3\) was added until the ionic strength of 10\(^{-1}\) mol dm\(^{-3}\) was achieved and remained practically constant. The glass electrode potentials were converted to pH values on the basis of calibration with five buffers (pH 3, 5, 7, 8, and 10). The surface potential \(\Psi_0\) was related \([29]\) to the electrode potential of the single-crystal electrode \(E_{ECS}\) by

\[\psi_0 = E_{ECS} - E_{cal},\] (6)

where \(E_{cal}\) can be obtained by calibration and represents all potential differences in the measuring circuit except the one at the crystal–electrolyte interface. As the \(E_{cal}\) value does not depend on the composition of the solution it may be taken as a constant for a given system and used for evaluation of \(\Psi_0\) by Eq. (6). At the point of zero potential (pH\(_{pZP}\); \(\Psi_0 = 0\)), \(E_{cal} = E_{ECS}\).

4. Results

Fig. 4 shows the hematite electrode potentials (vs reference electrode Ag|AgCl|KCl, 3 mol dm\(^{-3}\) |NaNO\(_3\), 10\(^{-3}\) mol dm\(^{-3}\)) of different planes of the hematite single crystal as a function of pH at \(I_c = 10^{-3}\) mol dm\(^{-3}\) and 22°C: \(\triangle\) (0 1 2); \(\bigcirc\) (1 0 2); \(\bigotimes\) (1 1 3); \(\square\) (1 1 2).

The Nernstian slope (\(\Psi_N\)) is represented by a dashed line.

4. Results

Fig. 4 shows the hematite electrode potentials (vs reference electrode Ag|AgCl|KCl, 3 mol dm\(^{-3}\) |NaNO\(_3\)) as a function of pH, as determined at low ionic strength (\(I_c = 10^{-3}\) mol dm\(^{-3}\)), for all examined crystal planes. It may be concluded that there was no significant difference in potential between the planes. The slope of −38 mV (\(\alpha = 64\%\)) agreed well with our previous findings when several different planes were exposed to the solution [27,28,34].

The p.z.p. value at low ionic strength was taken to correspond to that of i.e.p. at pH\(_{iEP}\) = pH\(_{pZP}\) = 8.5 [18,35]. At this pH the electrode potential was −35 ± 5 mV, so that the value of −35 mV was taken as \(E_{cal}\) and used for evaluation of the surface potentials \(\Psi_0\) (Eq. (6)). Had a different value been assigned to the p.z.p., the only consequence would have been a shift in experimental \(\Psi_0(pH)\) functions.

Fig. 5 shows the effect of sodium nitrate concentration on the surface potentials of the (1 0 2) hematite crystal plane. As expected, the slope was significantly lower at higher ionic strengths, from −38 to −19 mV. A shift in p.z.p. was observed from pH\(_{pZP}\) = 8.5 to pH\(_{pZP}\) = 9.0. Results for the (1 1 3) hematite plane are given in Fig. 6. At high ionic strength there was no significant changes in slope in the acidic region, but in the basic region a substantial reduction of slope was noticeable. The shift in p.z.p. was more pronounced, from pH\(_{pZP}\) = 8.5 to pH\(_{pZP}\) = 9.5.

5. Discussion

At low ionic strength (10\(^{-3}\) mol dm\(^{-3}\)) there was no significant difference in surface potential between the (1 0 2) and (1 1 3) planes of the hematite crystal, but at high ionic
From Figs. 5 and 6 it is therefore possible to conclude that at higher electrolyte concentrations there occurred a shift in i.e.p. to the acidic region, is a sign that anions are more prone to associate with oppositely charged surface groups than cations [36–39]. The shift in p.z.p. was shown to follow the shift (10⁻¹ mol dm⁻³) the difference was noticeable (Figs. 5 and 6). It is known that at higher ionic strengths the isoelectric point (i.e.p.) and the point of zero charge (p.z.c.) shift in opposite directions. A shift in p.z.c. to the basic region, accompanied with a shift in i.e.p. to the acidic region, is a sign that anions are more prone to associate with oppositely charged surface groups than cations [36–39]. The shift in p.z.p. was shown to follow the shift in p.z.c. [29]. From Figs. 5 and 6 it is therefore possible to conclude that at higher electrolyte concentrations there occurred a shift in p.z.c. to the basic region, which was more prominent for the (1 1 −3) plane than for the (1 0 −2) one, and that consequently, the affinity of NO₃⁻ ions for association at the interface was higher than that of Na⁺ ions. The difference in counterion association affinity was more pronounced for the (1 1 −3) plane. The question remains open whether this difference was due to the lowering of the association affinity of Na⁺ ions or to the increase in the association affinity of NO₃⁻ ions. Analysis of the slope of ψ₀(pH) function is not helpful in solving this problem. Depending on other parameters that characterize the interface, e.g., electrical capacitance of interfacial layers, the higher counterion association affinity may result in both increase and decrease of the surface potential [40]. This is in accordance with our previous results obtained with the hematite SCR-E (high ionic strength—lower surface potential) [27].

The shift in p.z.p. to the basic region was more pronounced for the (1 1 −3) plane than for the (1 0 −2) plane. It is known that at higher ionic strengths the isoelectric point (i.e.p.) and the point of zero charge (p.z.c.) shift in opposite directions. A shift in p.z.c. to the basic region, accompanied with a shift in i.e.p. to the acidic region, is a sign that anions are more prone to associate with oppositely charged surface groups than cations [36–39]. The shift in p.z.p. was shown to follow the shift in p.z.c. [29]. From Figs. 5 and 6 it is therefore possible to conclude that at higher electrolyte concentrations there occurred a shift in p.z.c. to the basic region, which was more prominent for the (1 1 −3) plane than for the (1 0 −2) plane, and that consequently, the affinity of NO₃⁻ ions for association at the interface was higher than that of Na⁺ ions. The difference in counterion association affinity was more pronounced for the (1 1 −3) plane. The question remains open whether this difference was due to the lowering of the association affinity of Na⁺ ions or to the increase in the association affinity of NO₃⁻ ions. Analysis of the slope of ψ₀(pH) function is not helpful in solving this problem. Depending on other parameters that characterize the interface, e.g., electrical capacitance of interfacial layers, the higher counterion association affinity may result in both increase and decrease of the surface potential [40]. This is in accordance with our previous results obtained with the hematite SCR-E (high ionic strength—lower surface potential) [27].

Electrokinetic measurements [41,42] on colloidal hematite samples showed a shift in pH<sub>isc</sub> to the acidic region at increased NaNO₃ concentration. This is in accordance with the results of this study where the i.e.p. shift to the acidic region was accompanied by p.z.c. and p.z.p. shifts to the basic region. As predicted by the Monte Carlo simulation for the 001 hematite plane [21] the ψ₀(pH) function is practically linear in the pH range between 4 and 10 with the slope lower than the Nernstian. This prediction agrees with our data. In fact, this function is not necessarily linear, and the slopes may be different in positive and negative regions due to the difference in association affinities of anions and cations, respectively.

It has been established that surface potential measurements help in understanding the specificity of different crystal planes and that they may contribute to verification of theoretical predictions [16,17,23].

However, the conclusions based solely on those measurements are semiquantitative, because for complete and quantitative characterization of individual planes the adsorption and electrokinetic data are necessary. Measurements of the surface potentials of individual planes may be extended to examine their mutual interactions taking place when a crystal with several different planes is exposed to an electrolyte solution. One can measure their potential separately and then connect them and find the output, which should be between the individual values. The measured “overall” value may suggest which plane is more dominant. However, such an experiment requires new design of the apparatus and will be subject of further attempts.

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