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Evaluation of surface potential from single crystal electrode potential

Application of Saddle point method for sapphire A crystal plane

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Abstract The new method of evaluation of the point of zero potential for the metal oxide exhibiting a saddle-like surface potential function $\Psi_0(\mathrm{pH})$, as obtained by acid base potentiometric titration using Single Crystal Electrode, was proposed. The electrode potential of sapphire single crystal electrode (A crystal plane, $11\bar{2}0$) was measured, point of zero potential and surface potentials were evaluated, and the results were analyzed using the Surface Complexation Model. The electroneutrality point corresponding to the point of zero potential was found to be at $\mathrm{pH_{pzp}} = 7.0$. Thermodynamic protonation equilibrium constants for the first and the second step of protonation were obtained as $\lg K_1^\circ = 12.7$; $\lg K_2^\circ = 1.2$.

Keywords Single crystal electrode · Sapphire · Surface potential · Electrical interfacial layer · Surface complexation · Equilibrium parameters · Surface charging

1 Introduction

The electrical interfacial layer forms at the contact of a metal oxide with the aqueous electrolyte solution. Electrical interfacial layer (EIL) could be described with various theoretical models differing in the number of proposed planes and layers (Delgado et al. 2007; Kallay et al. 2006). In all assumed models the electrical interfacial layer starts to form at the contact of solid surface with liquid phase. The surface sites are located at the solid surface and their state and electrical charge depend on the crystallographic structure, as well as on the binding and distribution of ions within the EIL. The process of electrical charging at a metal oxide surface in aqueous environment, assuming formation of charged surface groups and their partial association with counterions, has been commonly described by the Surface Complexation Model (SCM) (Schindler and Kamber 1968; Stumm et al. 1970; Schindler and Stumm 1987). The original concept was refined by Yates et al. (1974) introducing the Triple layer model and later by Hiemstra et al. (1989) who introduced advanced the MUSIC model. The original model, as well as the refined versions, agrees in the assumption that the state of charged surface sites is affected by the (inner) surface potential (Bousse et al. 1983; Piasecki 2003). Therefore, the (inner) surface potential Ψ_0 is an important parameter for describing the equilibrium of surface reaction so numerous attempts were made to measure this quantity.

The first effort of evaluation of surface potential was the preparation of an electrode consisting of conducting wire covered with deposited colloidal metal oxide particles (Kinoshita et al. 1986; Penners et al. 1986; Avena et al. 1993). The electrode potential was measured as a function of pH and a linear response was obtained with the slope equal to the Nernstian slope i.e. −59.1 mV at 25 °C, except for $\mathrm{TiO_2}$ (Avena et al. 1993). However, it is likely that due to the porosity of the oxide layer, the potential was predominantly determined by the redox equilibrium and influenced by the solubility of the oxide. Next attempt was the application of the Ion Sensitive Field Effect Transistors (ISFET) technique which produced more reliable results (Bousse et al. 1983; Cichos and Geidel 1983). The problem of porosity of the (metal) oxide electrode was first solved by the construction of an ice electrode (Kallay and Čakara 2000). A compact nonporous and stable ice layer, few millimeters thick,

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was formed by cooling on the platinum plate. The measured electrode potential of the ice electrode was the result of interfacial reactions involving H^+ and OH^- ions. Afterwards, a hematite single crystal electrode (SCrE) was constructed (Kallay et al. 2005) enabling measurements of surface potentials. Later, different metal oxides (Kallay et al. 2007; Preočanin and Kallay 2008; Kovačević et al. 2010), silver halogenides (Preočanin et al. 2009, 2011) and other minerals (Preočanin et al. 2007) were examined. In addition, the method enabled the determination of the surface potential of each crystal plane separately (Kallay and Preočanin 2008; Yanina and Rosso 2008; Boily et al. 2011; Shimizu et al. 2012), which is important when considering surface heterogeneity (Hiemstra and van Riemsdijk 2006).

There are however a few limitations of this method which make its application somewhat difficult. One of the hindrances is the calculation of the surface potential from the measured electrode potential i.e. the overall electromotive force of the cell E. Since $\Psi_0 = E + \textit{constant value}$, it is enough to determine the point of zero potential pH_{pzp} at which $\Psi_0 = 0$. Usually, the point of zero potential corresponds to other electroneutrality points i.e. to the point of zero charge pH_{pzc} (Sposito 1998) and to the isoelectric point pH_{iep} (Hunter 1981; Delgado et al. 2007). The point of zero charge, at which $\sigma_0 = 0$, could be obtained by potentiometric acid-base titrations (Parks and de Bruyn 1962; Lyklema 1995) or potentiometric mass titration (Noh and Schwarz 1989; Preočanin and Kallay 1998) while the isoelectric point, at which $\zeta = 0$, can be obtained by several electrokinetic techniques. All three zero charge points coincide ($pH_{pzp} = pH_{pzc} = pH_{iep}$) in the absence of specific adsorption and in the case of negligible or symmetrical counterion association. This state, when all electrical properties tend to zero ($\sigma_0 = \sigma_s = 0$, $\Psi_0 = \zeta = 0$), is called the electroneutrality point (pH_{eln}) or the pristine point of zero charge (pH_{ppzc}) which is determined by thermodynamic equilibrium constants of interfacial reactions (Pyman et al. 1979). In such a case the value of isoelectric point or the point of zero charge enables the evaluation of surface potentials from the measured electrode potentials. This approach can be tested by measuring the dependency of the isoelectric point on the electrolyte concentration. If pH_{iep} does not depend on the electrolyte concentration it may be assumed that pH_{pzp} correspond to pH_{iep}, and also to pH_{pzc}.

In the case of specific adsorption or unsymmetrical association of counterions, the pH_{pzc} and pH_{iep} values shift from the pH_{eln} in the opposite directions. The value of pH_{pzp} is also shifted and lies between pH_{eln} and pH_{pzc}. For example in the case of preferential association of cations $pH_{pzc} < pH_{pzp} < pH_{eln} < pH_{iep}$, whereas, for the preferential association of anions the opposite trend should be expected: $pH_{pzc} > pH_{pzp} > pH_{eln} > pH_{iep}$ (Kallay et al. 2007).

In the study of individual specific crystal surface faces the corresponding point of zero potential, or at least isoelectric point, should be known. These values are very difficult to determine and are thus rarely reported (Bullard and Cima 2006; Eggleston and Jordan 1998).

Apart from identifying the point of zero potential with the point of zero charge or the isoelectric point several methods for determination of the point of zero potential were proposed. Cyclic titration from acidic to basic pH (alkalimetric), and the reverse (acidimetric), often exhibits hysteresis (Preočanin et al. 2006), which was exploited for determination of the point of zero potential (Zarzycki et al. 2011). In the absence of hysteresis and counterion association another method was proposed which is based on a common-intersection point of measured electrode potential functions at different ionic strengths (Zarzycki and Preočanin 2012).

The aim of this work is to develop an accurate and simple method for pH_{pzp} determination. The proposed method applies to systems exhibiting a saddle-like surface potential function $\Psi_0(\mathrm{pH})$. In the proposed method acid base potentiometric titration is performed and electrode potential of Single Crystal Electrode is measured, pH_{pzp} is determined and electrode potentials are converted to the surface potentials. The method is demonstrated by measurements with the individual sapphire surface plane (A, $11\bar{2}0$). The results enable evaluation of corresponding equilibrium parameters, i.e. interfacial equilibrium constants.

2 Interfacial equilibrium

Interfacial equilibrium is commonly interpreted by Site Binding or Surface Complexation Model (SCM) (Schindler and Kamber 1968; Stumm et al. 1970; Yates et al. 1974; Schindler and Stumm 1987; Lützenkirchen 2006; Kallay et al. 2011). Charging of metal oxides is described either by Single-step protonation by 1-pK model (van Riemsdijk et al. 1986) or by two-step protonation (2-pK mechanism (Davis et al. 1978)). Since the 1-pK model does not result in the saddle like potential function, the 2-pK concept (two step protonation) will be employed. The electrical double layer was used as a model of the electrical interfacial layer.

The two-step protonation mechanism assumes the following surface reactions

$$\equiv\mathrm{MO}^- + \mathrm{H}^+ \rightarrow \equiv\mathrm{MOH}; \quad K_1^\circ \tag{1}$$

$$\equiv\mathrm{MOH} + \mathrm{H}^+ \rightarrow \equiv\mathrm{MOH}_2^+; \quad K_2^\circ \tag{2}$$

where species bound to the surface are denoted by ≡.

Corresponding thermodynamic equilibrium constants K_1° and K_2° are

$$K_1^\circ = \exp(\Psi_0 F/RT) \cdot \frac{\{\equiv\mathrm{MOH}\}}{\{\equiv\mathrm{MO}^-\} \cdot a_{\mathrm{H}^+}} \tag{3}$$

$$K_2^\circ = \exp(\Psi_0 F/RT) \cdot \frac{\{\equiv\mathrm{MOH}_2^+\}}{\{\equiv\mathrm{MOH}\} \cdot a_{\mathrm{H}^+}} \tag{4}$$

where curly brace denotes surface concentration (the amount or number of moles per surface area) and Ψ_0 stands for the inner surface potential affecting the state of ionic species being directly bound to the surface. Other symbols have their usual meaning. It is also a common practice to consider hydrated surface $\equiv$MOH species as amphotheric and to write the above stoichiometric equations as protonation, being identical to Eq. (2), and the deprotonation of neutral sites as opposite to the first step of protonation, Eq. (1). The effective (net) surface charge is reduced by the association of anions A^- and cations C^+ with oppositely charged surface groups.

$$\equiv\mathrm{MOH}_2^+ + \mathrm{A}^- \rightarrow \equiv\mathrm{MOH}_2^+ \cdot \mathrm{A}^-; \quad K_\mathrm{A}^\circ \tag{5}$$

$$\equiv\mathrm{MO}^- + \mathrm{C}^+ \rightarrow \equiv\mathrm{MO}^- \cdot \mathrm{C}^+; \quad K_\mathrm{C}^\circ \tag{6}$$

The corresponding thermodynamic equilibrium constants K_A° and K_C° are

$$K_\mathrm{A}^\circ = \exp(-\Psi_\beta F/RT) \cdot \frac{\{\equiv\mathrm{MOH}_2^+ \cdot \mathrm{A}^-\}}{\{\equiv\mathrm{MOH}_2^+\} \cdot a_{\mathrm{A}^-}} \tag{7}$$

$$K_\mathrm{C}^\circ = \exp(\Psi_\beta F/RT) \cdot \frac{\{\equiv\mathrm{MO}^- \cdot \mathrm{C}^+\}}{\{\equiv\mathrm{MO}^-\} \cdot a_{\mathrm{C}^+}} \tag{8}$$

where the outer surface potential Ψ_β at β-plane affects the state of associated counterions. The total density of surface sites is equal to

$$\begin{aligned}\Gamma_{\mathrm{tot}} = {} & \{\equiv\mathrm{MOH}\} + \{\equiv\mathrm{MOH}_2^+\} + \{\equiv\mathrm{MOH}_2^+ \cdot \mathrm{A}^-\} \\ & + \{\equiv\mathrm{MO}^-\} + \{\equiv\mathrm{MO}^- \cdot \mathrm{C}^+\}\end{aligned} \tag{9}$$

Surface charge densities in 0- and β-planes are

$$\begin{aligned}\sigma_0 = {} & F \cdot \big(\{\equiv\mathrm{MOH}_2^+\} + \{\equiv\mathrm{MOH}_2^+ \cdot \mathrm{A}^-\} - \{\equiv\mathrm{MO}^-\} \\ & - \{\equiv\mathrm{MO}^- \cdot \mathrm{C}^+\}\big)\end{aligned} \tag{10}$$

and

$$\sigma_\beta = F \cdot \big(\{\equiv\mathrm{MO}^- \cdot \mathrm{C}^+\} - \{\equiv\mathrm{MOH}_2^+ \cdot \mathrm{A}^-\}\big) \tag{11}$$

The effective (net) surface charge density σ_s is equal in magnitude and opposite in sign to the surface charge density of the diffuse layer σ_d

$$\sigma_\mathrm{s} = -\sigma_\mathrm{d} = \sigma_0 + \sigma_\beta = F \cdot \big(\{\equiv\mathrm{MOH}_2^+\} - \{\equiv\mathrm{MO}^-\}\big) \tag{12}$$

The relationships between surface charge densities and interfacial electrostatic potentials are often based on the concept of condensers of constant capacitance C (expressed per surface area) as

$$C_1 = \frac{\sigma_0}{\Psi_0 - \Psi_\beta} \tag{13}$$

$$C_2 = \frac{\sigma_\mathrm{s}}{\Psi_\beta - \Psi_\mathrm{d}} \tag{14}$$

where Ψ_d is the potential at the onset of the diffuse layer. Note that if $C_2 \rightarrow \infty$ then $\Psi_\mathrm{d} = \Psi_\beta$. According to the Gouy-Chapman theory

$$\sigma_\mathrm{d} = -\sigma_\mathrm{s} = -\sqrt{8RT\varepsilon I_c}\,\sinh(-F\Psi_\mathrm{d}/RT) \tag{15}$$

where ε ($\varepsilon = \varepsilon_0 \cdot \varepsilon_\mathrm{r}$) is permittivity and I_c is the ionic strength determined by the concentrations (c) and the respective charge numbers (z) of all ions present in the bulk of the solution as

$$I_c = \frac{1}{2} \sum_i c_i \cdot z_i^2 \tag{16}$$

According to the Surface Complexation Model (Eqs. (3), (4)), the inner surface potential Ψ_0 is given by

$$\Psi_0 = \frac{RT}{F} \ln K_1^\circ - \frac{RT}{F} \ln\left(\frac{\{\equiv\mathrm{MOH}\}}{\{\equiv\mathrm{MO}^-\}}\right) - \frac{RT \ln 10}{F} \cdot \mathrm{pH} \tag{17}$$

$$\Psi_0 = \frac{RT}{F} \ln K_2^\circ - \frac{RT}{F} \ln\left(\frac{\{\equiv\mathrm{MOH}_2^+\}}{\{\equiv\mathrm{MOH}\}}\right) - \frac{RT \ln 10}{F} \cdot \mathrm{pH} \tag{18}$$

Summation of Eqs. (17) and (18) leads to

$$\begin{aligned}\Psi_0 = {} & \frac{RT}{2F} \ln\big(K_1^\circ \cdot K_2^\circ\big) - \frac{RT}{2F} \ln\left(\frac{\{\equiv\mathrm{MOH}_2^+\}}{\{\equiv\mathrm{MO}^-\}}\right) \\ & - \frac{RT \ln 10}{F} \cdot \mathrm{pH}\end{aligned} \tag{19}$$

By introducing the electroneutrality point $\mathrm{pH}_{\mathrm{eln}}$

$$\mathrm{pH}_{\mathrm{eln}} = \frac{1}{2} \lg\big(K_1^\circ \cdot K_2^\circ\big) \tag{20}$$

the following relationship is obtained

$$\Psi_0 = \frac{RT \ln 10}{2F} \lg\left(\frac{\{\equiv\mathrm{MO}^-\}}{\{\equiv\mathrm{MOH}_2^+\}}\right) - \frac{RT \ln 10}{F}(\mathrm{pH} - \mathrm{pH}_{\mathrm{eln}}) \tag{21}$$

The second term in Eq. (21) is Nernstian, while the first term determines the deviation from the Nernst equation. Accordingly, surface potential measurements and the deviation

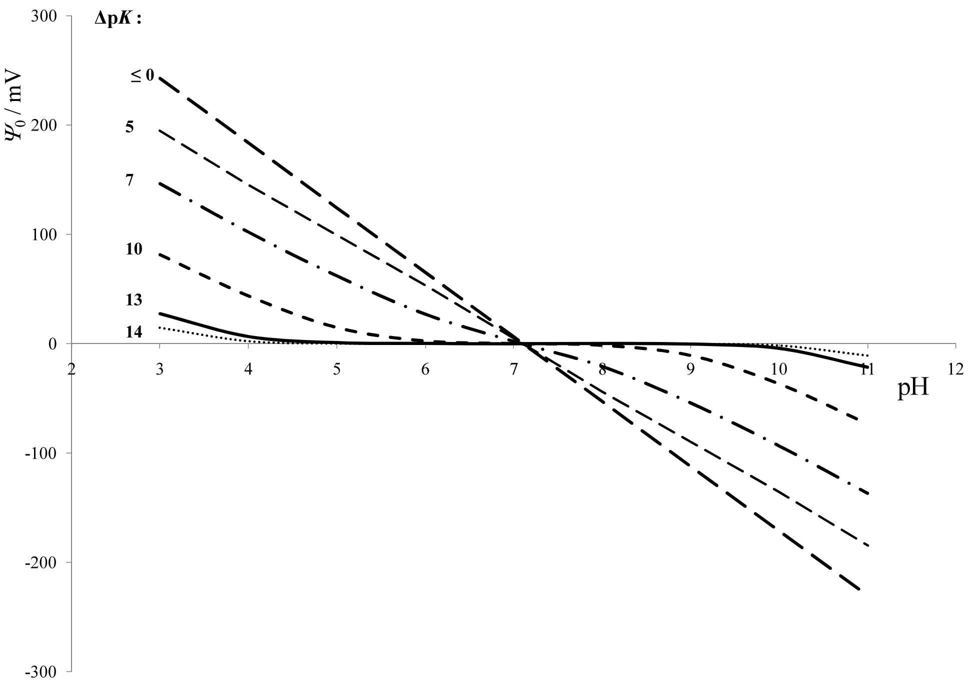


Fig. 1 Calculated surface potentials Ψ_0 at 25 °C for $\Gamma_{\mathrm{tot}} = 1.5 \times 10^{-5}\ \mathrm{mol\,m^{-2}}$, $\lg K_{\mathrm{A}}^{\circ} = \lg K_{\mathrm{C}}^{\circ} = 1$, $C_1 = 1.5\ \mathrm{F\,m^{-2}}$, $C_2 = \infty$, $I_c = 10^{-4}\ \mathrm{mol\,dm^{-3}}$, $\lg(K_1^{\circ} \cdot K_2^{\circ}) = 14.2$; $\mathrm{pH_{eln}} = 7.1$; assuming different $\Delta \mathrm{p}K$ values: ≤ 0 (— — —), 5 (– – –), 7 (–·–·–), 10 (- - -), 13 (—), 14 (·····)

from the Nernstian behavior may be used to obtain the ratio of surface concentrations of negative and positive sites, and thus the evaluation of interfacial equilibrium parameters. According to Eq. (21) the Ψ_0(pH) function may be (approximately) linear, but also a kind of a saddle may appear, depending on the values of equilibrium constants and the total density of surface sites. Figure 1 demonstrates that the saddle appears only at significant $\Delta \mathrm{p}K$ values defined by

$$\Delta \mathrm{p}K = \lg\left(K_1^{\circ}/K_2^{\circ}\right) \tag{22}$$

For $\Delta \mathrm{p}K \le 0$, i.e. $K_1^{\circ} \le K_2^{\circ}$, the function is linear with the Nernstian slope of -59.1 mV at 25 °C. For $\Delta \mathrm{p}K = 0$, both processes proceed with the same equilibrium constant ($K_1^{\circ} = K_2^{\circ}$). In such a case they are equivalent, and consequently cannot be distinguished. In fact such system corresponds to one-step protonation, i.e. to 1-pK concept.

If only the formation of positive sites, i.e. the binding of H^+ ions to neutral sites, is considered, an increase in pH would result in the decrease of positive surface potentials asymptotically approaching the zero value. If only the formation of negative sites, i.e. release of H^+ ions from the neutral sites (opposite to the first step of protonation), is considered a decrease in pH would result in the decrease of negative surface potentials asymptotically approaching the zero value. Figure 1 represents Ψ_0(pH) functions calculated by using Eqs. (3)–(21), for different assumed $\Delta \mathrm{p}K$ values. It is clear that the function is almost linear for $\Delta \mathrm{p}K < 6$ with the slope lower than Nernstian, but for $\Delta \mathrm{p}K$ values approaching to zero, and also for negative $\Delta \mathrm{p}K$ values ($K_1^{\circ} \le K_2^{\circ}$), the Ψ_0(pH) function becomes linear with the Nernstian slope.

Additionally the effect of total density of surface sites, Eq. (9), on surface potential was examined. From Fig. 2 it is clear that function Ψ_0(pH) become linear for high Γ_{tot} values. For example for $\Gamma_{\mathrm{tot}} = 10^{-3}\ \mathrm{mol\,m^{-2}}$ function is almost linear but slope was lower than the Nernstian slope (64 % lower). However, so high value of total density of surface sites is not realistic. From the physical and chemical properties of the sapphire crystal (for example the density of sapphire is $\rho = 3.98\ \mathrm{g/cm^3}$) the value of the total density of surface sites could be assumed to be around $1.5 \times 10^{-5}\ \mathrm{mol\,m^{-2}}$. Assuming the value of the total density of surface sites being near this value, the calculated surface potentials would only slightly change.

According to the results presented in Figs. 1 and 2, the Nernstian response is expected for low $\Delta \mathrm{p}K$ and high Γ_{tot} values. Increase in $\Delta \mathrm{p}K$ and decrease in Γ_{tot} results in the lowering of the slope. Moreover, high $\Delta \mathrm{p}K$ and low Γ_{tot} values causes deviation of the linearity and a saddle like Ψ_0(pH) function.

3 Experimental

All chemicals used in this study were of the analytical grade purity. The sapphire was obtained from TBL Kelpin (now MaTeck, Germany). The crystal was rectangular (10 × 10 mm) with a thickness of 0.5 mm. The single crystal electrode was constructed so that A-plane construction of sapphire $(11\bar{2}0)$ was exposed to the solution, Fig. 3. The nonporous SCr-sapphire electrode consisted of a plexiglas body with a single crystal mounted at its end and sealed with

Fig. 2 Calculated surface potentials Ψ_0 at 25 °C for different total surface sites concentration Γ_{tot}, $\lg K_{\mathrm{A}}^{\circ} = \lg K_{\mathrm{C}}^{\circ} = 1$, $C_1 = 1.5\ \mathrm{F\,m^{-2}}$, $C_2 = \infty$, $I_c = 10^{-4}\ \mathrm{mol\,dm^{-3}}$, $\lg(K_1^{\circ} \cdot K_2^{\circ}) = 14.2$; $\mathrm{pH_{eln}} = 7.1$; $\Delta \mathrm{p}K = 10$

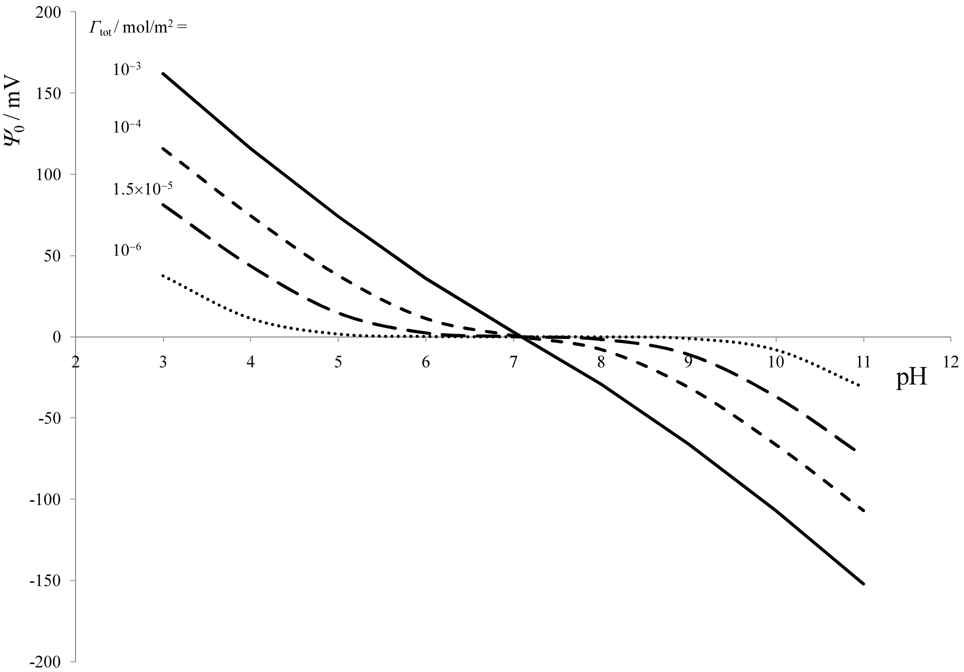
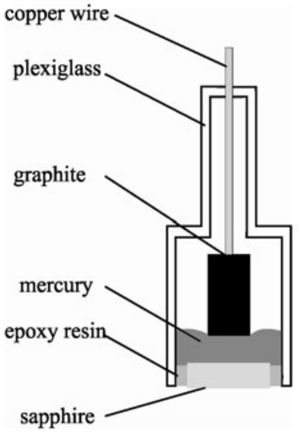


Fig. 3 Sapphire single Crystal Electrode for surface potential measurements



epoxy resin. Internal electric contact was ensured by mercury into which a graphite rod was immersed. A copper wire was connected to the graphite rod. The details are given elsewhere (Kallay et al. 2005; Preočanin and Kallay 2008; Zarzycki et al. 2010). The electric resistance (impedance) of the sapphire crystal was measured directly and found to be approximately 100 MΩ, so that the internal resistance of the pH-meter was sufficiently high to ensure reversible condition, i.e. the absence of potential drop due to the passage of current through the electrode. Accordingly, the measured electrode potential was the result of the ionic adsorption equilibrium within the sapphire EIL only.

Potentials of the SCr-sapphire electrode were measured by Metrohm 713 pH-meter. As a reference electrode the silver/silver chloride electrode, filled with 3 $\mathrm{mol\,dm^{-3}}$ KCl solution, with salt bridge (Metrohm, 6.0729.100), filled with the same electrolyte solution as the measuring system, was used. Separate pH-meter operated by batteries (Methrom 826) was used for the measurements of pH values so that a mutual influence through grounding was excluded. pH was measured using a glass electrode (Metrohm 6.0133.100.) and the same reference silver chloride electrode as used for the SCr-hematite electrode. Systems were thermostated at 25.0 °C and placed in a Faraday cage so that external electrical effects were avoided. In order to avoid $\mathrm{CO_2}$ contamination the experiments were performed under argon atmosphere. The surface of the SCr-sapphire electrode was cleaned with ethanol and rinsed with water before the measurements to remove possible organic impurities. As a background, the electrolyte KCl was used. The HCl solution was titrated with KOH. Time intervals between additions were 15 minutes to ensure the equilibration and stabilization of the reading signal.

4 Results and discussion

Figure 4 displays the electrode potential of sapphire crystal A-plane $(11\bar{2}0)$ as a function of pH in the presence of $10^{-3}\ \mathrm{mol\,dm^{-3}}$ KCl.

The problem of the conversion of electrode potentials to surface potentials was solved by interpretation based on the Surface Complexation model which suggests a possibility of "mirror symmetry" of the saddle-like surface potential function enabling the evaluation of the point of zero potential (Figs. 1 and 2). The procedure is simple: a certain pH is assumed as the point of zero potential $\mathrm{pH_{pzp}}$, corresponding to

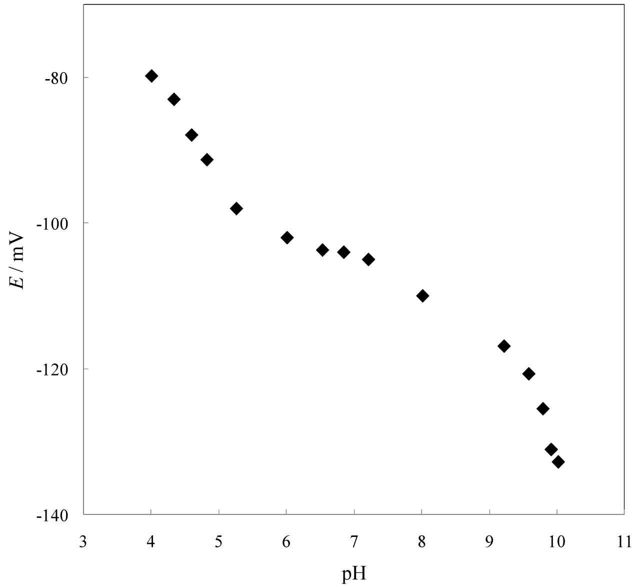


Fig. 4 Electrode potential of SCr- electrode (A crystal plane $11\bar{2}0$) vs. Ag/AgCl/KCl (3 mol dm^{-3}) reference electrode as a function of pH in presence of 10^{-4} mol dm^{-3} KCl. Temperature: 25 °C

pH_{eln}, and the absolute values of electrode potential difference is calculated

$$|\Delta E| = \left|E - E(pH_{pzp})\right| = |\Psi_0| \tag{23}$$

as a function of absolute values of pH with respect to assumed pH_{pzp}

$$|\Delta pH| = |pH - pH_{pzp}| \tag{24}$$

The plot of absolute values of such calculated surface potentials vs. the absolute difference of pH, should coincide for the acidic and for the basic branches. Figure 5 demonstrates such plots for the correct value of the $pH_{pzp} = 7.0$, and for too low and too high chosen pH_{pzp} values. It is clear that "mirror symmetry" was obtained only if the correct value of pH_{pzp} was used. Accordingly, the value of $pH_{pzp} = 7.0$ was used to evaluate surface potential Ψ_0 from electrode potentials (Fig. 6). This simple and accurate procedure for the evaluation of the point of zero potential may be used only for systems exhibiting a saddle-like surface potential function i.e. in the case of higher ΔpK values (i.e. above 7). Another procedure for the location of the point of zero potential is to fit the experimental pH(E) function with a polynomial and calculate the inflection point. This procedure is not so accurate since the function is flat with a broad zero potential region.

The saddle like function, as presented in Fig. 4, suggests the two-step protonation (2-pK) mechanism, one reaction being responsible for charging in the acidic medium and the second taking place in the basic medium. As expected the slopes in the acidic and in the basic regions were found to be lower with respect to Nernstian. Since the one-step mechanism (1-pK) cannot result in the saddle like function but rather in a more or less linear function, the results were interpreted on the basis of the two-step mechanism using Eqs. (3)–(21). The best fit for 10^{-4} mol dm^{-3} KCl solutions is presented in Fig. 6. In calculations, the commonly accepted total density of surface sites of $\Gamma_{tot} = 1.5 \times 10^{-5}$ mol m^{-2} as well as $\lg K_A^\circ = \lg K_C^\circ = 1$ and $C_1 = 1.5$ F m^{-2}, $C_2 = \infty$ were used. The fit is not perfect which is probably due to experimental uncertainty. The best fit values were obtained as $\lg K_1^\circ = 12.7$; $\lg K_2^\circ = 1.2$ resulting in $\Delta pK = \lg K_1^\circ - \lg K_2^\circ = 11.5$ and $pH_{pzp} = 7.0$.

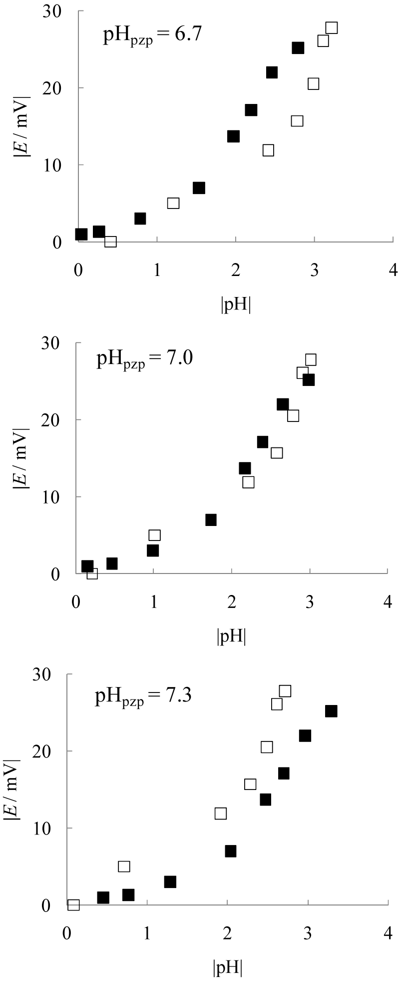


Fig. 5 Evaluation of the point of zero potential from single crystal electrode potentials. Absolute values of the surface potential of A crystal plane $(11\bar{2}0)$ calculated from corresponding electrode potentials as presented in Fig. 4 for 10^{-4} mol dm^{-3} KCl at 25 °C. The following values of pH_{pzp} were assumed: 6.7, 7.0 and 7.3

Measurements of surface potential of the single and defined crystal plane enable a proper choice of the reaction mechanism responsible for charging the surface. The appearance of the saddle-like function suggests the two step protonation mechanism. The importance of surface potential

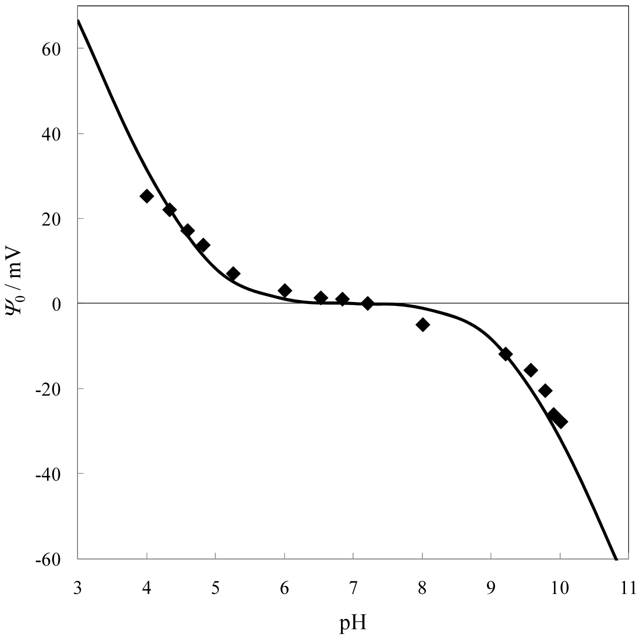


Fig. 6 Surface potential of sapphire A crystal plane $(11\bar{2}0)$ as a function of pH in presence of 10^{-4} (■) $\text{mol}\,\text{dm}^{-3}$ KCl. Full line presents the best fit for $\Gamma_{\text{tot}} = 1.5 \times 10^{-5}\ \text{mol}\,\text{m}^{-2}$, $\lg K_{\text{A}}^{\circ} = \lg K_{\text{C}}^{\circ} = 1$, $C_1 = 1.5\ \text{F}\,\text{m}^{-2}$, $C_2 = \infty$, and $\lg K_1^{\circ} = 12.7$; $\lg K_2^{\circ} = 1.2$; $\Delta\text{p}K = \lg(K_2^{\circ}/K_1^{\circ}) = 11.5$. Temperature: 25 °C

measurements lies in the fact that surface charge data cannot be used to distinguish between one- and two-protonation mechanisms, i.e. between the 1-pK and 2-pK concepts. If the mechanism or stoichiometry of surface reactions is not certain, the corresponding equilibrium constants do not have clear physical meaning. Also, surface potential measurements enable characterization of a single crystal plane and thus comparison with theoretical predictions based on the structure of the surface. According to the results presented in Figs. 1 and 2, the surface potential does not depend on the electrolyte concentration, which means that it does not depend on the degree of counterion association and on the compression of the diffuse layer. Consequently, fitting of the surface potential function is not sensitive to the choice of parameters characterizing the outer part of the interfacial layer, i.e. the calculated surface potentials did not depend on the choice of counterion association equilibrium constants and on the chosen values of the capacitance. The same Ψ_0 values were obtained by varying $\lg K_{\text{A}}^{\circ}$ and $\lg K_{\text{C}}^{\circ}$ values from 1 to 2.5 and C_1 values from $0.5\ \text{F}\,\text{m}^{-2}$ to $2.0\ \text{F}\,\text{m}^{-2}$. Accordingly, it may be concluded that the point of zero potential, contrary to the point of zero charge and the isoelectric point, is not sensitive to the degree of counterion association. At first sight it appears as a disadvantage, since only protonation equilibrium constants could be evaluated from surface potential measurements, but not the capacitances and equilibrium constants of the counterion association. However, the fit of an experimental function with four or even more adjustable parameters is at least questionable. Therefore, surface potential data enable more accurate and reliable determination of protonation equilibrium constants. The appearance of saddle suggests two-protonation mechanism and excludes the assumption of just one protonation reaction. However, as demonstrated in Fig. 1 the absence of the saddle does not exclude the possibility of the two-step mechanism (2-pK concept). The traditional 2-pK approximation includes just one kind of amphotheric surface sites, while the more advanced MUSIC model would consider different surface sites characterized by specific reaction mechanisms and values of corresponding equilibrium constants. Also, the advanced MUSIC model may result in the deviation from the mirror symmetry of the $\Psi_0(\text{pH})$ saddle like function. Therefore the values associated with 2-pK model could be considered as average.

The comparison between the $\Psi_0(\text{pH})$ saddle like function characterized with $\text{pH}_{\text{pzp}} = 7.0$ (Fig. 6) and electrokinetic $\zeta(\text{pH})$ characterized with $\text{pH}_{\text{iep}} \approx 4$ (Lützenkirchen et al. 2010) leads to the conclusion that the pH-dependent charge of interfacial water layer contributes to electrokinetic potential but not to surface potential. For example, in the pH region between 6 and 8, the surface potential is close to zero, but the electrokinetic potential has a significant negative value. The isolectric point of water at inert surfaces lies between 2 and 4 (Beattie and Djerdjev 2004; Healy and Fuerstenau 2007; Lützenkirchen et al. 2008; Kosmulski 2012) so that interfacial water is negatively charged at $\text{pH} > 4$ contributing to negative electrokinetic potential despite the zero value of the surface potential. The contribution of the pH-dependent charge of interfacial water layer was recently observed for silver halides (Kallay et al. 2012a, 2012b).

5 Conclusion

The proposed method of the evaluation of the point of zero potential pH_{pzp} from SCr-electrode potentials is simple and reliable tool if the electrode potential exhibits the saddle like function. It may be applied in case of mirror symmetry of the $\Psi_0(\text{pH})$ saddle like function. The deviation from mirror symmetry results in less accurate evaluation of the point of zero potential, but due to the plateau of the $\Psi_0(\text{pH})$ function in the zero potential region, this uncertainty does not affect the conversion of electrode potentials to surface potentials. Once the pH_{pzp} value is known it is easy to convert electrode potentials to corresponding surface potentials Ψ_0. Determination of surface potentials by Single Crystal electrodes enables the characterization of individual crystal planes. The sapphire A-crystal plane $(11\bar{2}0)$ exhibited saddle in $\Psi_0(\text{pH})$ function enabling the determination of the point of zero potential pH_{pzp} and thus the accurate conversion of measured electrode potentials to surface potentials. The saddle in Ψ_0(pH) function suggest the two step protonation mechanism with significantly different values of protonation interfacial equilibrium constants. The evaluation of equilibrium constants did not depend on the chosen values of counterion association equilibrium constants and values of inner layer capacitance, neither did it depend on the choice of the model for the electrical interfacial layer but was slightly influenced by the choice of the value of the total density of surface sites.

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