

Effect of electrolytes on the electroneutrality at the interface^{*}

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Recently, the measurements of the electrostatic potential at the inner plane of the electrical interfacial layer (surface potential φ_0) were introduced by using metal oxide electrodes. The evaluation of the surface potential from the electrode potential requires the knowledge of the point at which the surface potential is zero, i.e. the point of zero potential (p.z.p., pH_{pzp}). The numerical analysis based on the 2-pK mechanism of the Surface Complexation Model showed that pH_{pzp} approximately coincides with pH_{iep} if the ionic strength is kept enough low. At higher ionic strengths the values of pH_{iep} and pH_{pzc} might be different and pH_{pzp} lies between these two point and is still close to the original value at low ionic strength, i.e. the point of electroneutrality pH_{en} . The experimental results of electrode potential dependence on pH measured with hematite electrode showed appreciable reproducibility in the acidic region. The slope of the $\varphi_0(\text{pH})$ function is found to be significantly lower in magnitude than the Nernstian which is more pronounced at higher ionic strengths.

1. INTRODUCTION

Electrical charge at the solid liquid interface determines behavior of the system, such as colloid stability and also adhesion, adsorption and electrokinetic phenomena. To characterize solid liquid interface, e.g. a metal oxide in aqueous environment, one usually applies experimental methods such as potentiometric

^{*} This article is dedicated to Professor F. González-Caballero and Professor M. Jaroniec on the occasion of the celebration of their honorary professorships at Maria Curie-Skłodowska University in Lublin.

acid-base [1], electrolyte [2] and mass [3] titration, electrokinetics [4], adsorption measurements [5] and spectroscopy [6]. Recently, we have succeeded in preparation of metal oxide electrode that enables measurements of the electrostatic potential of the inner surface plane [7], i.e. of the surface potential φ_0 . These measurements, supported by data obtained with common methods, provide the complete information on the composition of the electrical interfacial layer (EIL). The idea on constructing the metal oxide electrodes originates from the discussion on the Sn-electrode with M. Koščec in the presence of Č. Frank. The success, which was the result of the mentioned discussion, encouraged us to proceed in this direction. The first result was the ice-electrode [8] and the second one the hematite electrode [7]. There are two problems with evaluation of surface potential from the measured electrode potential data. The first one is the slow equilibration at the interface resulting in hysteresis [9,10] and the second one is associated with the point of zero potential. Since the electrode potential includes several potential jumps in the measuring circuit one needs to know the condition at which the surface potential is zero. Therefore, we have introduced the additional zero point i.e. the point of zero potential (p.z.p.) characterized with pH_{pzp} [11]. This point is not available experimentally as are isoelectric point pH_{iep} and the point of zero charge pH_{pzc} . However, as it will be shown, all zero points coincide in the absence of counterion association but also in the case of their symmetric association taking place if the equilibrium constants of association of counterions with oppositely charged groups at the surface are equal for both kinds of counterions (cations and anions). Such a condition will be called electroneutrality condition and denoted as pH_{eln} . If the counterion affinities towards association are not equal, the pH_{iep} and pH_{pzc} are shifted from the original value of pH_{eln} . For location of the point of zero potential, i.e. for evaluation of the surface potential from the electrode potential data, it is important to examine the effect of the electrolyte on the possible shift of the pH_{pzp} from pH_{eln} . In this article we shall present some experimental data and the results of the numerical simulation that helps in solving the problem.

2. SURFACE COMPLEXATION MODEL

The process of the electrical charging at a metal oxide surface in aqueous environment is commonly described by the Surface Complexation Model (SCM). A general description of the interfacial reactions and the activity of surface species are based on our concept of standard states at the interface [12]. According to the 2-pK mechanism [13,14] surface charge is result of two step protonation (reaction 1 and 2) of the surface groups:



where K_1 and K_2 are equilibrium constants of corresponding surface reactions. Generally, a thermodynamic equilibrium constant K° is defined in terms of equilibrium activities a of species J that are involved in a specified chemical reaction [15]

$$K^\circ = \prod_{\text{J}} a_{\text{J}}^{\nu_{\text{J}}} \quad (3)$$

where ν denotes stoichiometric coefficient being positive for products and negative for reactants. For interfacial species the activity of surface species S may be defined [12] in terms of surface concentration Γ (amount of surface species per surface area) so that

$$a_{\text{S}} = y_{\text{S}} \frac{\Gamma_{\text{S}}}{\Gamma^\circ} = y_{\text{S}} \{\text{S}\} \quad (4)$$

where y denotes activity coefficient, and curly brace denotes relative value of surface concentration with respect to the chosen standard value. The value of $\Gamma^\circ = 1 \text{ mol m}^{-2}$ seems to be a convenient choice. Consequently $\{\text{S}\}$ becomes just a numerical value of surface concentration of species S; $\{\text{S}\} = \Gamma_{\text{S}}/\text{mol m}^{-2}$. The activity coefficient of surface species S, y_{S} , is defined through the difference in chemical potentials of real (μ^{real}) and ideal (μ^{id}) states

$$RT \ln y_{\text{S}} = \mu^{\text{real}} - \mu^{\text{id}} = z_{\text{S}} F \varphi \quad (5)$$

where F denotes the Faraday constant, z_{S} is charge number of the surface species S and φ the electrostatic potential affecting their state at the interface. Ideal state corresponds to zero value of electrostatic potential being equal to that in the bulk of the solution. Above equation can be rewritten as

$$y_{\text{S}} = \exp(z_{\text{S}} F \varphi / RT) \quad (6)$$

In the case of 2-pK model, reactions (1) and (2), the activity coefficients of charged interfacial species $\equiv\text{MO}^-$ and $\equiv\text{MOH}_2^+$ are

$$y(\equiv \text{MO}^-) = \exp(-F\varphi_0 / RT) \quad (7)$$

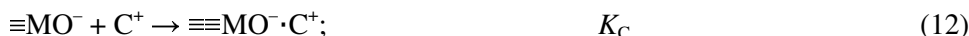
$$y(\equiv \text{MOH}_2^+) = \exp(F\varphi_0 / RT) \quad (8)$$

while the activity coefficient of neutral $\equiv\text{MOH}$ species is equal to 1. Consequently, the thermodynamic equilibrium constants for first (1) and second (2) step of protonation as defined on the basis of equations (3-8) are

$$K_1^\circ = \exp(F\varphi_0 / RT) \cdot \frac{\{\equiv \text{MOH}\}}{\{\equiv \text{MO}^-\} \cdot a_{\text{H}^+}} \quad (9)$$

$$K_2^\circ = \exp(F\varphi_0 / RT) \cdot \frac{\{\equiv \text{MOH}_2^+\}}{\{\equiv \text{MOH}\} \cdot a_{\text{H}^+}} \quad (10)$$

where φ_0 is potential at the inner plane of the electrical interfacial layer, i.e. 0-plane in which charged surface groups $\equiv\text{MOH}_2^+$ and $\equiv\text{MO}^-$ are located. Surface charge is reduced by association of anions A^- and cations C^+ from the bulk of solutions (reactions A and C) respectively



The counterions are exposed to potential φ_β . By taking into account that interfacial ion pairs behave as oriented dipoles with charged ends which are exposed to different potentials φ_β and φ_0 , activity coefficients of the $\equiv\text{MO}^- \cdot \text{C}^+$ and $\equiv\text{MOH}_2^+ \cdot \text{A}^-$ groups are

$$\gamma(\equiv \text{MO}^- \cdot \text{C}^+) = \exp\left(\frac{F(\varphi_\beta - \varphi_0)}{RT}\right) \quad (13)$$

$$\gamma(\equiv \text{MOH}_2^+ \cdot \text{A}^-) = \exp\left(\frac{-F(\varphi_\beta - \varphi_0)}{RT}\right) \quad (14)$$

so that corresponding thermodynamic equilibrium constants are

$$K_C^\circ = \frac{\exp(F(\varphi_\beta - \varphi_0)/RT) \cdot \{\equiv \text{MO}^- \cdot \text{C}^+\}}{\exp(-F\varphi_0/RT) \cdot \{\equiv \text{MO}^-\} \cdot a_{\text{C}^+}} = \exp(F\varphi_\beta/RT) \cdot \frac{\{\equiv \text{MO}^- \cdot \text{C}^+\}}{\{\equiv \text{MO}^-\} \cdot a_{\text{C}^+}} \quad (15)$$

$$K_A^\circ = \frac{\exp(-F(\varphi_\beta - \varphi_0)/RT) \cdot \{\equiv \text{MOH}_2^+ \cdot \text{A}^-\}}{\exp(F\varphi_0/RT) \cdot \{\equiv \text{MOH}_2^+\} \cdot a_{\text{A}^-}} = \exp(-F\varphi_\beta/RT) \cdot \frac{\{\equiv \text{MOH}_2^+ \cdot \text{A}^-\}}{\{\equiv \text{MOH}_2^+\} \cdot a_{\text{A}^-}} \quad (16)$$

Total surface concentration of active surface sites Γ_{tot} , within 2-pK model, as described by reaction equations (1), (2), (11) and (12), is equal to

$$\Gamma_{\text{tot}} = \Gamma(\equiv \text{MOH}) + \Gamma(\equiv \text{MOH}_2^+) + \Gamma(\equiv \text{MO}^-) + \Gamma(\equiv \text{MOH}_2^+ \cdot \text{A}^-) + \Gamma(\equiv \text{MO}^- \cdot \text{C}^+) \quad (17)$$

The corresponding surface charge densities in 0-plane (σ_0) and in β -plane (σ_β) are

$$\sigma_0 = F \left(\Gamma(\equiv \text{MOH}_2^+) - \Gamma(\equiv \text{MO}^-) + \Gamma(\equiv \text{MOH}_2^+ \cdot \text{A}^-) - \Gamma(\equiv \text{MO}^- \cdot \text{C}^+) \right) \quad (18)$$

$$\sigma_\beta = F \left(\Gamma(\equiv \text{MO}^- \cdot \text{C}^+) - \Gamma(\equiv \text{MOH}_2^+ \cdot \text{A}^-) \right) \quad (19)$$

The net surface charge density σ_s (the charge directly bound to the surface per surface area), being equal in magnitude but opposite in sign with respect to the so-called charge density of diffuse layer σ_d , is

$$\sigma_s = -\sigma_d = \sigma_0 + \sigma_\beta = F \left(\Gamma(\equiv \text{MOH}_2^+) - \Gamma(\equiv \text{MO}^-) \right) \quad (20)$$

At low ionic strength (I_c) and also at low surface potentials the association of counterions is negligible so that surface charge density in 0-plane could be approximated by

$$\sigma_0 \approx F \left(\Gamma(\equiv \text{MOH}_2^+) - \Gamma(\equiv \text{MO}^-) \right); \quad I_c \rightarrow 0 \text{ or } \varphi_0 \rightarrow 0 \quad (21)$$

The relationships between potentials at the surface are based on the concept of constant capacitance. For inner layer, the following relationship holds

$$C_1 = \frac{\sigma_0}{\varphi_0 - \varphi_\beta} \quad (22)$$

This concept was analyzed [16], and it was suggested that a more proper choice would be to replace σ_0 in equation (22) by $-\sigma_\beta$.

Some authors [17] introduced a Triple Layer Model with a second capacitor, assuming that onset of diffuse layer, i.e. d-plane, is shifted from the β -plane in which centers of the associated counterions are located. Accordingly

$$C_2 = \frac{\sigma_s}{\varphi_\beta - \varphi_d} \quad (23)$$

Another approach, based on the Double Layer Model [18], does not assume a potential drop between β -plane and d-plane, which corresponds to $C_2 = \infty$.

The zero charge condition at the interface is expressed by three quantities, i.e. by the point of zero charge (p.z.c.) corresponding to $\sigma_0 = 0$, by the isoelectric point (i.e.p.) corresponding to electrokinetic potential $\zeta = 0$ (and $\sigma_s = 0$), and by the point of zero potential (p.z.p.) corresponding to $\varphi_0 = 0$. In absence of specific adsorption of ions and in the case of negligible or symmetric association of counterions, all three points coincide and correspond to state in which all electrical properties diminish ($\sigma_0 = \sigma_s = 0$, $\varphi_0 = \zeta = 0$). This electroneutrality condition (pH_{eln}) is related to the protonation equilibrium constants by

$$\text{pH}_{\text{eln}} = \frac{1}{2} \log \left(K_1^\circ K_2^\circ \right) \quad (24)$$

Electroneutrality condition can be achieved at low electrolyte concentration, and in such a case

$$\text{pH}_{\text{eln}} \approx \text{pH}_{\text{pzc}} \approx \text{pH}_{\text{iep}} \approx \text{pH}_{\text{pzp}}; \quad I_c \rightarrow 0 \quad (25)$$

Since affinities of binding the cations and anions are not necessarily the same, the shift in pH_{pzc} , pH_{iep} and pH_{pzp} with respect to pH_{eln} is expected at higher

electrolyte concentration [19]. For example, in the case of preferential adsorption of cations ($K_C > K_A$), p.z.c. is shifted to lower pH values and i.e.p. is shifted to higher pH values with respect to pH_{eln} : $\text{pH}_{\text{iep}} > \text{pH}_{\text{eln}} > \text{pH}_{\text{pzc}}$.

Within the 2-pK model the surface potential at 0-plane is according to Eqs. (1 and 2) equal to

$$\varphi_0 = \frac{RT \ln 10}{F} (\text{pH}_{\text{pzp}} - \text{pH}) - \frac{RT}{2F} \ln \left(\frac{\{\equiv \text{MOH}_2^+\}}{\{\equiv \text{MO}^-\}} \right) \quad (26)$$

The first term in Eq. (26) is Nernstian while the second one is responsible for the lowering of the magnitude of the slope of the $\varphi_0(\text{pH})$ function. Potential φ_0 can be approximated [20] by the modified Nernst equation as

$$\varphi_0 = \frac{RT \ln 10}{F} (\text{pH}_{\text{pzp}} - \text{pH}) \cdot \alpha \quad (27)$$

where coefficient α describes the deviation from the ideal behavior being characterized by $\alpha = 1$. Note that the value of coefficient α is often expressed in percents (%). For real metal oxide surfaces the coefficient α is below 1 and depends on the type of metal oxide [11,21,22], and also on the composition of the electrolyte solution [23].

3. NUMERICAL SIMULATIONS

Performed numerical simulations are based on the Surface Complexation model, Eqs (1, 2, 9-12, 15-24) using the following equilibrium parameters that represent a common model system: $\Gamma_{\text{tot}} = 1,5 \cdot 10^{-5} \text{ mol m}^{-2}$; $C_1 = 1,50 \text{ F m}^{-2}$; $C_2 = \infty$; $K_1^\circ = 8,20 \cdot 10^8$, $K_2^\circ = 1,57 \cdot 10^4$; $T = 298 \text{ K}$. According to Eq. (24), the electroneutrality condition is at $\text{pH}_{\text{eln}} = 6.556$.

Three cases were examined: absence of counterion association ($K_A^\circ = K_C^\circ = 0$), symmetrical counterion association ($K_A^\circ = K_C^\circ = 100$), and the preferential association of cations ($K_A^\circ = 10$; $K_C^\circ = 1000$). The values of the surface potential φ_0 as a function of pH were calculated for relatively low ionic strength of $1 \cdot 10^{-4} \text{ mol dm}^{-3}$ and relatively high ionic strength of $1 \cdot 10^{-2} \text{ mol dm}^{-3}$. The values of pH_{pzp} , pH_{iep} and pH_{pzc} were evaluated. Figure 1 demonstrates results for the case of absence of counterion association at low and high ionic strength. At high ionic strength the function is almost linear with the slope of -43 mV which is 73 % of the Nernstian slope and for low ionic strength the slope is -51 mV ($\alpha = 86 \%$) calculated for the entire pH region $2 < \text{pH} < 12$.

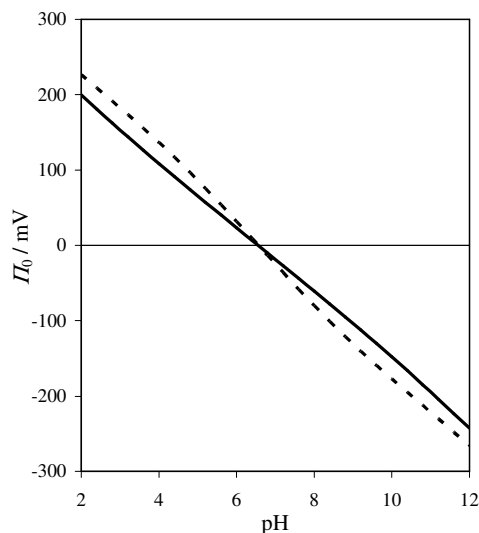


Fig. 1. Surface potential φ_0 as a function of pH obtained by numerical simulations in the absence of counterion association: $K_A^0 = K_C^0 = 0$. Full line: $I_c = 1 \cdot 10^{-2} \text{ mol dm}^{-3}$. Dashed line: $I_c = 1 \cdot 10^{-4} \text{ mol dm}^{-3}$. The point of zero potential, isoelectric point and the point of zero charge coincide with point of electroneutrality: $\text{pH}_{\text{pzp}} = \text{pH}_{\text{iep}} = \text{pH}_{\text{pzc}} = \text{pH}_{\text{eln}} = 6.556$.

In the case of significant, but symmetrical counterion association the situation is similar as it could be seen from Figure 2. The slope is -51 mV ($\alpha = 86 \%$) and -53 mV ($\alpha = 90\%$) for $I_c = 1 \cdot 10^{-2} \text{ mol dm}^{-3}$ and $I_c = 1 \cdot 10^{-4} \text{ mol dm}^{-3}$, respectively. As expected, the point of zero potential pH_{pzp} remains at pH_{eln} , just as pH_{iep} and pH_{pzc} . The magnitude of the slopes of $\varphi_0(\text{pH})$ function are higher with respect to the case of absent counterion association, but all three zero points remain the same and correspond to electroneutrality condition: $\text{pH}_{\text{pzp}} = \text{pH}_{\text{iep}} = \text{pH}_{\text{pzc}} = \text{pH}_{\text{eln}}$.

The results obtained for the case of preferential association of cations are presented in Figures 3 and 4. At high ionic strength (Fig. 3) the slope was found to be -51 mV ($\alpha = 87 \%$), and for low ionic strength -54 mV ($\alpha = 91 \%$). As expected, the isoelectric point is shifted to higher pH values while the point of zero charge is shifted in opposite direction. It is important to notice that the point of zero potential did not shift significantly from pH_{eln} .

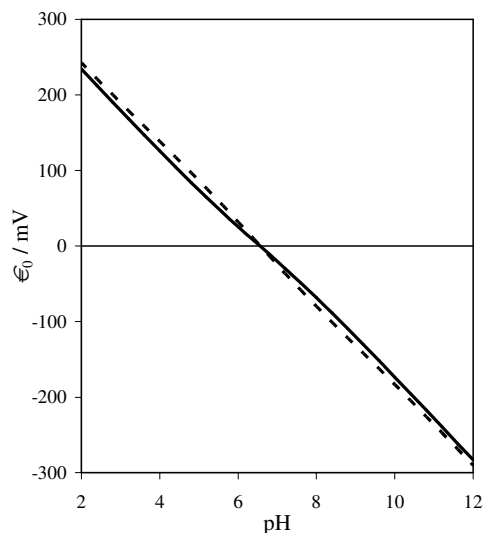


Fig. 2. Surface potential ϕ_0 as a function of pH obtained by numerical simulations in the case of symmetrical counterion association: $K_A^0 = K_C^0 = 100$. Full line: $I_c = 1 \cdot 10^{-2} \text{ mol dm}^{-3}$. Dashed line: $I_c = 1 \cdot 10^{-4} \text{ mol dm}^{-3}$. The point of zero potential, isoelectric point and the point of zero charge coincide with point of electroneutrality: $\text{pH}_{\text{pzp}} = \text{pH}_{\text{iep}} = \text{pH}_{\text{pzc}} = \text{pH}_{\text{eln}} = 6.556$.

The similar situation, but significantly less pronounced, was obtained at low ionic strength. The shift of pH_{iep} and pH_{pzc} from pH_{eln} is less significant. The point of zero potential pH_{pzp} practically coincides with pH_{eln} , just as pH_{iep} .

The above analysis shows that the zero value of the surface potential could be assumed on the basis of the measurements of the isoelectric point and the point of zero charge. If these two points coincide counterion association is either negligible or symmetrical. In both cases one can take this point as the point of zero potential. If pH_{pzc} differs from pH_{iep} one can approximate the pH_{iep} as pH_{pzp} which is correct at the low ionic strength where $\text{pH}_{\text{pzp}} \approx \text{pH}_{\text{eln}} \approx \text{pH}_{\text{iep}}$. The error introduced by such a procedure is lower if the ionic strength is lower. Regarding the determination of the point of the zero charge, it should be mentioned that the common intersection point of the surface charge function cannot be used accurately for that purpose. It is better to apply the mass titration method which enables the examination of the dependency of pH_{pzc} on ionic strength [3]. In most of the cases only electrokinetic measurements are possible. One can crush the crystal and disperse the powder in the liquid medium.

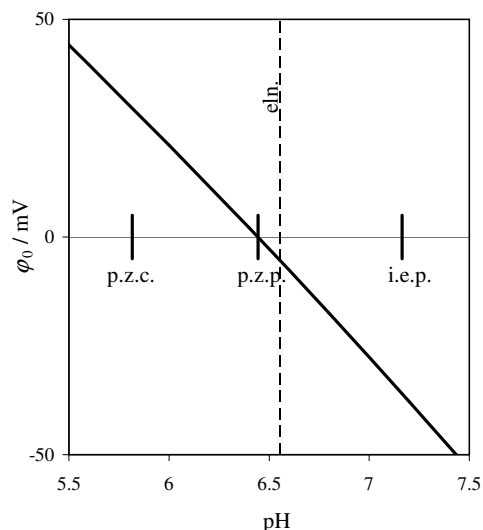


Fig. 3. Surface potential φ_0 as a function of pH obtained by numerical simulations in the case of preferential association of cations: $K_C^0 = 1000$; $K_A^0 = 10$. Calculations were performed for $I_c = 1 \cdot 10^{-2} \text{ mol dm}^{-3}$. The isoelectric point and the point of zero charge are shifted in opposite direction with respect to point of electroneutrality: $\text{pH}_{\text{iep}} > \text{pH}_{\text{eln}} > \text{pH}_{\text{pzc}}$. The point of zero potential remains close to point of electroneutrality: $\text{pH}_{\text{pzp}} \approx \text{pH}_{\text{eln}}$.

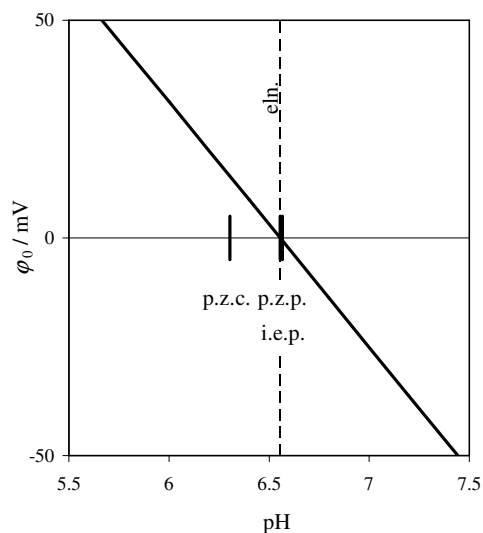


Fig. 4. Same as for Figure 3 but at $I_c = 1 \cdot 10^{-4} \text{ mol dm}^{-3}$. The effects are the same as for higher ionic strength, but less pronounced. The point of zero potential and isoelectric point coincide with point of electroneutrality: $\text{pH}_{\text{pzp}} \approx \text{pH}_{\text{iep}} \approx \text{pH}_{\text{eln}}$.

The large particle would settle and one may use electrophoresis for the dispersion of fine particles. On other hand, large particles could be used for the streaming potential technique. The point of zero potential could be estimated from electrokinetic measurements only. In such a case one should perform experiment at different ionic strengths and obtain the pH_{iep} value by extrapolation of the $\text{pH}_{\text{iep}}(I_c)$ function to zero ionic strength. If the isoelectric point does not change with the ionic strength, this means that counterion association is symmetrical ($K_A^\circ = K_C^\circ$) and the measured pH_{iep} may be simply taken as pH_{pzp} .

4. EXPERIMENTAL METHODS

Hematite electrode (Fig. 5) was made from the hematite monocrystal (Vesuvius, Italy) and was described earlier [7].

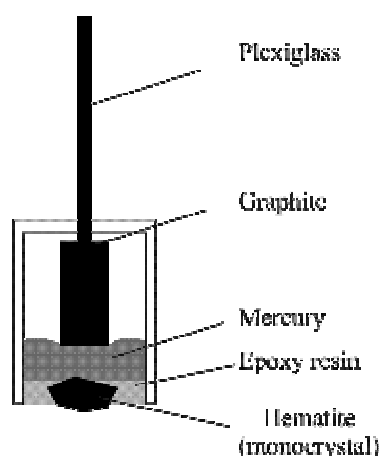


Fig. 5. Schematic presentation of the hematite electrode.

Materials: NaNO_3 (Fluka), NaCl (Fluka), HNO_3 (0.1 mol dm^{-3} , titrival, Fluka), NaOH (0.1 mol dm^{-3} , titrival, Fluka), standard buffers (Merck), redistilled water.

Potentiometric measurements were performed with pH-meter (Metrohm 713) using hematite electrode and glass electrode (Metrohm, 6.123.100). As the reference electrode Ag/AgCl electrode with salt bridge (Metrohm, 6.0729.100) was used. The salt bridge was filled with same electrolyte solution of approximately same concentration as in the examined system. Acid - base titrations were performed using thermostated cell containing initially 150 cm^3 of NaOH or HNO_3 solution. Ionic strength was adjusted with NaNO_3 . The system was thermostated at $25 \text{ }^\circ\text{C}$ and kept under argon atmosphere. Titrant,

0.1 mol dm⁻³ HNO₃ or NaOH, was added by a micro burette. Electrokinetic measurements were performed earlier [7] with the dispersion of fine hematite particles obtained by crushing the crystalline sample. The large particles were separated by decantation. The isoelectric point was found to be at pH_{iep} = 6.1 at NaNO₃ concentration of 5·10⁻⁴ mol dm⁻³. This point was taken as the point of zero potential at which $\varphi_0 = 0$.

5. EXPERIMENTAL RESULTS

Figure 6 displays the results obtained at NaNO₃ concentrations of 10⁻³ mol dm⁻³ and 10⁻¹ mol dm⁻³. The values of the surface potentials were calculated from hematite electrode potentials by taking pH_{pzp} = 6.1.

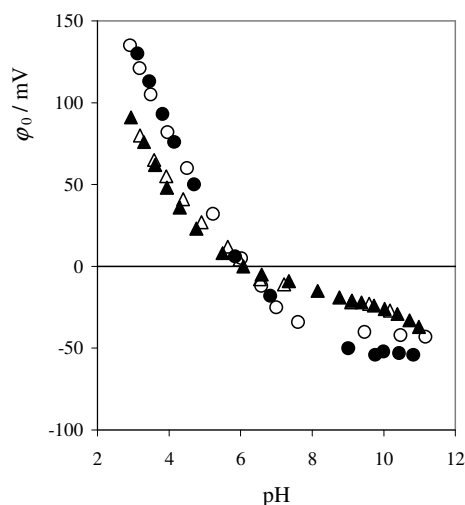


Fig. 6. Effect of ionic strength on surface potential of hematite at 25 °C. Titration of acidic solution with NaOH (full symbols) and of basic solution with HNO₃ (open symbols). $I_c = 10^{-3}$ mol dm⁻³: (●, ○); $I_c = 10^{-1}$ (▲, Δ).

Only the data in acidic region are reproducible and therefore reliable. These data are presented in Figure 7. The problem in the basic region is the equilibration of the electrode surface and the hysteresis. This phenomenon was investigated in details and will be published separately [9]. The slope in acidic region is significantly lower than the Nernstian. At 10⁻³ mol dm⁻³ NaOH the slope was found to be 87 % of the Nernstian, while at higher concentration the magnitude of the slope was lower, i.e. 70 % of the Nernstian.

The effect of the electrolyte concentration on the slope of the $\phi_0(\text{pH})$ function is presented on Figure 8. The results indicate that the slope decreases in magnitude by increasing the electrolyte concentration.

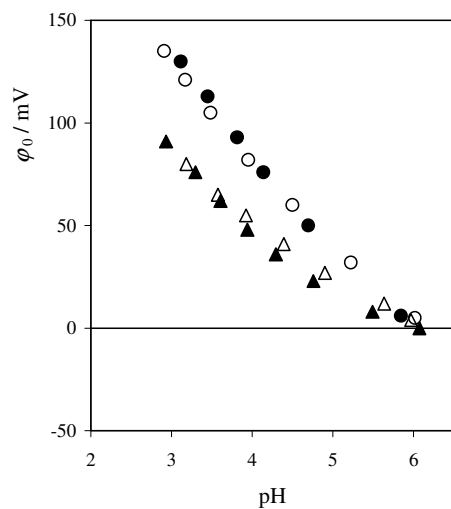


Fig. 7. Data in acidic region taken from Figure 6.

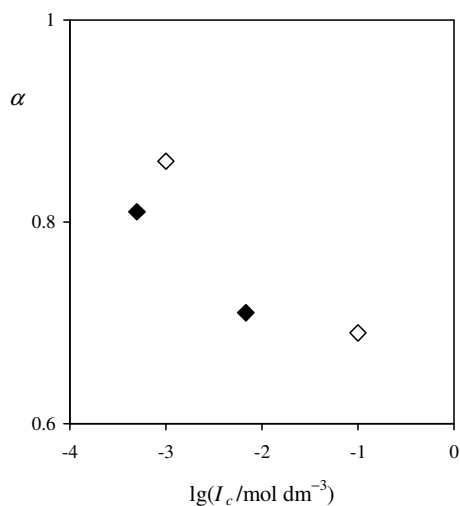


Fig. 8. Effect of ionic strength on the slope of $\phi_0(\text{pH})$ function in the acidic region at 25 °C. Two data points (\blacklozenge) were taken from results presented in Figure 7 while two points (\diamond) were taken from our already published article [7].

Figure 9 shows the specific effect of counterions on the surface potential. In the acidic region, the surface is positively charged so that counterions are anions. Two experimental runs are presented, one with nitrate and the other one with chloride counterions. The ionic strength was the same in both runs ($0,1 \text{ mol dm}^{-3}$). The slope obtained in the presence of chloride ions ($\alpha = 62 \%$) was found to be lower than in the presence of nitrate ions ($\alpha = 70 \%$) indicating higher affinity towards association of Cl^- ions with respect to NO_3^- ions. This finding agrees well with our previous results on the lyotropic effect in surface charge ($\text{Cl}^- > \text{ClO}_4^- > \text{NO}_3^-$) [24].

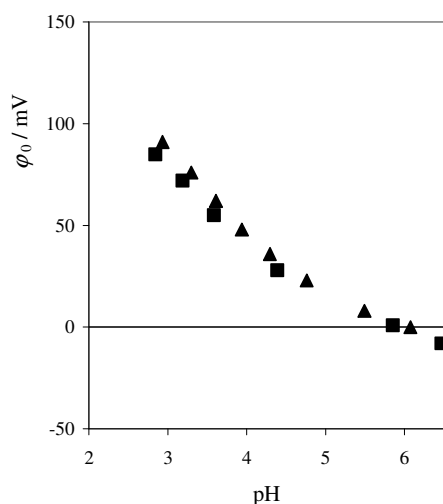


Fig. 9. Effect of counterion specificity on surface potential of hematite at 25 °C. Acidic solutions were titrated with NaOH: (▲) $c(\text{NaNO}_3) = 0.1 \text{ mol dm}^{-3}$ (data taken from Fig. 7) and (■) $c(\text{NaCl}) = 0.1 \text{ mol dm}^{-3}$.

6. CONCLUSIONS

In case of absent or symmetrical counterions association all three zero points coincide, i.e. $\text{pH}_{\text{pzp}} = \text{pH}_{\text{iep}} = \text{pH}_{\text{pzc}} = \text{pH}_{\text{eln}}$. In case of preferential association of one kind of counterions (anions or cations), the pH_{iep} and pH_{pzc} shift in opposite direction with respect to pH_{eln} , and this shift depends on electrolyte concentration. In case of low ionic strength the shift of pH_{pzc} is significant, while pH_{iep} remains close to pH_{eln} . The shift of pH_{pzp} is not significant and does not depend markedly on the ionic strength.

Determination of the electrostatic potential of the inner plane of the electrical interfacial layer (surface potential φ_0) on the basis of measurements of the electrode potential of metal oxide electrode meets a problem of the location of

the zero value of φ_0 , i.e. of the point of zero potential pH_{pzp} . Numerical simulation showed that pH_{pzp} could be approximated by the pH_{iep} if the ionic strength is enough low. For evaluation of the values of the surface potential from the electrode potential data one needs to subtract all other potential jumps (E_{cal}) in the circuit

$$\varphi_0 = E - E_{\text{cal}} \quad (28)$$

Since the value of E_{cal} does not depend on the composition of the liquid medium, only one calibration is necessary for a given electrode system. In order to obtain E_{cal} value one needs to measure pH_{iep} as a function of the ionic strength. At low ionic strength, the pH_{iep} approaches pH_{eln} value and becomes constant. This value could be taken as pH_{pzp} at which $\varphi_0 = 0$ so that $E_{\text{cal}} = E(I_c \rightarrow 0)$.

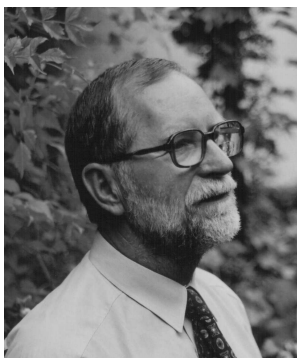
Regarding the slope of the $\varphi_0(\text{pH})$ function one may conclude that it is always significantly lower in magnitude than the Nernstian, but the effect of electrolyte concentration would depend on all of the parameters characterizing the surface equilibrium.

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CURRICULA VITAE



Nikola Kallay. Born in 1942, Zagreb, Croatia. In 1967 he received diploma in Chemical Engineering from the Faculty of Chemical Technology at the University of Zagreb, Zagreb. In 1972 he received M. Sc., and in 1973 Ph. D., in chemistry, from Faculty of Science at the University of Zagreb. In 1978 he completed his habilitation there. Since 1969 he is a member of Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, where he became research full professor in 1984, and full professor in 1988. He served as Vice Dean of the Faculty (1982), Head of the Laboratory of Physical Chemistry (1999) and at present he is Chairman of

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famous IUPAC Green Book (Quantities, Units and Symbols in Physical Chemistry), which was first published in 1988, and later had several editions and translations. His research is devoted to physical chemistry of colloids and surfaces, i.e. to development of experimental methods and theoretical interpretations. He was dealing with coagulation, adhesion, preparation, kinetics of crystal growth and dissolution, surface complexation (mechanism, equilibrium and enthalpy), electrical interfacial layer, dissolution of surfactants, micellization, microemulsions, effect of electromagnetic radiation and magnetic field etc. Recently, he solved the problems related to determination of enthalpy of interfacial processes (standard reaction enthalpy and electrostatic contribution), introduced electrokinetic potential in the interpretation of interfacial equilibria ("umbrella effect"), constructed ice-electrode (surface potential, interfacial equilibrium), developed theory for aggregation of nanoparticles (complete overlap of electrical interfacial layer), considered counterion association with micelles, etc. His future projects are related to determination and use of surface potentials, effects of electromagnetic radiation on interfaces, nanocoagulation, application of the van't Hoff equation to ionic reactions in dielectric media, etc. His approach is demonstrated in the Feature article published in *Journal Colloid Interface Science* (2000) and in the review article published in *Croatica Chemica Acta* (2001). He concluded that further scientific progress in the interfacial chemistry requires new experimental techniques combined with new theoretical concepts. Another route is to choose one sample, to standardize the treatment - purification, to measure properties of such uniform samples with all available techniques, and to critically test and refine present theoretical concepts. For that purpose the extensive international cooperation is necessity. He published over ten books (textbooks, recommendations on quantities and units, chapters in monographs) and is editor (and co-author) of *Interfacial Dynamics*, (1999). He is the author of more than hundred scientific articles in prestigious international journals, and over thirty other professional articles. For his scientific achievements he received "Ruđer Bošković" award of the State of Croatia (1992), award from Croatian Academy of Sciences and Arts (1999), and award of the City of Zagreb (2000).

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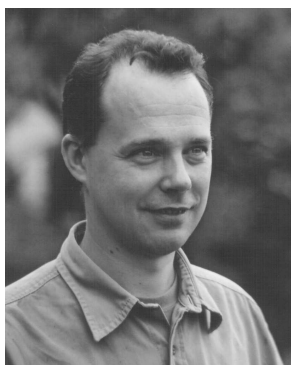
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