

Electrokinetic Data: Approaches, Interpretations and Applications*

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The article presents a review of the solid/liquid interface research with emphasis on the complementary role of electrokinetic data in the overall concept of the electrical interfacial layer (EIL), potential energy of interaction and, consequently, colloidal stability of suspensions. The significance of electrokinetic (zeta) potential is particularly discussed. It is suggested that the absolute zeta potential values are hardly comparable from case to case. However, the isoelectric point (IEP) can be ascribed to a certain substance under defined conditions as a kind of material property. Selected theoretical tenets are involved in interpreting the solid/liquid interactions, including the surface complexation model, structure of the electrical interfacial layer and energy of surface interactions. Some cases are analyzed in more detail, such as simple oxides, mixed oxides, heterogeneous surfaces with two types of surface functional groups. Finally, several applications of electrokinetic data in ceramic processing, textile processing, and in natural water suspensions are described.

INTRODUCTION

Does zeta potential characterize a certain substance, *i.e.*, is it a property of material? The answer should be negative, because if we describe a certain substance by the zeta potential value, indicating, for instance, $\zeta = -50$ mV under predetermined conditions, we should know at least the following:

- form (crystalline, amorphous, particulate, dispersions, macro-bodies *e.g.*, discs, rods, spheres, capillaries, *etc.*)
- size of particles and purity of the substance
- electrolyte: purity, concentration, conductivity
- pH value
- temperature

- type of electrokinetic measurement and the corresponding conditions.

Even if all the mentioned conditions were requested and defined by a convention, the absolute values of zeta potential on most solid-liquid interfaces achieved in different laboratories are hardly reproducible. Therefore, a comparison of absolute values of the zeta potential obtained by different techniques, *e.g.*, microelectrophoresis or streaming potential or other, does not make much sense, even if the same class of substances (materials) is analyzed under the same basic conditions. On the other hand, in an isolated experiment, the zeta potential values obtained under the quite identical conditions could be highly reproducible and therefore very useful for the interpretation of the behavior of that particular investigated interface.

* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

Much more useful, in general, is the *isoelectric point* (IEP), which represents the concentration (activity) of potential determining ions at which the zeta potential is zero. In interpreting and improving the electrical interfacial layer (EIL) models for many years, Kallay and his group were developing an approach of using three sets of data: on the one side, potentiometric titration and the *point of zero charge* (PZC) and, on other side, zeta potential (ζ) and the isoelectric point (IEP), and additionally adsorption data.¹⁻⁷ In recent years, they have developed direct measurements of surface potential (Ψ_0), initially with an ice electrode^{8,9} and after that with a hematite single crystal electrode.^{10,11} To calculate the surface potential from the measured electrode potential, the precise IEP has to be known. Under the surface zero-charge conditions, in the absence of specific ions adsorption, the electrokinetic isoelectric point (IEP) and the point of zero charge (PZC) coincide with the point of zero surface potential (PZP). Here, it is worth mentioning that, in order to accurately determine IEP and PZC values, Kallay and his group have introduced new experimental methods, such as »adhesion«, a method for IEP determination and »mass titration« for determination of PZC.^{2,3,12-14}

After the very well known and frequently quoted source of the so-called »pristine points of zero charge« of oxides published by Parks,¹⁵ the new, most comprehensive compilation of the point of zero charge conditions was recently published by Kosmulski.¹⁶ This report emphasizes predominantly metal oxides, but also mixed oxides, aluminosilicates, some salts and a few other materials. The presented data are mostly based on potentiometric titrations (PZC from a common intersection point, CIP) and classical electrokinetic measurements (electrophoresis, electroosmosis), including the electroacoustic methods. Also, direct electrometric methods have been discussed, yielding, for example, the PZC of hematite¹¹ at pH = 6.1. A common point emphasizing the presented data is the pH-dependent charging. However, in the case of solid salts, the surface reactions, involving potential determining ions or molecules other than H⁺ and OH⁻ ions, should be considered. An example is the case of CaCO₃ where the activity of Ca²⁺ and of CO₃²⁻ or CO₂ will have a determining role as well. A comprehensive table provides a description of the tested material, the type of electrolyte and its concentration, the temperature and method for the determination of IEP or PZC.

Within the domain of colloidal stability, the IEP in many cases coincides with the condition of rapid aggregation.¹⁷ Apart from the IEP region, neutral electrolytes promote aggregation of colloid particles. Combining the results on surface complexation of potential determining ions and association of counterions at the interface with the electrokinetic data, Kallay *et al.* produced a scheme

of theoretical contributions to the overall theory of colloid stability.^{6,18}

The aim of this paper is to present, mainly in a descriptive way, the analyses of various approaches to electrokinetic data. In the following few sections, the broad context of using electrokinetic data, their significance, interpretations and selected applications are presented.

ELECTROKINETIC PHENOMENA

Surface Charging

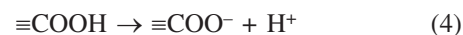
According to the Surface Complexation Model, the origin of charge at solid/liquid interfaces is due to the interaction of active surface groups with the ions in the bulk of liquid solution. There are several proposed mechanisms of surface reactions:

a) According to the 2-pK model, metal oxides and hydroxides undergo protonation and deprotonation of surface sites, which can be also formulated as binding of H⁺ and OH⁻ ions from the surrounding aqueous solution:^{1-5,19}



where the species $\equiv\text{MOH}\cdot\text{OH}^-$ can be considered as hydrated species $\equiv\text{MO}^-$.

b) Acids and bases of Brönstead type would donate or accept protons:



c) Association of counterions, as well as binding of various charged, simple or complex, ligands may take place and change the surface charge.

d) Specific adsorption of surfactant ions leads to surface charging and modification of surface properties.

Mechanisms (a) – (d) cover the charging of metal oxides, metal hydroxides and of the majority of natural and synthetic polymers, including starch, cellulose, tannins, humic acids, as well as polyacrylate, polyvinyl-alcohol, polyethyleneimine, *etc.*^{5,19,20} Due to isomorphous replacement, the unit of lattice network may carry an electrical charge. For instance, in the case of replacement of Si⁴⁺ in SiO₂ tetrahedra with Al³⁺, which has one electron more than Si⁴⁺, the unit net charge would be negative.¹⁹ Such a situation is typical of clays. A similar mechanism is responsible for the charge at the borosilicate glass/solution interface²¹ where boron replaces silicon in the glass network, as shown in Figure 1. It is worth mentioning that such electrical charge, created in the interior of the solid bulk either due to isomorphous

exchange or generally to lattice imperfections, would be independent of the pH of the solution. By fracturing of crystals, a new surface of different properties can be obtained. For instance, as shown in Figure 2, by breaking siloxane bridges, a pair of positive and negative charges will be created, which in the presence of moisture will recombine into two silanol groups.²¹

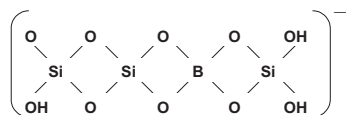


Figure 1. An example of the source of surface charge arising from isomorphous exchange in silicates (example of boron/silicon exchange).

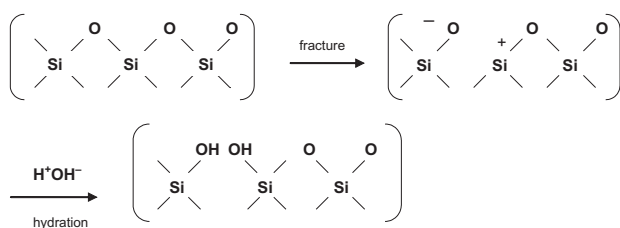


Figure 2. An example of the source of surface charge arising from fracturing defects in silicates (example of siloxane bridges).

Electrical Interfacial Layer and Electrokinetic (Zeta) Potential

The model of electrical interfacial layer (EIL), formed as a consequence of electrical charge distribution at the solid-liquid interface, is schematically presented in Figure 3. The expression *electrical interfacial layer* is a generalization of the more common term *electrical double layer*. The reason for such a rename is the fact that the theoretical development in the last decades offered the concept of a 3-layer model as well as a 4-layer model, so the term *double layer* lost its original classical meaning.^{5,22–24}

The surface charge density (σ) at a certain plane, created by some kind of surface reactions shown above, is related to the corresponding surface potential (Ψ). Quantitative relationships between surface charge densities and surface potentials depend on the assumed model of EIL. It is reasonable to use the model that best satisfies the experimental findings and the assumptions of the mechanism of surface charging. All models introduce the concept of several imaginary planes going from the »hard« surface at 0-plane, characterized by σ_0 and Ψ_0 , towards the liquid bulk. For each x -plane, one can relate the given charge density (σ_x) to the corresponding electrostatic potential (Ψ_x). According to classical theories, the Stern layer is located between the »hard« sur-

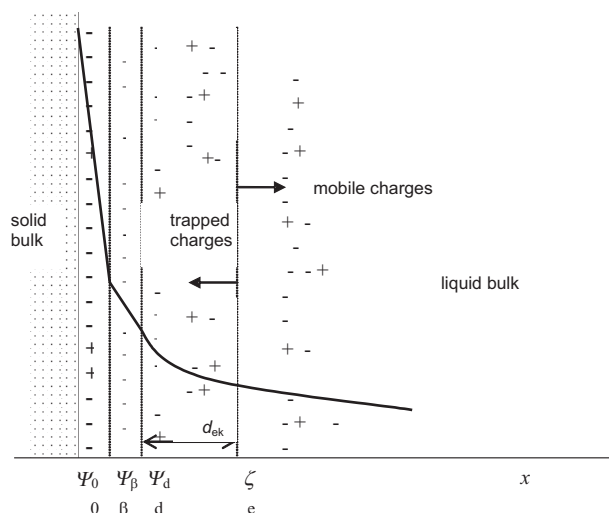


Figure 3. Schematic presentation of the structure of the electrical interfacial layer (EIL). Surface potential decay with indicated positions of Ψ_0 , Ψ_β , Ψ_d , and ζ potentials.

face (0-plane) and the »beginning« or »onset« of the diffuse layer (d-plane), from which the diffuse layer or Gouy-Chapman layer extends toward the liquid bulk. Subdivision of the Stern layer into the inner Helmholtz layer (between 0- and β -plane) and outer Helmholtz layer (between β - and d-plane) is reasonable because the charge reversal, due to specific chemical binding of some adsorbing ions, may occur within these inner layers, e.g., at β -plane. The diffuse layer starts at d-plane and is characterized by charge density σ_d and potential Ψ_d . At some distance d_{ek} from the d-plane, the so called electrokinetic slip plane (e-plane) is assumed to exist. This slip plane is the border of the hydrodynamically stagnant layer where the space charge is hydrodynamically immobile. It is important to note that within the hydrodynamically stagnant layer, electrical conductivity of ions takes place, which may have a significant role in the evaluation of electrokinetic data. For distances $x > d_{ek}$, the space charge is hydrodynamically mobile.

The potential at the slip plane, corresponding to the charge density σ_{ek} , is the *electrokinetic or zeta (ζ) potential*. Since $d_{ek} \geq 0$, the magnitude of the electrokinetic potential will be smaller or equal to the diffuse layer potential; thus $|\zeta| \leq |\Psi_d|$. Owing to the existence of the slip plane, several electrokinetic phenomena can be detected and by using the model that properly describes the investigated system, the zeta potential can be evaluated. In an excellent IUPAC document by Delgado *et al.*, the evaluation of zeta potential was pointed out as the main problem of the electrokinetic studies.²⁴

In summary, for the sake of electroneutrality of EIL, the sum of charge densities within EIL is:

$$\sigma_0 + \sigma_\beta + \sigma_d = 0 \quad (5)$$

where the charge density of the diffuse part of the interfacial layer σ_d is equal in magnitude but opposite in sign to the net surface charge density σ_s .

The sequence of electrostatic potential is:

$$|\Psi_0| > |\Psi_\beta| \geq |\Psi_d| \geq |\zeta| \quad (6)$$

The charge density at 0-plane, σ_0 , is obtainable by potentiometric titration of colloid suspension. Two limiting potentials, on the left (Ψ_0) and right hand sides (ζ) of relation (6) are in principle measurable. The other two potentials (Ψ_β , Ψ_d) can be obtained by calculation, using an EIL model and applying appropriate approximations. Electrokinetic ζ -potential can be evaluated from the electrokinetic phenomena, while the surface potential Ψ_0 can be measured using the single crystal electrode.⁸⁻¹¹ One should not confuse the Ψ_0 potential with the potential of a metal electrode or an electrode of another type (e.g., Ag/AgCl electrode) defined by the Nernstian equation, since the Nernst potential depends on the redox equilibrium, while Ψ_0 potential is caused by the binding of ionic species at the interface. Indeed, measurements with ice and single crystal metal oxides (hematite) resulted in the $d\Psi/dpH$ slope some 10–20 % lower than the Nernstian slope of 59 mV at 25 °C.^{10,11} Thus, the sequence shown above can be extended, by adding the Nernst potential Ψ_N , as follows:

$$|\Psi_N| > |\Psi_0| > |\Psi_\beta| \geq |\Psi_d| \geq |\zeta| \quad (7)$$

The surface potential, Ψ_0 , can be used in testing the theoretical postulates of the EIL structure but also for determination of ionic activities, as an analytical tool, by constructing ion-selective electrodes.

On the right hand side of the above potentials sequence (7) is the zeta potential (ζ), which can be relatively easily obtained by electrokinetic measurements. The potential at the onset of the diffuse layer Ψ_d is, according to the Gouy-Chapman theory, related to the electrokinetic potential ζ by:

$$\Psi_d = \frac{2RT}{F} \ln \left(\frac{\exp(-\kappa d_{ek}) + \text{th}(F\zeta / 4RT)}{\exp(-\kappa d_{ek}) - \text{th}(F\zeta / 4RT)} \right) \quad (8)$$

where d_{ek} is the separation distance of the electrokinetic e-plane from the d-plane, and κ is the Debye-Hückel parameter given by:

$$\kappa = \sqrt{\frac{2I_c F^2}{\varepsilon RT}} \quad (9)$$

where ε is the permittivity of solution, I_c is the ionic strength and other symbols have their usual meaning. Equations (8) and (9) may be used for evaluation of Ψ_d from electrokinetic data by assuming $d_{ek} \approx 1 \dots 2$ nm.

Electrokinetic potential is directly related to the surface charging process and to the adsorption of various

ionic and non-ionic species within the inner-layer of the EIL. It means that, if the negative charge dominates due to the surface charging mechanism, the potential at surface Ψ_0 will be negative and consequently the electrokinetic ζ potential will be negative, in accordance with sequence (7). The same is true of positively charged surfaces. However, if in the total standard Gibbs energy of adsorption, $\Delta_{ads}G$, defined as

$$\Delta_{ads}G = \Delta_{ads}G^\circ + zF\Psi \quad (10)$$

the chemical part of the adsorption energy $\Delta_{ads}G^\circ$ exceeds the electrostatic effect ($zF\Psi$), like e.g. in the case of adsorption of organic ions, the charge reversal may occur, i.e., electrokinetic ζ potential may have the opposite sign with respect to the surface potential Ψ_0 . It was found¹⁹ that van der Waals interactions between CH_2 groups are about 2.5 kJ mol⁻¹. Multiplying this value by the number of CH_2 groups in the hydrocarbon chain of adsorbing ions, it seems possible that »hydrophobic interactions« could result in charge reversal. Such a phenomenon could be easily detected by electrokinetic methods.

Zero Charge and Isoelectric Condition

H^+ and OH^- are the potential determining ions for oxide (and many other) surfaces, so surface charging is a consequence of protonation and deprotonation processes. If binding of counterions or other ions is negligible or equivalent, the point of zero charge pH_{pzc} ($\sigma_0 = 0$) will correspond to the point of zero potential pH_{pzp} ($\Psi_0 = 0$) and also to the isoelectric point pH_{iep} ($\zeta = 0$). At this condition, the potential at the onset of the diffuse layer, the net surface charge density and the electrokinetic ζ potential will be equal to zero ($\Psi_d = 0$, $\sigma_s = 0$, $\zeta = 0$). Data on surface charge density as a function of pH, i.e. the $\sigma_0(\text{pH})$ function, and the pH_{pzc} , can be obtained by potentiometric titration of the suspension,¹⁻⁴ while electrokinetic methods are used for pH_{iep} .

Besides the pH_{iep} determination, electrokinetic methods are in some cases suitable for determination of pH_{pzc} . It is necessary to measure some electrokinetic phenomenon, such as electrophoretic mobility, of particles suspended in the so-called indifferent electrolyte at different concentrations. If the pH_{iep} value does not depend on electrolyte concentration, one may conclude that anions and cations have the same affinity towards association at the interface and that the isoelectric point corresponds to the point of zero charge, $\text{pH}_{iep} = \text{pH}_{pzc}$. This finding is important, since relative values of surface charge density ($\sigma_{0,rel}$) are obtained by potentiometric titration of the suspension, so that the value of pH_{pzc} is necessary for data evaluation. The procedure based on the common intersection point CIP of $\sigma_{0,rel}(\text{pH})$ curves obtained at different ionic strengths is not always accurate,

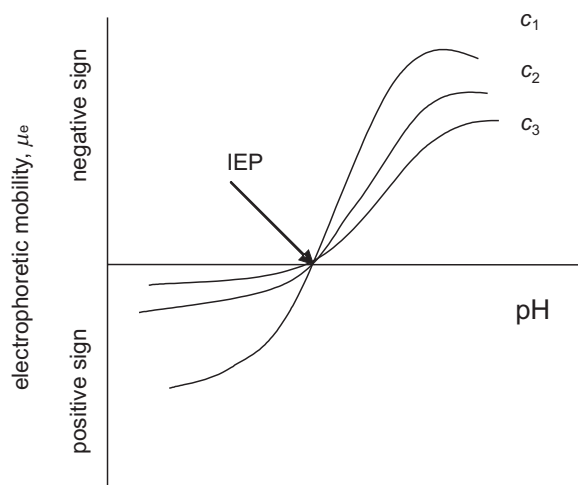


Figure 4. An arbitrary presentation of electrophoretic mobility (μ_e) as a function of pH and electrolyte concentration. Isoelectric point (IEP) is indicated by the common intersection point (CIP). Concentrations are shown in the sequence $c_1 < c_2 < c_3$.

since it is based on the assumption of same association affinities of cations and anions. In the mentioned case, shown in Figure 4, the isoelectric point is independent of the ionic strength, so for such an electrolyte the common intersection point may be used for setting the σ_0 scale.

Relevance of Electrokinetic Data to Colloid Stability

The zeta potential, as a measurable part of the potential decay in the interfacial layer, acts as an important parameter in studying colloidal stability of suspensions *via* the DLVO theory developed by Derjaguin, Landau, Verwey and Overbeek and other contributing theories.^{17,22} The balance between the repulsive electrical forces, acting within the interfacial layer, and van der Waals attractive forces is considered in the DLVO prediction of colloid stability. The common criterion of colloid stability is the stability coefficient W being equal to the ratio of the rate constant of rapid aggregation, k_d (diffusion controlled process related to the collision frequency), and actual aggregation rate constant, k .^{5,25} According to Fuchs, the stability coefficient is related to the integral that includes the dependency of the total interaction energy on the distance between interacting particles. In the simplest case of aggregation of hydrophobic particles dispersed in electrolyte solution, total interaction is the sum of electrostatic and dispersion (van der Waals) contributions, whereas the short range repulsion prevails at the closest distance (hard wall). Electrostatic forces between particles of the same composition are always repulsive, since the particles bear the charge of the same sign. They depend on the activity of potential determining ions and on the electrolyte concentration. At the isoelectric point, the particles are uncharged and the electrostatic repulsion diminishes. Consequently, rapid dif-

fusional aggregation takes place ($W = 1$). Apart from the isoelectric region, the particles are charged but the charge effect could be reduced by addition of electrolyte. The electrostatic interaction energy can be approximated by the HHF theory²⁶ as:

$$E_{el} = \epsilon r \pi \Psi_d^2 \left(\ln \frac{1 + \exp(-\kappa x_s)}{1 - \exp(-\kappa x_s)} \pm \ln(1 - \exp(-2\kappa x_s)) \right) \quad (11)$$

where r and x_s are the radius of interacting particles and their mutual surface-to-surface distance, respectively, while κ is the Debye-Hückel parameter given by Eq. (9). The plus sign applies to relaxed interfacial layers in the course of interaction (constant Ψ_d potential) while the minus sign applies to constant surface charge density, *i.e.*, to the non-relaxed case. It is obvious that the electrostatic potential determining the interaction energy is the potential at the onset of the diffuse part of the electrical interfacial layer Ψ_d . As discussed above, this potential is directly related to the electrokinetic ζ potential. According to Eq. (8), depending on the separation distance of the electrokinetic slip plane d_{ek} and the ionic strength, the magnitude of ζ potential is lower than that of the Ψ_d potential. However, for metal oxides the functions $\Psi_d(\text{pH})$ and $\zeta(\text{pH})$ have both zero value at the isoelectric point. Equation (11) clearly shows that the electrostatic contribution to the interaction energy is proportional to the square of potential Ψ_d . Therefore, approximately, especially at low ionic strengths, the value of E_{el} is proportional to the ζ potential. However, Ψ_d (and ζ) is not the only parameter determining the E_{el} value. As it can be concluded from Eq. (11), the E_{el} value will be reduced at high ionic strengths. As stated by Kallay,^{6,27} the value of Ψ_d will be reduced at higher electrolyte concentrations due to a pronounced counterion association. This effect markedly depends on the charge of the counterions (Schulze-Hardy rule) and less, but still significant, on the specificity of counterions of the same charge number (lyotropic series). The other effect on colloid stability is due to the distribution of counterions within the diffuse part of the interfacial layer. At higher electrolyte concentrations, the κ value is higher and the potential drop is steeper, causing a lower value of E_{el} . Accordingly, the stability of dispersions is determined by both the Ψ_d potential and the ionic strength. Electrokinetic measurements are a useful tool to deduce the effect of electrolyte concentration on Ψ_d . However, one should not forget that stability is not determined by the Ψ_d value (*i.e.*, ζ value) only.

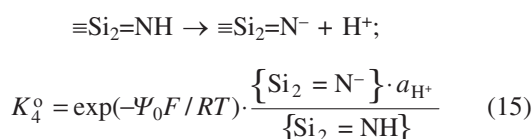
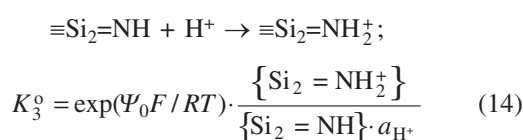
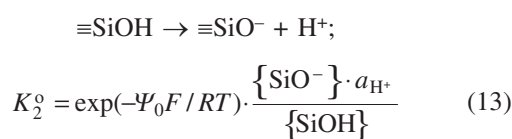
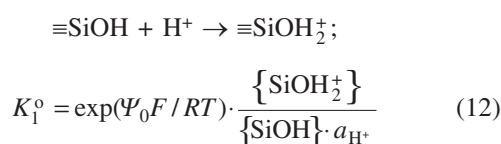
Relevance of Electrokinetic Data to Mixed Oxides and Heterogeneous Surfaces

In the case of »mixed oxide« systems, the situation can be complicated although the same type of reaction is occurring at the surface, *i.e.*, protonation and deprotonation

of surface sites. For example, inclusion of a minute amount of aluminum oxide ($\delta\text{-Al}_2\text{O}_3$) having pH_{iep} about 8 in the structure of vitreous silica, which typically has pH_{iep} about 3, could cause either a neutralizing or a *doping effect*. Due to isomorphous substitution, the *doping effect* would cause additional acidic Lewis-type sites and consequently higher negative surface charge density, higher negative zeta potential values, and shift of the pH_{iep} toward lower pH. On the other hand, the *surface neutralization* due to two pairs of amphoteric reactions of $\equiv\text{AlOH}$ and $\equiv\text{SiOH}$ groups would give an average result, which can be indicated by the PZC and/or IEP shift within the limits of $3 < \text{pH}_{\text{iep}} < 8$.

Some of such dilemmas were discussed in an earlier work²⁸ where the electrokinetic data on borosilicate glasses (Pyrex and Vycor) supported the idea that isomorphous substitution was the main mechanism in that case.

Even more complicated is the situation involving the existence of two types of surface functional groups, such as silanol ($\equiv\text{Si-OH}$) and silazane ($\equiv\text{Si}_2=\text{NH}$) groups, which is the case in silicon nitride suspensions ($\equiv\text{Si}_3\text{N}_4$), an important raw material in fine ceramic production. The diversity of PZC and IEP of Si_3N_4 can be found in the literature.^{29,30} One of the reasons may be the not adequately prepared material. Biščan *et al.*^{12,13} have found that basically four processes create the surface charge with the corresponding thermodynamic equilibrium constants:



Note that surface concentrations are denoted by curly braces.

According to the above reactions, the surface charge density σ_s (being opposite in sign with respect to the

charge density of the diffuse layer σ_d) is related to surface concentrations of charged species by:

$$\sigma_s = -\sigma_d = F(\{\text{SiOH}_2^+\} + \{\text{Si}_2=\text{NH}_2^+\} - \{\text{SiO}^-\} - \{\text{Si}_2=\text{N}^-\}) \quad (16)$$

By using Eqs. (12–16), one obtains the characteristic point of zero charge for -NH and -OH surface groups as:

$$\text{pH}_{\text{IEP}}(-\text{NH}) = 0.5 \cdot \lg(K_3^0 / K_4^0) \quad (17)$$

$$\text{pH}_{\text{IEP}}(-\text{OH}) = 0.5 \cdot \lg(K_1^0 / K_2^0) \quad (18)$$

These two characteristic IEP values were determined: one at $\text{pH}_{\text{IEP}} = 4.2$, characterizing the oxidized surface of Si_3N_4 where SiOH groups dominate, and the other at $\text{pH}_{\text{IEP}} = 8.2$, characterizing »pure Si_3N_4 «, achieved after the sample was thoroughly and carefully leached.

Two processes take place between these limiting pH_{IEP} values, *i.e.*, deprotonation of silanol groups and protonation of silazane groups, so that:

$$\text{pH}_{\text{IEP}} = 0.5 \cdot \lg(K_3^0 / K_2^0) \quad (19)$$

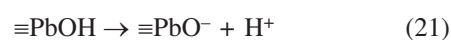
Similarly, such a model can be applied for any other two types of surface functional groups.

Complex Ceramic Oxides

Typically, in ceramic technology one has to deal with complex ceramic compounds like, for instance, $\text{Pb}_{1+x}\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ ($x = 0; 0.025; -0.01$) (PZT).

It was found²⁰ that TiO_2 and ZrO_2 behaved like the majority of metal oxides to which the approach of amphoteric surface equilibria of protonation and deprotonation can be applied. The »problematic« composite for quantitative interpretation was PbO. While the pH of the suspension of TiO_2 and ZrO_2 was almost constant in a wide range of suspension concentrations, the pH of PbO suspension rose from $\text{pH} = 6$ to $\text{pH} = 10$ in the range $0.2\text{--}1.0 \text{ g dm}^{-3}$, becoming stable at about 0.5 g dm^{-3} . The pH dependence of zeta potential gave the IEP for PbO at $\text{pH}_{\text{IEP}} = 11$ in $10^{-4} \text{ mol dm}^{-3}$ NaCl electrolyte, while the pH_{IEP} was 3.5 for TiO_2 , and 7 for ZrO_2 .

In the case of PbO, the following surface reactions are expected:



In addition, a number of other surface and bulk reactions are possible, resulting in the following species: $\text{Pb}_{(\text{aq})}^{2+}$, $\equiv\text{PbOH}^+$, $\text{HPbO}_{(\text{aq})}^{2-}$, $\text{Pb}(\text{OH})_{2(\text{s})}$. Also, the follow-

ing species are possible in sodium chloride solutions: $\text{PbCl}_{2(s)}$, $\text{PbCl}_{(aq)}^+$, $\text{PbCl}_{3(aq)}^-$.

For PZT, being the complex mixture of all three oxides, the impact of each composite can be detected by electrokinetic data. For instance, lower and higher concentration levels of PbO in non-stoichiometric PZT ($\text{P}_{0.99}\text{ZT}$ and $\text{P}_{1.025}\text{ZT}$) were detected qualitatively as the IEP shifts in opposite directions.

Natural Waters

Another complex system is suspended matter in natural waters. The process of aggregation interpreted in terms of colloid stability is of enormous importance, particularly in estuaries where river-born suspended solids enter the saline environment. Due to the great and sudden increase of ionic strength, the energy barrier against aggregation eventually disappears, causing sedimentation, which is an extremely important step in biogeochemical processes. However, it is worth mentioning that other kinds of colloidal stabilization, such as steric stabilization, could have an important role here, so rapid aggregation need not necessarily occur, or may be postponed.³¹

The complexity of the system arises from the coexistence of organic and inorganic particles or complex particles having a mineral core and organic cover, but also pure minerals of different kind and origin: clay minerals, carbonates, oxides, *etc.*

In order to solve at least some surface reactions and the related solid/liquid behavior, one should invent experimental (laboratory) models representing a simplified »natural« system. Besides the salinity gradient in estuaries, the other parameters, such as temperature, pH and oxygen content, undergo significant changes.

Several »model« minerals, such as kaolinite, artificial (synthetic) calcite, natural calcite, natural sea sediment, were investigated by microelectrophoresis.³² The aim was restricted to analyzing the electrokinetic response of selected mineral/solution models to changes in pH, salinity and to the addition of selected organic substances, representative of the natural water constituents (amino acids, polyelectrolytes, polysaccharides). The additives used were: polyethyleneglycol PEG 4000, of $M_r = 3500\text{--}4000$, which is a non-ionic, long-chain, surface-active molecule of general structure $\text{HO}-(\text{C}_2\text{H}_4\text{O})_n\text{-H}$; dextran, a neutral polysaccharide consisting of glucose units bounded by α -1,6 or α -1,3 glycosidic links, and β -alanine, $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-COOH}$, which is a short-chain amino acid often present in natural waters. The assumption was that all kinds of mineral particles in contact with natural seawater undergo surface modifications due to association of organic ions, which compensate the surface charge and in some cases cause charge reversal.

If slow »titration« of pure model minerals, kaolinite, synthetic calcite, natural calcite suspended in 10^{-3} mol

dm^{-3} NaCl, with the so-called »artificial« seawater is performed, the electrokinetic response would be »normal« as expected, *i.e.*, a decrease of electrophoretic mobility with increasing salinity as a consequence of compression of the electrical interfacial layer. However, if »titration« of model minerals is performed with natural seawater, the charge reversal occurs on positively charged species (calcite).

If selected organic compounds, introduced above, were added into artificial seawater, the results confirmed, in qualitative manner, the assumption that organic molecules and ions have the main role in modifying the surface charge and surface potential of particles and consequently the electrokinetic data. The results for calcite and added dextran in Table I give an extra emphasis to this discussion. Fast coagulation of synthetic calcite in artificial seawater with added dextran was observed. It is quite reasonable to assume that interparticle bridging by adsorbed dextran is the cause of rapid aggregation.

TABLE I. Influence of organic additives on the electrophoretic mobility ($10^8 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$) of minerals in »artificial seawater«

Solid	Added organic substance/mg mL^{-1}			
	Blank ^(a)	PEG	dextran	β -alanine
Kaolinite	-1.91	-1.92	-1.94	-1.94
Calcite artificial	+0.72	+1.12	$\leq \pm 0.1$	+1.02
Calcite natural	-0.42	-0.35	-0.45	-0.52

^(a) Artificial seawater of composition: 0.56 mol dm^{-3} NaCl, 0.05 mol dm^{-3} $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.01 mol dm^{-3} $\text{CaCl}_2 \cdot \text{H}_2\text{O}$, pH = 8.1 adjusted by $0.3 \text{ mL } 1 \text{ mol dm}^{-3}$ Na_2CO_3 and $3 \text{ mL } 1 \text{ mol dm}^{-3}$ NaHCO_3 , which resulted in 37.2 ‰ salinity, diluted to $\approx 3.8 \text{ ‰}$ (after Ref. 32)

Textile Fibers

In the production of textile fibers (both processing and finishing), electrokinetic measurements seem to be of essential help in characterizing the surface properties of fibers such as the adhesivity of dyestuffs or various additives, mechanism of washing, modification of surfaces by adsorption of ionic surfactants, adhesion of soil particles, *etc.*^{33–35}

The electrokinetic potential at the textile fibers/solution interface is commonly measured by the streaming potential or streaming current^{33,36} technique. A plug of fibers is usually formed and the hydrodynamic pressure difference is applied across the plug. The laminar flow of electrolyte through the plug induces the electrokinetic effect, *i.e.*, potential difference at both ends of the plug sensed by a pair of reversible electrodes, such as Ag/AgCl reference electrodes. The extended Helmholtz-

-Smoluchowski^{33,34} equation can be used to calculate the zeta potential.

Zeta potential measurements in characterization of textile fibers can provide an insight into the progress and efficiency of various pretreatments performed in order to remove non-cellulose compounds from the primary wall of fibers. Alkaline, acid or enzymatic treatments are most common in textile preparation. Since surface charging by dissociation of surface acidic and basic groups is the intrinsic property of the cellulose surface, it is quite clear that by removing non-cellulose substances like waxes, pectins, proteins, *etc.*, the fresh cellulose surface will be disclosed, bearing the active adsorbing sites capable of association of water molecules (wetting), surface active ionic compounds, dyestuffs and other additives required for textile finishing.

At each stage of pretreatment and treatment, the zeta potential, as a function of pH or of the concentration of a surface active agent, could indicate surface modification. Thus, the shifts of the isoelectric point (IEP) or the charge reversal concentration (CRC) are indicative of the surface dissociation mechanism and association of surfactants, respectively.³⁶

Another treatment that causes morphological changes of fibers, along with modification of their mechanical and adsorption abilities, is mercerization. Electrokinetic measurements seem to be of significant help in detecting treatment efficiency and in optimizing the processes of fibers modification.^{37,38}

In conclusion, the suggestion is to continue to improve and apply electrokinetic data in the solid/liquid interface investigations as a complementary parameter in determining interaction energy between solid particles or solid surfaces with suspended particles or molecules. Another role of electrokinetic data is to give a »framework« of optimal conditions for certain technological processes. Apart from a model needed for calculation of electrokinetic potential, the streaming potential, electrophoretic mobility or electroacoustic analyses may provide such optimal conditions.

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SAŽETAK

Elektrokinetički podaci: pristupi, tumačenja i primjene

Jasenka Bišćan

Rad predstavlja pregled istraživanja međupovršina čvrsto/tekuće s naglaskom na komplementarnoj ulozi elektrokinetičkih podataka u općem konceptu električnog međupovršinskog sloja (EIL), potencijalne energije interakcije i , kao posljedice, koloidne stabilnosti suspenzija. Posebno se raspravlja o elektrokinetičkom (zeta) potencijalu. Sugerira se, da se apsolutne vrijednosti elektrokinetičkih podataka (potencijal ili struja strujanja, elektroforetska pokretljivost i dr.) od slučaja do slučaja teško mogu uspoređivati. Naprotiv, izo-električna se točka (IEP) može pripisati određenoj supstanciji kao neka vrsta konstante, pod točno definiranim uvjetima. Odabrane teorijske postavke korištene su pri interpretaciji interakcija na granici čvrsto/tekuće, uključujući i model površinskog kompleksiranja (SCM). Posebno su analizirani neki slučajevi, kao na pr. jednostavni oksidi, miješani oksidi, heterogene površine s dva tipa površinskih funkcionalnih skupina. Naposljetku se navodi nekoliko primjera primjene elektrokinetičkih podataka u području keramičke tehnologije, međupovršinskih procesa u prirodnim vodama i obradi tekstila.