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Authors' review

Equilibria in the Electrical Interfacial Layer Revisited*

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Equilibrium at the solid-liquid interface is the subject of numerous experimental and theoretical investigations. Several different models describing the structure of the electrical interfacial layer (EIL) and the mechanism of surface reactions are suggested in the literature. At present it seems impossible to decide which of them describe the real situation best. One of the routes towards the solution of this problem is the development of new experimental methods and simultaneous interpretation of different sets of data (*e.g.*, adsorption data, Ψ_0 data, σ_0 data, ζ -potential data, *etc.*). Interpretation based on such an approach may eventually enable differentiation between models and a better choice of appropriate ones. Another route is to refine or develop a new, more realistic and less approximate, theoretical concept. This article presents a review of such efforts (EIL structure, electroneutrality condition, surface potential measurements, capacitors within EIL, enthalpy of surface reactions, colloid stability, *etc.*), with special emphasis on the role of Nikola Kallay in this field, to whom this article is dedicated on the occasion of his 65th birthday.

INTRODUCTION

Equilibria at the solid/liquid interface have been intensively studied since Gouy and Chapman developed their theory in the beginning of the 20th century. Although basic principles and equations proposed almost 100 years ago are still commonly used, we have witnessed continuous improvements in this important field of colloid chemistry. Among other scientists who substantially contributed to a better understanding of interfacial phenomena, the name of Nikola Kallay, to whom we dedicate this article on the occasion of his 65th birthday, should not be omitted. It

should be stated here that, contrary to most of the other scientists in the field, he was, and still is, trying to approach the problem from both experimental and theoretical points of view. He realized that the introduction of new, or modification of already known, experimental techniques as well as simultaneous interpretation of different experimental data could lead to results that can distinguish between several proposed theoretical models and accordingly enable the choice of the proper ones. In this article, we will give just a few examples of where such an approach was successfully applied.

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

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ELECTRICAL INTERFACIAL LAYER

Properties of the solid/liquid interface are influenced by chemical and electrostatic interactions of ions with the surface. Since the distribution of ions in the bulk solution is different from that in the vicinity of the solid surface, and properties of the solid differ inside and at the surface, it is necessary to assume a theoretical model for the structure of the interfacial layer and also for the mechanism of surface charging.

Models that describe the electrical interfacial layer (EIL) at the solid/liquid interface generally differ in the number of postulated layers, *i.e.*, planes that divide these layers. The most comprehensive model, as proposed by Kallay,^{1,2} would be the so called General Model of the Electrical Interfacial Layer (GM-EIL) in which three layers and four different planes (with corresponding potentials) are postulated. This model, shown in Figure 1, could be reduced to any specific EIL model used in the literature by a proper choice of characteristic parameters. The (inner) surface potential Ψ_0 affecting the state of surface charges corresponds to the 0-plane in which the surface charges are located. Centers of the associated counterions are located in the β -plane, which is separated from the "solid surface plane" by a distance depending on their effective size. Consequently, the associated counterions are exposed to potential Ψ_β . The layer between the 0-plane and β -plane is called the Helmholtz layer.

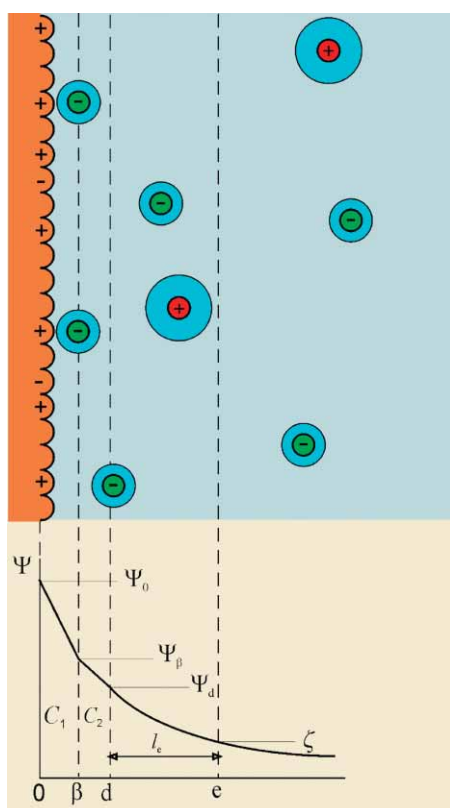


Figure 1. General model of the Electrical Interfacial Layer.¹

The part of the EIL, governed only by electrostatic forces, starting from the d-plane is called the diffuse layer. The distribution of ions in the diffuse layer is affected by the electrostatic potential in the d-plane Ψ_d , permittivity of the interfacial region, thermal energy and the concentration of ions, and is described by the Gouy-Chapman theory. The layer between β - and d-planes is called the outer layer. Sometimes the layer between 0- and β -planes is called the inner Helmholtz layer in order to distinguish it from the outer Helmholtz layer, *i.e.*, the layer between the β -plane and d-plane.

The electrokinetic ζ -potential corresponds to the imaginary slip or shear plane (e-plane) that is located within the diffuse layer and close to the d-plane.

The surface charge densities of interfacial planes are related to the corresponding surface concentrations of interfacial ions: the surface charge density of the 0-plane, β -plane and of the diffuse layer are denoted σ_0 , σ_β , σ_d , respectively. As the system is electroneutral, it follows:

$$\sigma_0 + \sigma_\beta + \sigma_d = 0 \quad (1)$$

The net surface charge density σ_s is equal in magnitude but opposite in sign to σ_d :

$$\sigma_s = -\sigma_d = \sigma_0 + \sigma_\beta \quad (2)$$

In the case of (1:1) symmetrical electrolytes the relationship between the surface charge densities σ_d , σ_s and the electrostatic potential at the onset of the diffuse layer Ψ_d is for planar geometry, according to the Gouy-Chapman theory, given by:

$$\sigma_d = -\sigma_s = -\sqrt{8RT\varepsilon I_c} \sinh(-F\Psi_d / RT) \quad (3)$$

or

$$\Psi_d = \frac{2RT}{F} \operatorname{ar} \sinh \frac{\sigma_d}{\sqrt{8RT\varepsilon I_c}} \quad (4)$$

where I_c is ionic strength (here it corresponds to the concentration of the 1:1 electrolyte), ε is the permittivity of the medium, while other symbols have their usual meaning. According to the same theory, the potential drop within the diffuse layer can be expressed by:

$$\Psi_d = \frac{2RT}{F} \ln \left(\frac{\exp(-\kappa l) + \tanh(F\Psi_l / 4RT)}{\exp(-\kappa l) - \tanh(F\Psi_l / 4RT)} \right) \quad (5)$$

where l is a distance from d-plane and κ is the Debye-Hückel parameter given by:

$$\kappa = \sqrt{\frac{2I_c F^2}{\varepsilon RT}} \quad (6)$$

Equation (5) provides the relationships between Ψ_d and potential Ψ_l at a certain distance l from the onset of the diffuse layer. The potential drop within the hydrody-

namically stagnant part of the diffuse layer, *i.e.*, between the d-plane and the electrokinetic e-plane, is also given by Eq. (5); thus $\Psi_x = \zeta$ at $l = l_e$ (where l_e is the separation distance of the electrokinetic e-plane from the d-plane).

According to the GM-EIL (Figure 1), the (inner) Helmholtz layer can be considered a capacitor with two planes; 0-plane and β -plane. Since the distance between planes (d) is determined by effective sizes of the ionic species, the capacitance C_1 , expressed "per surface area", depends on the apparent distance d and the permittivity of the layer:

$$C_1 = \frac{\varepsilon}{d} \quad (7)$$

The capacitance C_1 is assumed to be constant and is commonly defined as:

$$C_1 = \frac{\sigma_0}{\Psi_0 - \Psi_\beta} \quad (8)$$

However, as suggested by Kallay,³ it might be more appropriate to introduce surface charge density at the β -plane ($-\sigma_\beta$) instead of σ_0 in equation (8). This problem, as well as the questionable constancy of capacitance, will be discussed later in the text. The outer layer, the layer between the β -plane and d-plane, is sometimes⁴ considered as a second capacitor of capacitance C_2 defined by:

$$C_2 = \frac{\sigma_s}{\Psi_\beta - \Psi_d} = \frac{-\sigma_d}{\Psi_\beta - \Psi_d} \quad (9)$$

More than a hundred years ago, first attempts to describe EIL considered mercury and other metal electrodes. The first model of the electrical interfacial layer was proposed by Helmholtz (1879).⁵ In his model, the interface is considered as an electrical capacitor in which charged planes (metal surface and adsorbed counterions at the surface) are fixed and parallel. Later on, Gouy (1910) and Chapman (1913) assumed that the surface is flat, infinite and uniformly charged and that counterions are distributed statistically in the vicinity of the surface.⁵ They developed a theory that is known as the diffuse layer theory (DL). Stern (1924) extended that theory⁵ and considered the possibility of specific adsorption of ions. He proposed a model in which the interfacial layer is divided in two parts separated by the plane located at about a hydrated ion radius from the surface; the surface charge is compensated by both specifically adsorbed counterions and by the ions distributed in the diffuse layer. In fact, the Stern model could be considered as a combination of the Helmholtz and Gouy-Chapman models and is in agreement with the proposed GM-EIL.

The above theories were further developed and applied for the electrical interfacial layer formed at colloid particles. The general model (Figure 1) includes all of the proposed models for the description of EIL at the metal oxide/aqueous electrolyte solution. For example, the ori-

ginal Triple Layer Model (TLM), proposed by Leckie and coworkers,⁴ is in accord with the GM-EIL. It assumes that the onset of the diffuse layer corresponds to the electrokinetic slip plane so that $l_e = 0$ and $C_2 \ll \infty$, which corresponds to $|\Psi_\beta| > |\Psi_d| = |\zeta|$. The general model of EIL may be also reduced to the Double Layer Model (DLM)⁶ assuming that the onset of the diffuse layer is the β -plane and the slip plane separation $l_e > 0$, which corresponds to $|\Psi_\beta| = |\Psi_d| > |\zeta|$. Both approaches are consistent with the general model and satisfy the experimentally verified requirement according to which $|\Psi_\beta| > |\zeta|$.

INTERFACIAL EQUILIBRIA

When discussing the interfacial equilibria, it should be noted that these equilibria were in the past very often interpreted on the basis of semiempirical adsorption isotherms. The adsorption process was observed just as an accumulation of molecules or ions at the surface. But since the early nineteen-seventies, the process of electrical charging at a metal oxide surface in aqueous environment, which assumes reactions of charged surface groups with counterions, has been commonly described by the Surface Complexation Model⁷⁻⁹ (SCM). At that time, Kallay^{10,11} approached the problem in a similar way, but by considering colloid particles as "colloidal molecules" with the "valence" equal to the number of surface active sites. The solution was provided only for the hypothetical extremes; zero and infinite ionic strengths. This approach could be extended to real situations and might be useful for treating nano-particle dispersions, since it provides the distribution of charges among the particles; statistically they do not bear the same charge.

The Surface Complexation Model (SCM) is commonly applied to metal oxides dispersed in aqueous medium, taking into account the structure of EIL, and assuming different mechanisms of surface protonation: one-step protonation mechanism¹²⁻¹⁴ (1-pK), two-step protonation mechanism^{4,15} (2-pK), multi-site complexation (MUSIC) model¹⁶ allowing different types of surface groups, charge distribution model¹⁷ (CD model), *etc.*

Within the SCM, the equilibria of interfacial reactions were traditionally considered by the so called "intrinsic concept"; an ion from the bulk of the solution is first accommodated in the "intrinsic state" (Boltzmann distribution) and then bound to a certain surface group (intrinsic equilibrium constant). As shown by Kallay *et al.*,¹⁸ such a cumbersome hypothetical concept is unnecessary and the equilibrium of interfacial reactions could be treated by standard thermodynamics in the same way as for reactions in homogeneous medium, providing the activities of interfacial species are properly defined. The thermodynamic equilibrium constant, K° , of any reaction is defined as:¹⁹

$$K^\circ = \prod_B a_B^{v_B} \quad (10)$$

where a_B denotes relative activities and v_B refers to stoichiometric coefficients of species B involved in a chemical reaction. Relative activity depends on the arbitrary choice of the standard state, and for interfacial species is defined as:¹⁸

$$a_B = \gamma_B \cdot \Gamma_B / \Gamma^\circ \quad (11)$$

where Γ_B is surface concentration (could be also denoted with curly braces), while the standard value of surface concentration could be taken, for example, as $\Gamma^\circ = 1 \text{ mol m}^{-2}$. The activity coefficient γ_B is related to the difference of chemical potentials between the real and ideal states. The ideal state is defined as a state in the absence of the electrostatic effect, *i.e.*, at the zero value of the corresponding electrostatic potential. Accordingly, for interfacial species B, of the charge number z_B , exposed to the electrostatic potential Ψ_B :

$$RT \ln \gamma_B = \Delta\mu_B = \mu_B^{\text{real}} - \mu_B^{\text{ideal}} = z_B \cdot F \cdot \Psi_B \quad (12)$$

For ionic associates (ion pairs) in the interfacial layer, one should take into account that they act as oriented dipoles in such a way that two charged (ionic) end-groups are exposed to different electrostatic potentials. For example, association of (monovalent) counterions C^+ with surface sites S^- results in surface ion pairs $S^- \cdot C^+$. These interfacial ion pairs are oriented in such a way that the charged side S^- is exposed to the electrostatic potential Ψ_0 while the C^+ side is oriented towards the liquid phase and exposed to electrostatic potential Ψ_β so that the following relationship holds:

$$RT \ln \gamma_{S^- \cdot C^+} = F(-\Psi_0 + \Psi_\beta) \quad (13)$$

According to the 1-pK mechanism,¹²⁻¹⁴ surface equilibrium is described by one-step protonation:



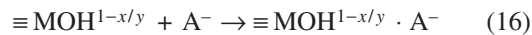
Charge numbers of surface groups ($-x/y$ and $1 - x/y$) depend on the coordination of metal atoms in metal oxides.¹³ The thermodynamic equilibrium constant $K_{x/y}^\circ$ of the above reaction is, according to Eqs. (10), (11) and (13), equal to:

$$K_{x/y}^\circ = \frac{\exp[(1-x/y) \cdot \Psi_0 F / RT]}{\exp[(-x/y) \cdot \Psi_0 F / RT]} \cdot \frac{\{\equiv \text{MOH}^{1-x/y}\}}{\{\equiv \text{MO}^{-x/y}\} \cdot a_{\text{H}^+}} = \exp(\Psi_0 F / RT) \cdot \frac{\{\equiv \text{MOH}^{1-x/y}\}}{\{\equiv \text{MO}^{-x/y}\} \cdot a_{\text{H}^+}} \quad (15)$$

Ψ_0 is the electrostatic potential affecting the state of charged surface groups $\equiv \text{MO}^{-x/y}$ and $\equiv \text{MOH}^{1-x/y}$. The corrective exponential term in the right hand side of rela-

tionship (15) is the ratio of the activity coefficients of surface groups. Note that the original charge of surface groups does not affect the corrective exponential term.

Effective surface charge is reduced by association of anions A^- and cations C^+ with oppositely charged surface sites according to:



where thermodynamic equilibrium constants of the above surface reactions, K_{A1}° and K_{C1}° , are:

$$K_{A1}^\circ = \frac{\exp[(1-x/y) \cdot \Psi_0 + (-1) \cdot \Psi_\beta] F / RT]}{\exp[(1-x/y) \cdot \Psi_0] F / RT]} \cdot \frac{\{\equiv \text{MOH}^{1-x/y} \cdot A^-\}}{\{\equiv \text{MOH}^{1-x/y}\} \cdot a_{A^-}} = \exp(-\Psi_\beta F / RT) \cdot \frac{\{\equiv \text{MOH}^{1-x/y} \cdot A^-\}}{\{\equiv \text{MOH}^{1-x/y}\} \cdot a_{A^-}} \quad (18)$$

$$K_{C1}^\circ = \frac{\exp[(-x/y) \cdot \Psi_0 + (+1) \cdot \Psi_\beta] F / RT]}{\exp[(-x/y) \cdot \Psi_0] F / RT]} \cdot \frac{\{\equiv \text{MOH}^{-x/y} \cdot C^+\}}{\{\equiv \text{MOH}^{-x/y}\} \cdot a_{C^+}} = \exp(\Psi_\beta F / RT) \cdot \frac{\{\equiv \text{MO}^{-x/y} \cdot C^+\}}{\{\equiv \text{MO}^{-x/y}\} \cdot a_{C^+}} \quad (19)$$

Ψ_β is the electrostatic potential affecting the state of associated counterions. The corrective exponential terms in the right hand side of relationships (18) and (19) are the ratios of the activity coefficients of surface groups and are again not affected by the original charge of surface groups. Also, they depend only on the outer surface potential Ψ_β .

According to the 2-pK mechanism,^{4,15} surface charge is the result of two-step protonation of surface groups on the metal oxide surface:



The stoichiometric equation (20) could be written in the opposite direction, *i.e.*, as deprotonation of amphoteric $\equiv \text{MOH}$ groups. The thermodynamic equilibrium constants of the corresponding surface reactions, K_1° and K_2° , are:

$$K_1^\circ = \frac{\exp[(0) \cdot \Psi_0 F / RT]}{\exp[(-1) \cdot \Psi_0 F / RT]} \cdot \frac{\{\equiv \text{MOH}\}}{\{\equiv \text{MO}^-\} \cdot a_{\text{H}^+}} = \exp(\Psi_0 F / RT) \cdot \frac{\{\equiv \text{MOH}\}}{\{\equiv \text{MO}^-\} \cdot a_{\text{H}^+}} \quad (22)$$

$$K_2^\circ = \frac{\exp[(+1) \cdot \Psi_0 F / RT]}{\exp[(0) \cdot \Psi_0 F / RT]} \cdot \frac{\{\equiv \text{MOH}_2^+\}}{\{\equiv \text{MOH}\} \cdot a_{\text{H}^+}} = \exp(\Psi_0 F / RT) \cdot \frac{\{\equiv \text{MOH}_2^+\}}{\{\equiv \text{MOH}\} \cdot a_{\text{H}^+}} \quad (23)$$

Ψ_0 is the electrostatic potential affecting the state of charged surface groups $\equiv \text{MOH}_2^+$ and $\equiv \text{MO}^-$. According to the above formalism, K_2° is identical to the protonation equilibrium constant, while K_1° is equal to the reciprocal value of the deprotonation equilibrium constant.

Within the 2-pK mechanism, the effective surface charge is reduced by association of anions A^- and cations C^+ with oppositely charged surface sites (reactions (24) and (25), respectively) by:



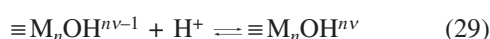
where thermodynamic equilibrium constants $K_{\text{A}2}^\circ$ and $K_{\text{C}2}^\circ$ are:

$$K_{\text{A}2}^\circ = \frac{\exp[(+1) \cdot \Psi_0 + (-1) \cdot \Psi_\beta] F / RT}{\exp[(+1) \cdot \Psi_0 F / RT]} \cdot \frac{\{\equiv \text{MOH}_2^+ \cdot \text{A}^-\}}{\{\equiv \text{MOH}_2^+\} \cdot a_{\text{A}^-}} = \exp(-\Psi_\beta F / RT) \cdot \frac{\{\equiv \text{MOH}_2^+ \cdot \text{A}^-\}}{\{\equiv \text{MOH}_2^+\} \cdot a_{\text{A}^-}} \quad (26)$$

$$K_{\text{C}2}^\circ = \frac{\exp[(-1) \cdot \Psi_0 + (+1) \cdot \Psi_\beta] F / RT}{\exp[(-1) \cdot \Psi_0 F / RT]} \cdot \frac{\{\equiv \text{MO}^- \cdot \text{C}^+\}}{\{\equiv \text{MO}^-\} \cdot a_{\text{C}^+}} = \exp(\Psi_\beta F / RT) \cdot \frac{\{\equiv \text{MO}^- \cdot \text{C}^+\}}{\{\equiv \text{MO}^-\} \cdot a_{\text{C}^+}} \quad (27)$$

Ψ_β is the electrostatic potential affecting the state of associated counterions.

A more refined approach,¹⁶ the *MUSIC Model*, considers the heterogeneous surface of the metal (hydr)oxide surface. Heterogeneity is treated in terms of several discrete surface groups of potentially different reactivity. The proton affinity, which is linked to the formal charge of the surface oxygen, is in a generic way described by the following reactions:



where n is the number of the underlying metal ions and v is the bond valence. Hiemstra *et. al.*¹⁴ calibrated a relationship between formal charge and log K values using Pauling bond valence principle. A more accurate estimation of the oxygen excess charge was later obtained using the actual bond valence instead of Pauling bond valence which takes into account the actual metal-oxygen distances.²⁰ The corresponding equilibrium constants are:

$$K_{nv-2}^\circ = \frac{\exp[(nv-1) \cdot \Psi_0 F / RT]}{\exp[(nv-2) \cdot \Psi_0 F / RT]} \cdot \frac{\{\equiv \text{M}_n \text{OH}^{nv-1}\}}{\{\equiv \text{M}_n \text{O}^{nv-2}\} \cdot a_{\text{H}^+}} = \exp(\Psi_0 F / RT) \cdot \frac{\{\equiv \text{M}_n \text{OH}^{nv-1}\}}{\{\equiv \text{M}_n \text{O}^{nv-2}\} \cdot a_{\text{H}^+}} \quad (30)$$

$$K_{nv-1}^\circ = \frac{\exp[nv \cdot \Psi_0 F / RT]}{\exp[(nv-1) \cdot \Psi_0 F / RT]} \cdot \frac{\{\equiv \text{M}_n \text{OH}^{nv}\}}{\{\equiv \text{M}_n \text{O}^{nv-1}\} \cdot a_{\text{H}^+}} = \exp(\Psi_0 F / RT) \cdot \frac{\{\equiv \text{M}_n \text{OH}^{nv}\}}{\{\equiv \text{M}_n \text{O}^{nv-1}\} \cdot a_{\text{H}^+}} \quad (31)$$

Note that the original charge of surface groups nv , $(nv-1)$ and $(nv-2)$ does not affect the correction term in the right hand side of relationships (30) and (31), so that the final expression is not sensitive to the assumption of the charge distribution among sites at the surface. The correction term includes solely the potential Ψ_0 and the increase of the charge number of interacting surface groups due to their protonation.

The MUSIC model takes into account the crystallographic distribution of surface sites on the dominant crystal faces of particles and charge distribution (CD) model¹⁷ accounts for the distribution of the charge of adsorbed ligands (and metal ions) within EIL and its effect on the respective equilibrium constants. By applying the CD-concept, surface complexes are no longer treated as point charges, but are considered to have a spatial distribution of charge in the interfacial region.

As shown above, equilibrium expressions based on the common thermodynamic approach are the same as those obtained by the "intrinsic concept". The advantage of the thermodynamic concept lies in the following:

1. The derivation is exact and simple.
2. The concept of thermodynamic equilibrium constant is clear so that the relationship with other thermodynamic quantities, such as Gibbs energy, enthalpy and entropy, is straightforward.
3. The interfacial thermodynamic equilibrium constant can be related with those for solute species.

ASSOCIATION SPACE MODEL

The definition of equilibrium constants for association of counterions with oppositely charged surface groups (Eqs. (18), (19), (26), (27)) is based on the assumption that as-

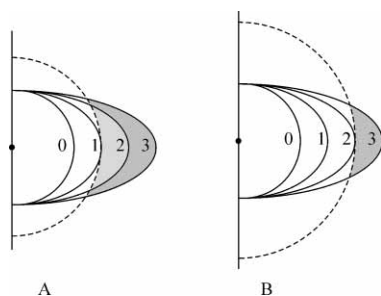


Figure 2. Schematic presentation of critical boundaries of the counterion association space around a fixed central surface charged group for gradually increasing surface potentials. Dashed lines are minimum distances between the centers of the central ion and counterion for relatively small (A) and large (B) counterions. The numbers represent the values of the surface potential on an arbitrary scale. The shadowed area is the association space: for relative potential 2 (---) and for relative potential 3 (---).

sociated counterions are fixed and exposed always to just one potential Ψ_β . However, it is well known that ionic associates in the bulk of the solution, formed due to electrostatic forces, are not characterized by a fixed distance. According to Bjerrum,²¹ they are rather distributed in the "association space", *i.e.*, they are distributed between the distance of the closest approach and the critical distance. On the basis of the Bjerrum concept of ionic association, Kallay and Tomić^{22,23} explained the association of counterions in the EIL (Figure 2). The original Bjerrum theory was modified for the situation at the interface. First, half of the space is forbidden, and second, in addition to the Coulombic potential due to surface charged groups, counterions are exposed to the overall interfacial potential caused by the presence of other ions at the interface.

The resulting equations are complicated and are not suitable for interpretation of the interfacial equilibrium, so that this method is not in use. The Association Space (AS) model explains why ions of a strong electrolyte that are almost completely dissociated in the bulk solution would associate in EIL. It also explains the promoted association at higher surface potentials and predicts the absence of association in the vicinity of the isoelectric point. The association starts at critical values of the surface potential depending on the nature of a counterion, *i.e.*, on their "effective" size which includes the hydration shell. If the hydration shell is not destroyed in the association process, the "effectively" larger counterions would show lower affinity towards association. "Effectively larger" ions are "smaller" ions, since they bind more water molecules. This explains the lyotropic series in coagulation. However, the reverse order may be observed if the water shell is destroyed.

SURFACE POTENTIAL

One of the important variables affecting the interfacial equilibrium of metal oxide aqueous systems is the elec-

trostatic potential at the inner plane of the Helmholtz interfacial layer (0-plane), *i.e.*, the surface potential Ψ_0 . According to Eqs. (15), (22) and (23), the surface potential in the 0-plane is equal to:

$$\Psi_0 = \frac{RT \ln 10}{F} \left(\lg \frac{K_{x/y}^\circ (y-x)}{x} - \text{pH} \right) + \frac{RT}{F} \ln \left(\frac{\{\equiv \text{MOH}^{1-x/y}\} \cdot (y-x)}{\{\equiv \text{MO}^{-x/y}\} \cdot x} \right); \quad 1\text{-pK} \quad (32)$$

and

$$\Psi_0 = \frac{RT \ln 10}{F} \left(\frac{1}{2} \lg(K_1^\circ \cdot K_2^\circ) - \text{pH} \right) - \frac{RT}{2F} \ln \left(\frac{\{\equiv \text{MOH}_2^+\}}{\{\equiv \text{MO}^-\}} \right); \quad 2\text{-pK} \quad (33)$$

The first term of the right hand sides of Eqs. (32) and (33) is the Nernst-type or the "Nernstian" term suggesting that the slope of $\Psi_0(\text{pH})$ function should be -59.2 mV at 25°C . However, the second term reduces the slope. The information on the surface potential is essential for obtaining activity coefficients of the charged species directly bound to the surface,¹⁸ Eqs. (15), (22) and (23). For example, if the surface potential Ψ_0 , at room temperature and 4 pH units below the zero point, is $+190$ mV, the activity coefficient of surface $\equiv \text{MO}^-$ groups would be 0.0006, of $\equiv \text{MOH}_2^+$ 1600, while the activity coefficient of uncharged $\equiv \text{MOH}$ groups would be 1.

It is clear that measurements of the surface potential would enable a critical examination of the theoretical models describing the interfacial equilibrium. First attempts at surface potential measurements used a conducting wire covered with colloidal metal oxide particles and the electrode potential was measured as a function of pH.²⁴⁻²⁶ But probably 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. Consequently, these results do not provide information on the surface potential. However, the Ion Sensitive Field Effect Transistors (ISFET) technique seems to produce more reliable results.^{27,28}

The problem of porosity was solved by Kallay and Čakara²⁹ by construction of an ice electrode. A compact ice layer was formed on the platinum and the measured potential was a result of interfacial reactions. These surface potential data, along with the electrokinetic measurements, enabled evaluation of interfacial equilibrium constants at the ice/water interface.³⁰ More recently, a single crystal hematite electrode was constructed by Kallay, Dojnović and Čop³¹ (Figure 3). This design enables measurements of the surface potentials of different metal oxides.

Single Crystal Electrodes (SCrE) showed²⁹⁻³³ that the dependency of the surface potential on pH does not obey the Nernst equation; the magnitude of the slope was found

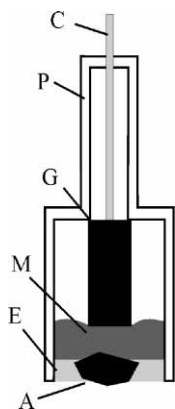


Figure 3. Single Crystal Electrode for surface potential measurements: A – metal oxide single crystal, M – mercury, G – graphite, C – copper wire, P – Plexiglas, E – epoxy resin.

to be significantly lower, which confirms the applicability of SCM, Eqs. (32) and (33). There are several problems in surface potential evaluation from the measured electrode potential data. Since the measurements with single crystal oxide electrodes provide only relative values of surface potential, it is necessary to locate the point of zero potential pH_{pzc} . This problem will be discussed in detail later. Another problem is the slow equilibration at the interface, resulting in hysteresis.^{33,34} Hysteresis was observed in the pH region close to neutrality where concentrations of potential determining H^+ and OH^- ions are low, while the equilibration was fast in acidic and basic regions. These results were explained on the basis of surface reactions kinetics.

Electrodes with single crystal metal oxides provide additional information on the electrical interfacial layer, and thus enable a more rigorous interpretation of the interfacial equilibrium. Surface charge data are related to the difference in surface concentration, while the surface potential measurements provide their ratio (Eqs. (32) and (33)), so a combination of these data yields the values of the surface concentration of surface charges. Simultaneous interpretation of three sets of data (surface charge densities, electrokinetic potential and surface potential) enabled the calculation of surface concentrations of all species, and thus evaluation of thermodynamic equilibrium constants and the inner layer capacitance for individual pH values.³² Also, crystalline electrodes allow measurements of surface potentials of each crystal plane separately, which is important when considering surface heterogeneity.³⁵

ELECTRONEUTRALITY CONDITION

Introduction of surface potential measurements forced Kallay to carefully consider the concept of interfacial electroneutrality. The experimental zero charge conditions at the surface are 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 $\Psi_0 = 0$. In the absence of specific adsorption of ions and in the case of negligible or symmetric association of counterions, all three zero charge points coincide and correspond to the state in which all electrical properties tend to zero ($\sigma_0 = \sigma_s = 0$, $\Psi_0 = \zeta = 0$). Such zero charge condition could be approached by lowering the neutral electrolyte concentration. This electroneutrality point (pH_{eln}), or the pristine point of zero charge (pH_{ppzc}), is related to the equilibrium constants of surface reactions by:

$$\text{pH}_{\text{eln}} = \lg K_{x/y}^\circ + \lg \frac{y-x}{x}; \quad 1\text{-pK} \quad (34)$$

$$\text{pH}_{\text{eln}} = \frac{1}{2} \lg (K_1^\circ \cdot K_2^\circ); \quad 2\text{-pK} \quad (35)$$

The value of pH_{eln} can be experimentally obtained at a sufficiently low ionic strength where pH_{eln} coincides with pH_{pzc} , pH_{iep} and pH_{pzp} .

Some methods for determination of the above zero-points, developed or modified in Kallay's laboratory, are presented in the following paragraphs.

Determination of pzc – Mass Titration Method

As commonly accepted, determination of the point of zero charge ($\sigma_0 = 0$) requires potentiometric titration of the suspension at different ionic strengths or addition of salt to suspensions at different pH. These methods assume that pH_{pzc} does not depend on ionic strength, which is not the case of asymmetric counterion association (different association affinities of anions and cations). Therefore, in some cases, the common interception point obtained by titrations of suspensions at different ionic strengths does not provide the point of zero charge ($\text{pH}_{\text{cip}} \neq \text{pH}_{\text{pzc}}$), so surface charge data obtained on the basis of this concept are not correct. The problem was solved by potentiometric mass titration, originally developed by Noh and Schwarz³⁶ and refined by Kallay and Žalac.^{37–40} Subsequent portions of a purified metal oxide powder should be added to the electrolyte solution (or water) and the pH of the dispersion should be measured. The pH of the system gradually changes with the mass concentration of the solid approaching a constant value pH_∞ (Figure 4), which is equal to pH_{pzc} if the powder was sufficiently purified. The pH_∞ value of contaminated dispersion is higher (basic impurities) or lower (acidic impurities) compared to the point of zero charge. The method was later extended³⁷ to determination of the point of zero charge of contaminated samples and provides information on the fraction of impurities in the powder. Mass titration was found extremely suitable for determination of temperature dependency of the point of zero charge and therefore for evaluation of surface reaction enthalpy.³⁸ One simply measures the temperature dependency of pH of a sufficiently

concentrated metal oxide dispersion in the absence of impurities. The mass titration method was also further developed for determination of surface charge density, Figure 4.^{39,40}

The advantage of this method is that experiments can be performed at just one ionic strength and also at an extremely low electrolyte concentration. Moreover, comparison of the dispersion with blank titration is avoided. Mass titration was applied⁴⁰ to determination of the effect of electrolyte concentration on the point of zero charge in order to deduce the difference in surface association affinities of cations and anions. Counterion association shifts the pH_{pzc} either to the acidic region (preferential adsorption of cations) or to the basic region (preferential adsorption of anions). Mass titration therefore enables detection of the difference between association affinities of counterions (cations and anions), which is important information about the equilibrium within the electrical interfacial layer.

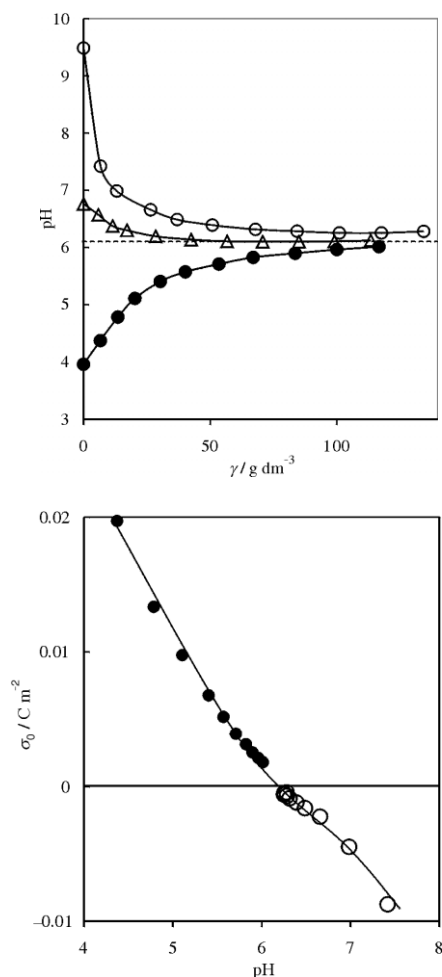


Figure 4. Mass titrations of TiO_2 for different initial pH: $\text{pH}_{\text{in}} = 9.8$ (○); 6.7 (△); 4 (●). When necessary, ionic strength of $I_c = 10^{-4}$ mol dm^{-3} was adjusted with NaCl. Temperature: 25 °C. Surface charge densities were calculated from mass titration data⁴⁰ (with permission of Croatica Chemica Acta).

Determination of iep – Adhesion Method

Common methods for determination of the isoelectric point (pH_{iep}) are electrophoresis, electroosmosis, streaming potential, streaming current, acoustophoresis and sedimentation potential measurements. If applied to metallic surfaces, these classical methods involve serious problems due to sample conductivity. For characterization of electrically conductive samples, Kallay⁴¹ developed the adhesion method. In such adhesion experiments, a suspension of small (sensor) colloid particles is passed through a bed consisting of collector beads. Adhesion of colloid sensor particles (at low ionic strength) is fast if they are oppositely charged with respect to the sample (collector beads). For example, if the deposition of negatively charged colloidal latex particles on relatively large copper particles in a packed column is measured and if pH is changed from *e.g.* 10 to 4, an abrupt increase in the adhesion rate will be observed at pH_{iep} of copper.^{42,43} The most important application of the adhesion method is determination of the pH_{iep} values of different metals,⁴⁴ which were found to be equal to those of the corresponding oxides. Additionally, the adhesion method can be used for various other fundamental and applied investigations. For example, it was shown that it may serve to deduce the nature of the oxide layer at a metal surface. This approach was used to monitor the corrosion process at the stainless steel surface.⁴⁵

Determination of pzp

As mentioned above, the surface potential values could be deduced from potentials of single crystal electrodes if the point of zero potential (pH_{pzp}) is known. At a sufficiently low ionic strength, pH_{pzp} is equal to pH_{pzc} , pH_{iep} and to the electroneutrality point pH_{eln} . The method for determination of pH_{pzp} at higher ionic strengths was recently proposed by Kallay *et al.*⁴⁶ For that purpose, one should, at the defined ionic strength, measure the single crystal electrode potential and the ζ -potential dependency on pH. Also, one should obtain pH_{eln} by performing the measurements at a sufficiently low ionic strength where $\text{pH}_{\text{iep}} \approx \text{pH}_{\text{pzc}} \approx \text{pH}_{\text{eln}}$. From Eqs. (32) and (33), it follows that the potential at the isoelectric point (*i.e.*, at pH_{iep}) for the 1-pK model is:

$$\Psi_0(\text{iep}) = \frac{RT \ln 10}{F} \lg \frac{K_{x/y}^\circ (y-x)}{x} - \frac{RT \ln 10}{F} \text{pH}_{\text{iep}} = \frac{RT \ln 10}{F} (\text{pH}_{\text{eln}} - \text{pH}_{\text{iep}}) \quad (36)$$

and for 2-pK model of surface charging is

$$\Psi_0(\text{iep}) = \frac{RT \ln 10}{2F} \lg(K_1^\circ \cdot K_2^\circ) - \frac{RT \ln 10}{F} \text{pH}_{\text{iep}} = \frac{RT \ln 10}{F} (\text{pH}_{\text{eln}} - \text{pH}_{\text{iep}}) \quad (37)$$

Equations (36) and (37) show that, regardless of the mechanism of surface charging, the surface potential at the isoelectric point pH_{iep} is the same. The value of $\Psi_0(\text{iep})$ can be simply calculated from the predetermined values of pH_{eln} and pH_{iep} . From $\Psi_0(\text{iep})$ and the measured value of the electrode potential of SCrE , $E(\text{iep})$, it is possible to recalculate measured electrode potentials of SCrE , E , to surface potentials Ψ_0 and thus determine the pH_{pZP} .

CAPACITORS WITHIN ELECTRICAL INTERFACIAL LAYER

One of the limitations in interpretation of the interfacial equilibrium at the solid/liquid interface by the Surface Complexation Model is that interpretation of *e.g.* $\sigma_0(\text{pH})$, experimental function requires a set of constant parameters characterizing the interfacial equilibrium. Therefore, one is forced to introduce the concept of constant capacitance of the inner layer capacitor, Eqs. (8) and (9), *i.e.*, one should assume that C_1 does not depend on pH . An additional problem is the definition of C_1 . Within the double layer approximation (DLM), one deals with two capacitors, *i.e.*, with the diffuse layer capacitor and the inner layer capacitor. The diffuse layer capacitor (expressed per surface area) has variable capacitance:

$$C_{\text{dif}} = \frac{\sigma_s}{\Psi_d} \quad (38)$$

which can be deduced from the Gouy-Chapman theory. Due to the variation of the capacitance C_{dif} , the concept of differential capacitance was introduced, which can also be inferred from the same theory. The definition of the capacitance of the inner layer C_1 (expressed per surface area) requires introduction of the corresponding surface charge density. There are two possible approximations. The commonly accepted model is that of serial connection of these two capacitors, but it may happen that the parallel connection better represents reality. These two approximations are shown schematically in Figure 5.

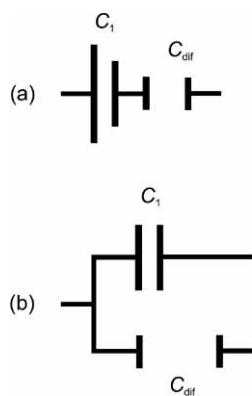


Figure 5. Schematic presentation of the concepts of serial (a) and parallel (b) connection of capacitors.

In the case of serial connection of capacitors, the following equation holds:

$$C_{1,\text{ser}} = \frac{\sigma_0}{\Psi_0 - \Psi_\beta} \quad (39)$$

while parallel connection requires the following definition of C_1 :

$$C_{1,\text{par}} = \frac{-\sigma_\beta}{\Psi_0 - \Psi_\beta} \quad (40)$$

Within the DLM approximation, one takes $\Psi_\beta = \Psi_d$. According to the concept of parallel connection of capacitors, the charges divided in the inner layer capacitor are $-\sigma_\beta$ and σ_β , but not σ_0 and $-\sigma_0$ as in the case of the commonly accepted concept, *i.e.*, the model of serial connection of capacitors.

Since the model of the inner layer capacitor is an approximation of the reality, it is hard to distinguish between these two concepts, *i.e.*, between the models of serial and parallel connection of capacitors as defined by Eqs. (39) and (40). Kallay³ examined the consequences of these two opposite assumptions on measurable characteristics of the solid/liquid interfaces both experimentally and by numerical simulation. Numerical simulation was performed with the parameters of an ordinary metal oxide system. As expected, by a sufficiently high value of counterion association ($\approx 100\%$), achieved by the high value of the association equilibrium constant, no significant difference between the two concepts was observed, even at ionic strength as low as $10^{-4} \text{ mol dm}^{-3}$. In the case of a low degree of counterion association, *i.e.*, for a low value of the association equilibrium constant, again no significant difference between these two different concepts was observed, which was attributed to the mutual effect of several parameters governing the equilibration in the electrical interfacial layer.

The behavior of an alumina suspension ($\gamma\text{-Al}_2\text{O}_3$, Degussa) was examined in experimental work: the net surface charge density σ_s was found to be markedly lower than the surface charge density in the inner layer σ_0 so that $\sigma_\beta \approx -\sigma_0$, and both concepts were found to be practically equivalent.³ The obtained results suggest that the choice between the concepts of serial (Eq. (39)) and parallel connection of the capacitors (Eq. (40)) cannot be made unambiguously on the basis of experimental findings, even for systems in which counterion association is low. It was concluded that, for the time being, both concepts are equally applicable.

The next question that was previously unsolved is the commonly assumed constancy of the capacitance of the inner layer capacitor C_1 . This commonly used assumption is necessary when one performs nonlinear regression analysis of experimental $\sigma_0(\text{pH})$ function. Several attempts to analyze the constancy of C_1 could be found in the literature.⁴⁷⁻⁵⁶ It was shown^{47,50,51} that the C_1 value depends

on pH, *i.e.*, on the surface potential Ψ_0 . However, the analysis assumed that the Ψ_0 potential obeys the Nernst equation, which is not necessarily valid. The recently introduced surface potential measurements with the anatase single crystal electrode provided the answer.³² It was shown that capacitance C_1 in acidic pH region increases by approaching the isoelectric point from 1 to 3 F m⁻².

SIMULTANEOUS INTERPRETATION OF ADSORPTION DATA

The problem of different models used for interpretation of interfacial equilibrium was analyzed a long time ago by Westal and Hohl.⁵² They showed that surface charge data could be interpreted successfully by several different models, so that these data cannot be used to distinguish between them. In order to solve the problem, Kallay's group introduced the concept of simultaneous interpretation of more than one set of experimental data.⁹ Such an approach was enabled by construction of single crystal electrodes but also by proper interpretation of electrokinetic results. Single crystal electrodes provide information on the surface potential Ψ_0 , while the electrokinetic data may be used for evaluation of the potential at the onset of the diffuse layer Ψ_d , being approximately equal to Ψ_β . To evaluate Ψ_d from the ζ -potential, one should have information on the slip plane separation distance s . This concept was devised on the basis of the results obtained by Eversole and Lahr.⁵³ They measured the dependency of ζ -potential on the ionic strength at constant pH and used the Gouy-Chapman theory, Eq. (3), yielding the following expression:

$$\ln[\tanh(F\zeta/4RT)] = \ln[\tanh(F\Psi_d/4RT)] - \kappa l_e \quad (41)$$

Accordingly, the slope of the function $\ln[\tanh(F\zeta/4RT)]$ *vs.* κ should provide the value of the slip plane separation l_e . However, such a procedure is correct only if Ψ_d is independent of the ionic strength at constant pH, which is not the case. Kallay and coworkers⁶ suggested that, since Ψ_d decreases in magnitude with increasing ionic strength, the function $\ln[\tanh(F\zeta/4RT)]$ *vs.* κ should not be linear, and the slope of the tangent should be always larger than l_e . It was concluded that it is possible to calculate Ψ_d from the ζ -potential by taking $l_e \approx 1$ nm.

The Surface Complexation Model is a general concept considering the interfacial equilibrium caused by specific reactions of bulk species with active surface groups. It was shown⁹ that both the Langmuir and Freundlich isotherms may be derived from the general expression for the interfacial equilibrium constant (Eq. (10)). These isotherms describe an ideal case, in which there are no interactions between adsorbed species, *i.e.*, the activity coefficients of interfacial species are equal to 1. In addition to the assumed ideality, the Freundlich isotherm

considers surface association or dissociation, but is limited to low surface coverage. Therefore, since due to the improvement of computational methods the linear forms of the relationships are no more necessary, and therefore the proper to apply general expression can be applied (Eq. (11)) to introduce activity coefficients and possible association or dissociation of adsorbable species at the interface.

In numerous cases, the semi-empirical Langmuir isotherm was used for interpretation of adsorption data without considering the model on which this isotherm is based. Kallay and Kovačević introduced the interpretation based on the extended Langmuir isotherm,^{54,55} as well as on the modified Surface Complexation Model.⁵⁶⁻⁵⁸ These were among the first examples of simultaneous interpretation of data obtained by different experimental methods (adsorption and electrokinetic measurements) for evaluation of equilibrium parameters in the EIL.

In the commonly used version of the Langmuir isotherm for ionic adsorption, at least one requirement is violated – the ions at the interface are not mutually independent but they rather exhibit pronounced electrostatic interactions. Additionally, in the case of association-dissociation equilibrium in the bulk of the solution, one should use the equilibrium concentration or activity of the species that actually adsorb. Accordingly, the refined adsorption isotherm of the Langmuir type for ionic species i of the charge number z would read:

$$\frac{1}{\Gamma_i} = \frac{1}{\Gamma_{\max}} + \frac{1}{\Gamma_{\max} K_i \exp(-z_i F \Psi_a / RT) a_i} \quad (42)$$

where a_i is the bulk activity of adsorbing species i , Γ_i and Γ_{\max} are equilibrium and maximum surface concentrations of adsorbed species i , respectively, and Ψ_a is the interfacial electrostatic potential affecting the state of adsorbed species i . In the interpretation of adsorption experiments, one uses electrokinetic data to evaluate Ψ_d and the approximation $\Psi_a \approx \Psi_d$. In doing so, one calculates Ψ_d from the ζ -potential by Eq. (5), using the slip plane separation as an adjustable parameter. The above treatment was successfully applied to the adsorption of citric, oxalic and iminodiacetic ions on hematite.^{59,60} Interpretation based on the extended Langmuir isotherm resulted in the charge number of species that actually adsorb at the surface (thus indicating the mechanism of the surface binding process), as well as in the values of the adsorption equilibrium constant, occupied area per molecule and the slip plane separation.

Surface equilibrium for adsorption of organic acid and heavy metal ions on metal oxides was also deduced from simultaneous interpretation of electrokinetic and adsorption measurements using the Surface Complexation Model.⁵⁶⁻⁵⁸ It was confirmed that, for the salicylic acid/hematite system, the singly charged salicylate ions are adsorbed. For adsorption of relatively large organic

species, one should also consider the fact that a bound organic molecule does not cover just one surface site (the one to which it is bound) but also several adjacent surface groups, excluding them from the further adsorption process. This so called "umbrella effect" should be significant in the case of salicylate ions and is reflected in the summation of surface sites.⁵⁶ The following equation takes into account the fact that one adsorbed L^- salicylate ion, forming a $\equiv ML^-$ surface complex, excludes from the binding process the f neutral $\equiv MOH$ species, one to which it is bound and others that are covered, preventing them from being active in the adsorption process:

$$\Gamma_{\text{tot}} = \Gamma(\equiv MOH) + \Gamma(\equiv MOH_2^+) + \Gamma(\equiv MO^-) + f \Gamma(\equiv ML^-) \quad (43)$$

Adsorption of lead and cadmium species at the goethite aqueous interface,^{57,58} as well as the electrokinetic properties of the system, were also measured as a function of pH and the data were interpreted simultaneously using the Surface Complexation Model. It was found that singly charged lead ($\equiv PbOH^+$) and cadmium ($\equiv CdOH^+$) species are bound to negatively charged surface sites. The adsorption equilibrium constants, the capacitance of the Helmholtz layer, the potentials of the inner Helmholtz plane and the slip plane separation were determined.

Simultaneous interpretation of potentiometric, electrokinetic and coagulation experiments^{50,51} yielded the average values of the inner layer capacitance and equilibrium constants of counterion association. It was found that larger ions, which are, due to less pronounced hydration, "effectively" smaller, have higher values of both parameters, indicating stronger affinity towards association in the interfacial layer. This finding explains the lyotropic effect in surface charge, as well as in electrokinetics and coagulation phenomena.

Recently, measurement of surface potential by means of the SCrE was introduced³¹ and used for interpretation of the adsorption of salicylic acid on hematite.⁶¹ This potential (Ψ_0) directly affects the state of ionic species created by interactions of surface groups with the potential determining ions. Other ions may be either associated to these surface charges or bound directly to the surface. It may be concluded that simultaneous interpretation of surface potential data together with electrokinetic and adsorption data enables elucidation of the adsorption mechanism of charged inorganic and organic species and evaluation of the corresponding equilibrium parameters.

ENTHALPY OF SURFACE REACTIONS

Two approaches for determination of the enthalpy of surface reactions are commonly used: direct calorimetric

experiments and measurements of temperature dependency of an equilibrium parameter, *e.g.*, the point of zero charge. The heat (enthalpy change) measured in the calorimeter is the sum of contributions of several interfacial reactions (Eqs. (20), (21), (24), (25)) and also of the accompanying processes in the bulk of the solution (*i.e.*, neutralization, dilution, *etc.*). The interaction of ions with charged surface sites is influenced by the electric field in EIL, so the electrostatic contributions to enthalpies should also be taken into account. To avoid electrostatic effects, the "symmetric" calorimetry experiment was designed by Kallay and coworkers in such a way that the point of zero charge was in the middle between the initial and final pH.⁶² In that case the heat of the reaction corresponds to the sum of standard reaction enthalpies of surface protonations (Eqs. (20) and (21)). Electrostatic contribution outside the point of zero charge region is significant because the interpretation of calorimetric titration data is no more simple. To solve this problem, Kallay and Preočanin⁶³ designed the experiment in such a way that the extent of neutralization in the bulk solution was minimized (titrations of slightly acid suspension with acidic solution and slightly basic suspensions with base solution). The extent of counterion association was minimized by performing the titrations at low ionic strength. Heats and pH-values were measured simultaneously for each titration step. The extents of surface protonation and deprotonation were calculated from their difference and ratio, for which the values of surface potential (Eq. (33)) were used. This method enabled evaluation of standard enthalpies of the first and second steps of protonation separately, as well as the electrostatic contribution to these quantities.

Temperature dependency of the point of zero charge is another route for evaluation of surface reactions enthalpy. To obtain reliable results, the accuracy of pH_{pzc} values is essential. According to the mass titration method,³⁶ the equilibrium pH of the suspension at high mass concentration corresponds to pH_{pzc} , so one could simply measure the pH of a sufficiently concentrated suspension as a function of temperature.³⁸ It was shown that the enthalpy obtained by this method is the standard reaction enthalpy and does not include the electrostatic contribution. It has the same physical meaning as the enthalpy obtained from the "symmetrical calorimetric experiment".

COLLOID STABILITY – KINETICS OF AGGREGATION

An important contribution of the colloid chemistry to the field of chemical kinetics is the collision theory originally developed for colloidal dispersions by Marian Smoluchowski.⁶⁴ According to this theory, the rate constant of aggregation controlled by diffusion (rapid coagulation) involving spherical particles of radii r_1 and r_2 is equal to:

$$k_{\text{dif}} = 4\pi(D_1 + D_2)(r_1 + r_2) = \frac{2k_{\text{B}}T}{3\eta} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) (r_1 + r_2) \quad (44)$$

where D_1 and D_2 are diffusion coefficients of particles 1 and 2, respectively, η is medium viscosity and k_{B} is the Boltzmann constant. Colloidal systems may be used as a perfect model to test this theory. The diffusion coefficient of uniform spherical particles in a viscous medium could be exactly evaluated from their measured radii. In the absence of electrostatic repulsion (high electrolyte concentration), all collisions result in aggregation since the direction (steric parameter) is not influential. The theory is "absolute" and the experimental rate constants were found to be close to the prediction, but still lower by a factor of two, which is usually explained on the basis of hydrodynamics affecting the movement of colliding particles. Temperature dependency of the rate coefficient of diffusional aggregation is according to Eq. (44):

$$\ln(k_{\text{dif}} / T) = \ln \left[\frac{2k_{\text{B}}T}{3} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) (r_1 + r_2) \right] - \ln B - \frac{E_v}{RT} \quad (45)$$

In the above equation, the semiempirical expression for the temperature dependency of viscosity was introduced: B is the "pre-exponential factor" and E_v is the "viscosity activation energy". At the beginning of his carrier, Kallay measured the temperature dependency of the diffusion rate constant of aggregation of silver iodide particles.^{65,66} The diffusional condition was achieved by adding $\text{Mg}(\text{NO}_3)_2$ to the negatively charged system at concentration above the critical coagulation concentration. The activation energy of $E_v = 18.6 \text{ kJ mol}^{-1}$ agrees well with the value of 17.8 kJ mol^{-1} obtained from the temperature dependency of water viscosity.

There are several reasons for the stability of colloidal systems. One of them is the electrostatic repulsion between dispersed colloidal particles. During the Second World War, the famous DLVO theory was developed.^{67,68} This theory enabled calculation of the electrostatic interaction energy between colloid particles. This theory was the last missing step in solving the colloid stability problem; short-range repulsion could be treated by the "hard wall" concept, dispersion attraction between particles was solved, Smoluchowski developed a theory for collision frequency, while Fuchs provided the general expression for collision efficiency (stability coefficient). Once the electrostatic interaction energy could be calculated on the basis of the DLVO theory, colloid stability could be predicted. Three problems still remained. The first is the value of the Hamaker constant (which may be treated as

an adjustable parameter), the second is relaxation of overlapping diffuse layers, and the third is the electrostatic potential at the onset of the diffuse layer, Ψ_{d} , governing the distribution of ions in that space and thus affecting the electrostatic interaction energy of two approaching particles. As shown by Kallay,⁶⁹ the introduction of the Surface Complexation Model into the "family" of theories that comprise the Theory of Colloid Stability makes this theory "absolute", Figure 7. Under the "absolute" theory we have in mind the theory which does not include adjustable parameters, *i.e.* the theory which may predict the behavior of the system on the basis of parameters that could be determined by independent measurements. Using the equilibrium parameters that characterize the electrical interfacial layer, it is possible to evaluate the potential at the onset of the diffuse layer Ψ_{d} and calculate the electrostatic interaction energy yielding the stability coefficient and the rate constant of aggregation. It was also demonstrated that counterion association plays an important role in the aggregation process by reducing the value of Ψ_{d} ; thus the colloid stability decreases by the addition of electrolyte due to association of counterions (reduction of surface charge and Ψ_{d}) and "compression" of the diffuse layer.

It is known that the colloidal nano-particle dispersions can hardly be stabilized by electrostatic repulsion forces.⁷⁰ The rate of aggregation of nano-particles cannot be properly interpreted by the DLVO theory, since the overlap of two electrical diffuse layers in the course of collision is not partial but almost complete. To solve this problem, Kallay combined the collision and the transition state theory⁶⁹ by introducing the Brønsted concept, originally developed for the primary salt effect in the kinetics of ionic reactions, and explained the low stability of nano-colloid dispersions. The following expression was found applicable for calculation of the stability coefficient W of nano-dispersions:

$$\log W = \log \frac{k_{\text{dif}}}{k} = z_1 z_2 \left(\frac{F^2 \ln 10}{4\pi\epsilon LRT(r_1 + r_2)} - 2A_{\text{DH}} \frac{\sqrt{I_c / \text{mol dm}^{-3}}}{1 + ab_{\text{DH}} \sqrt{I_c / \text{mol dm}^{-3}}} \right) \quad (46)$$

where k is rate constant of aggregation, z_1 and z_2 ions charge number, L Avogadro's constant, a distance of the closest approach, while A_{DH} and b_{DH} are Debye-Hückel constants depending on the temperature and the relative permittivity, ϵ_r , of the medium:

$$A_{\text{DH}} = 1.825 \times 10^6 (\epsilon_r \cdot (T / \text{K}))^{-3/2} \quad (47)$$

$$b_{\text{DH}} / \text{nm}^{-1} = 502.9 (\epsilon_r \cdot (T / \text{K}))^{-1/2} \quad (48)$$

At 25 °C and water $A_{\text{DH}} = 0.509$ and $b_{\text{DH}} = 3.28 \text{ nm}^{-1}$.

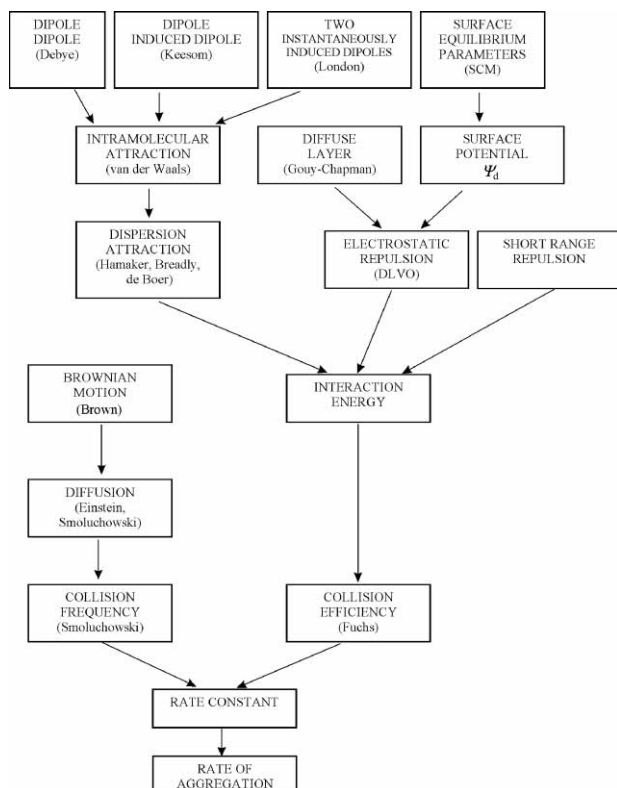


Figure 7. Different theoretical contributions to the Theory of Colloid Stability. Reproduced with permission from *Croatia Chemica Acta*, Ref. 69.

The distance of the closest approach a at higher ionic strengths may be approximated by the radius of nano-particles. The charge numbers of interacting nano-particles z are given by their absolute charges Q and are related to the corresponding net surface charge densities σ_s by:

$$z = \frac{Q}{e} = 4r^2\pi \cdot \sigma_s \quad (49)$$

where e denotes the elementary charge. As described in previous paragraphs, the charge of nano-particles could be obtained on the basis of adsorption and/or electrokinetic measurements.

SUMMARY

In this article, several theoretical and experimental approaches to the Electrical Interfacial Layer based on the ideas of Nikola Kallay are presented and discussed. New experimental methods have been developed (e.g., surface potential measurements, adhesion method for determination of the isoelectric point of metallic surfaces) or modified (e.g., mass titration). Simultaneous interpretation of different sets of experimental data has been introduced (e.g., Ψ_0 , ζ -potential and adsorption data). Some theoretical concepts (e.g., the general model of the electrical

interfacial layer, standard states and activity coefficients) and theories (e.g., counterion association space, stability of nano-dispersions) have been developed. The controversy relating to the definition and constancy of the capacitors within the electrical interfacial layer is discussed. The relation of interfacial equilibrium and colloid stability, including nano-dispersions, is analyzed.

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REFERENCES

1. N. Kallay, D. Kovačević, and A. Čop, *Interpretation of Interfacial Equilibria on the Basis of Adsorption and Electrokinetic Data*, in: N. Kallay (Ed.) *Interfacial Dynamics*, Marcel Dekker, Inc., New York, 2000.
2. A. V. Delgado, F. Gonzalez-Caballero, R. J. Hunter, L. K. Koopal, and J. Lyklema, *Pure Appl. Chem.* **77** (2005) 1753–1805.
3. N. Kallay, D. Kovačević, A. Čop, and M. Medvidović, *Croat. Chem. Acta.* **77** (2004) 243–249.
4. J. A. Davis, R. O. James, and J. O. Leckie, *J. Colloid Interface Sci.* **63** (1978) 480–499.
5. J. Lyklema, *Fundamentals of Interface and Colloid Science*, Volume II: *Solid-Liquid Interface*, Academic Press, London, 1995.
6. N. Kallay, R. Sprycha, M. Tomić, S. Žalac, and Ž. Torbić, *Croat. Chem. Acta* **63** (1990) 467–487.
7. W. Stumm, C. P. Huang, and S. R. Jenkins, *Croat. Chem. Acta* **42** (1970) 223–245.
8. D. E. Yates, S. Levine, and T. W. Healy, *J. Chem. Soc., Faraday Trans. I* **70** (1974) 1807–1818.
9. N. Kallay, S. Žalac, and D. Kovačević, *Thermodynamics of the Solid/Liquid Interface. Its Application to Adsorption and Colloid Stability*, in: J. Lützenkirchen (Ed.), *Surface Complexation Modelling*, Interface Science and Technology series, Elsevier, 2006.
10. N. Kallay, *Croat. Chem. Acta* **48** (1976) 271–276.
11. N. Kallay, *Croat. Chem. Acta* **50** (1977) 209–217.
12. W. H. van Riemsdijk, G. H. Bolt, L. K. Koopal, and J. Blaakmeer, *J. Colloid Interface Sci.* **109** (1986) 219–228.
13. R. H. Yoon, T. Salma, and G. Donnay, *J. Colloid Interface Sci.* **70** (1979) 483–493.
14. T. Hiemstra, P. Venema, and W. H. van Riemsdijk, *J. Colloid Interface Sci.* **184** (1996) 680–692.
15. W. Rudzinski, R. Charmas, W. Piasecki, J. M. Cases, M. Francois, F. Villieras, and L. J. Michot, *Colloids Surf., A* **137** (1998) 56–87.
16. T. Hiemstra, W. H. van Riemsdijk, and G. H. Bolt, *J. Colloid Interface Sci.* **133** (1989) 91–104.
17. T. Hiemstra and W. H. van Riemsdijk, *J. Colloid Interface Sci.* **179** (1996) 488–508.
18. N. Kallay, T. Preočanin, and S. Žalac, *Langmuir* **20** (2004) 2986–2988.
19. I. Mills, T. Cvitaš, K. Homann, N. Kallay, and K. Kuchitsu, *Quantities, Units and Symbols in Physical Chemistry*, 2nd ed., Blackwell Scientific Publications, Oxford, 1993.

20. I. D. Brown and R. D. Shannon, *Acta Crystallogr., Sect. A* **32** (1973) 266–282.
21. N. Bjerrum, *Ergeb. Exakten Naturwiss.* **6** (1926) 125.
22. N. Kallay and M. Tomić, *Langmuir* **4** (1988) 559–564.
23. M. Tomić and N. Kallay, *Langmuir* **4** (1988) 565–569.
24. E. Kinoshita, F. Ingman, and G. Edwall, *Electrochim. Acta* **31** (1986) 29–38.
25. N. G. H. Penners, L. K. Koopal, and J. Lyklema, *Colloids Surf., A* **21** (1986) 457–468.
26. M. J. Avena, O. R. Camara, and C. P. De Pauli, *Colloids Surf., A* **69** (1993) 217–228.
27. L. Bousse, N. F. de Rooij, and P. Bergveld, *Surf. Sci.* **135** (1983) 479–496.
28. C. Cichos and Th. Geidel, *Colloid Polym. Sci.* **261** (1983) 947–953.
29. N. Kallay and D. Čakara, *J. Colloid Interface Sci.* **232** (2000) 81–85.
30. N. Kallay, A. Čop, E. Chibowski, and L. Holysz, *J. Colloid Interface Sci.* **259** (2003) 89–96.
31. N. Kallay, Z. Dojnović, and A. Čop, *J. Colloid Interface Sci.* **286** (2005) 610–614.
32. T. Preočanin, W. Janusz, and N. Kallay, *Colloids Surf., A* **297** (2007) 30–37.
33. T. Preočanin, A. Čop, and N. Kallay, *J. Colloid Interface Sci.* **299** (2006) 772–776.
34. W. Piasecki, *Langmuir* **19** (2003) 9526–9533.
35. T. Hiemstra and W. H. van Riemsdijk, *J. Colloid Interface Sci.* **301** (2006) 1–18.
36. J. S. Noh and J. A. Schwarz, *J. Colloid Interface Sci.* **130** (1989) 157–164.
37. S. Žalac and N. Kallay, *J. Colloid Interface Sci.* **149** (1992) 233–240.
38. N. Kallay and S. Žalac, *Croat. Chem. Acta* **67** (1994) 467–479.
39. T. Preočanin and N. Kallay, *Croat. Chem. Acta* **71** (1998) 1117–1125.
40. T. Preočanin and N. Kallay, *Croat. Chem. Acta*, **79** (2006) 95–106.
41. E. Matijević and N. Kallay, *Croat. Chem. Acta* **56** (1983) 649–661.
42. N. Kallay, M. Tomić, B. Biškup, I. Kunjašić, and E. Matijević, *Colloids Surf.* **28** (1987) 185–197.
43. N. Kallay and E. Matijević, *J. Colloid Interface Sci.* **83** (1981) 289–300.
44. N. Kallay, Ž. Torbić, M. Golić, and E. Matijević, *J. Phys. Chem.* **95** (1991) 7028–7032.
45. N. Kallay, D. Kovačević, I. Dedić, and V. Tomašić, *Corrosion* **50** (1994), 598–602.
46. N. Kallay, T. Preočanin, and T. Ivšić, *J. Colloid Interface Sci.* **309** (2007) 21–27.
47. W. Smit and C. L. M. Holten, *J. Colloid Interface Sci.* **78** (1980) 1–5.
48. N. Sahai and D. A. Sverjensky, *Geochim. Cosmochim. Acta* **61** (1997) 2801–2826.
49. J. Lützenkirchen, *J. Colloid Interface Sci.* **217** (1999) 8–18.
50. M. Čolić, D. W. Fuerstenau, N. Kallay, and E. Matijević, *Colloids Surf.* **59** (1991) 169–185.
51. N. Kallay, M. Čolić, D. W. Fuerstenau, H. M. Jang, and E. Matijević, *Colloid Polym. Sci.* **272** (1994) 554–561.
52. J. Westall and H. Hohl, *Adv. Colloid Interface Sci.* **12** (1980) 265–294.
53. W. G. Eversole and P. H. Lahr, *J. Chem. Phys.* **9** (1941) 530–534.
54. D. Kovačević, N. Kallay, I. Antol, A. Pohlmeier, H. Lewandowski, and H.-D. Narres, *Colloids Surf., A* **140** (1998) 261–267.
55. N. Kallay, A. Čop, D. Kovačević, and A. Pohlmeier, *Prog. Colloid Polym. Sci.* **109** (1998) 221–226.
56. D. Kovačević, I. Kobal, and N. Kallay, *Croat. Chem. Acta* **71** (1998) 1139–1153.
57. D. Kovačević, A. Pohlmeier, G. Özbas, H.-D. Narres, and N. Kallay, *Prog. Colloid Polym. Sci.* **112** (1999) 183–187.
58. D. Kovačević, A. Pohlmeier, G. Özbas, H.-D. Narres, M. J. Schwuger, and N. Kallay, *Colloids Surf., A* **166** (2000) 225–233.
59. N. Kallay and E. Matijević, *Langmuir* **1** (1985) 195–201.
60. Y. Zhang, N. Kallay, and E. Matijević, *Langmuir* **1** (1985) 201–206.
61. N. Kallay, T. Preočanin, J. Marković, and D. Kovačević, *Colloids Surf., A* (2007), in press.
62. N. Kallay, S. Žalac, and G. Štefanić, *Langmuir* **9** (1993) 3457–3460.
63. N. Kallay, T. Preočanin, S. Žalac, H. Lewandowski, and H. D. Narres, *J. Colloid Interface Sci.* **211** (1999) 401–407.
64. M. von Smoluchowski, *Physik. Z.* **17** (1916) 557–585.
65. N. Kallay and I. Krznarić, *Indian J. Chem., Sect A* **15** (1977) 396–398.
66. N. Kallay, *Kinetic Interpretation of the Coagulation Processes*, Ph.D. Thesis, Faculty of Science, University of Zagreb, Zagreb, 1973.
67. B. V. Derjaguin and L. Landau, *Acta Physicochim., URSS* **14** (1941) 733–762.
68. E. J. W. Verwey and J. Th. Overbeek, *Theory of Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.
69. N. Kallay and S. Žalac, *Croat. Chem. Acta* **74** (2001) 479–497.
70. P. G. De Gennes, *Croat. Chem. Acta* **71** (1998) 833–836.

SAŽETAK

Ravnoteže u električnom međupovršinskom sloju

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Ravnoteža na međupovršini kruto/tekuće predmet je brojnih eksperimentalnih i teorijskih istraživanja. U literaturi su predloženi različiti modeli koji opisuju strukturu električnog međupovršinskog sloja i mehanizme površinskih reakcija. Za sada se čini nemogućim odrediti koji od modela najbolje opisuje stanje na površini. Jedan od putova prema rješenju ovog problema je razvoj novih eksperimentalnih metoda i simultana interpretacija dobivenih rezultata (npr. adsorpcijska mjerenja, mjerenja površinskog potencijala, površinske gustoće naboja, elektrokinetičkog potencijala, itd.). Takav pristup interpretaciji rezultata omogućava uočavanje razlika među predloženim modelima i odabir najboljeg. Drugi mogući put je razvoj novih, realističnijih teorijskih koncepata koji sadrže manje pretpostavki. Ovaj članak donosi pregled takvih pokušaja (opis strukture električnog međupovršinskog sloja, uvjet elektroneutralnosti površine, mjerenje površinskog potencijala i entalpije površinskih reakcija, određivanje električkih kapaciteta unutar električnog međupovršinskog sloja i koloidne stabilnosti, itd.), s posebnim naglaskom na ulogu Nikole Kallaya u području koloidne i međupovršinske kemije, kome i posvećujemo ovaj rad povodom šezdeset i petog rođendana.