

Electrical interfacial layer at solid/liquid interface*

N. Kallay, A. Čop, D. Kovačević, K. Majorinc, T. Preočanin and S. Žalac
*Laboratory of Physical Chemistry, Department of Chemistry, Faculty of
Science, University of Zagreb, Marulićev trg 19, P.O. BOX 163,
10 001 Zagreb, Croatia*

Some problems related to the theoretical concepts applied in studying interfacial equilibria at solid/liquid interfaces are discussed. It was shown that assumptions related to the mechanism of surface reactions and the structure of interfacial layer need to be reconsidered. The commonly used 3-layer models were considered as simplification of the general 4-layer model. The concept of the capacitors of constant capacitances was discussed. The equilibrium at the electrical interfacial layer was used to discuss the colloid stability phenomenon. The Schulze-Hardy rule, *i.e.* the effect of the lyotropic series was explained on the basis of equilibrium constants of counterion association with charged surface groups. It was concluded that new experimental methods are necessary for further progress in this area. The second route is to apply all existing experimental methods to one sample and to interpret the data simultaneously.

* Based on the lecture presented by N. Kallay on the occasion of his 60th birthday, who is grateful to his old friend Fritz Krempler for endless discussions on the subject of the electrical interfacial layer. These discussions resulted in inspiration and determination for science and scientific approach to the research.

We would also like to express appreciation for extensive collaboration with scientists from UMCS, which was initiated by a dear friend, late Professor Jerzy Szczypa.

*Non in fortuna sed labore
In asperis et prosperis
Vivit post funera virtus*

1. INTRODUCTION

Surface Complexation Model (SCM), together with the Electrical Interfacial Layer Model (EIL), serves as a tool for understanding the equilibria at solid/liquid interfaces [1,2]. In their quantitative form, they are used for evaluation of equilibrium parameters by interpreting the experimental data. These two concepts are enough general, so that they may be in principle applied to any system. However, they are still approximative and should be further refined. The problem is that some assumptions are not verified, and the fact that they do not contradict to experimental findings cannot be used as the test of their validity. It is known that several different variations of the original models agree with the experiments, which is mainly due to numerous adjustable equilibrium parameters, and due to relatively low accuracy of the measured data. The question is in which direction one should orient the research. Accumulation of data for different systems and interpretation by chosen models does not solve the problem. It is clear that we need better experiments, we need to apply new techniques for determination of the structure of interfacial complexes, but we also need to have more accurate data and to apply the correct mathematical analysis that takes into account the statistical weights of the experimental points. Another concept would be to use all available data, obtained with different techniques, and to interpret them simultaneously. Such an approach would result in constraints that will probably distinguish between different variations of SCM and EIL and may lead to the choice of the most representative theoretical concept. Applying this approach, we have introduced electrokinetic data and have interpreted them simultaneously together with adsorption [3-9], surface charge [10] or surface potential [11] data. An additional question is how far one may proceed in refining the basic SCM and EIL models. It is obvious that more refined model contains more (adjustable) equilibrium parameters and consequently will better fit the experimental data. However, it does not mean that such a model represents the physical situation at the interface better. Therefore, it is reasonable to conclude that one should proceed with refinement if significantly better fit is obtained, but also if there are other theoretical or experimental evidences that support such attempts.

In this article we shall discuss some theoretical and experimental aspects of the problems related to examination of the interfacial equilibria at the solid/liquid interface.

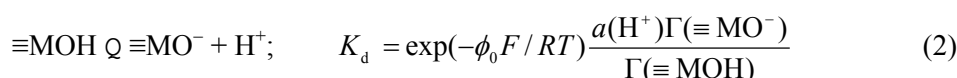
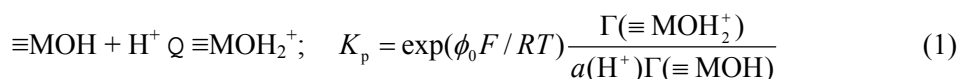
2. SOLID/LIQUID INTERFACE

Surface Complexation Model and Equilibrium Constants. Surface Complexation Model considers equilibrium of the reactions of defined surface groups with bulk ions and/or molecules. This concept is, from the chemical point of view, superior to those based on accumulation of bulk species at the interface. The model based on defined surface reactions was for the first time suggested more than thirty years ago [12]. The model was in 1974 refined by Yates, Levine and Healy [13] as Site Binding Model. Later, the name Surface Complexation Model was introduced [14-16]. Our early attempts were essentially similar to that concept. We have considered a colloid particle as "molecular entity" with the "valency" equal to the number of active surface sites [17-19]. The statistical treatment enabled us to obtain the number of bound ions to one colloid particle, *i.e.* the particle charge. The advantage of this approach was that the distribution among particles was also obtained. The problem was solved only for two limiting cases; for zero and also for infinite ionic strength. The second shortcoming of the treatment of colloid particles as a "molecules" is that their "valency" depends directly on their size; it is proportional to the surface area. This problem was avoided in the SCM by introducing surface concentrations of reactant and product species at the interface. In addition, the definition of the equilibrium constants with an exponential term that takes into account electrostatic interactions makes SCM model superior in common use.

There are two assumptions involved in SCM. The first one is postulation of the mechanism of the surface reaction, and the second one is related to the definition of the surface equilibrium constant. Several different mechanisms of surface reactions were assumed to be responsible for the charging mechanism at the solid/liquid interface, namely 1-pK [20], 2-pK [21], MUSIC [22-24] and CD-MUSIC [25,26] models. All mentioned models could fit the measured data so that interpretation of the experiments cannot be used to decide which concept is more realistic. In our work, we were using the 2-pK concept for simple reason; this original approach was enough refined to successfully interpret the measured data. The physical reason for not using 1-pK concept is that it seems to us that the charge number of surface species should be +1 or -1 (± 1), but not e.g. $\pm \frac{1}{2}$, in order to produce enough electrostatic attraction towards counterions so that they could be bound. Another reason is that 2-pK concept predicts, in some cases, change in the slope in the zero charge region, which is not the case if 1-pK concept is applied. We consider this question still open for discussion and further research, concluding that probably some systems are more close to 1-pK concept while other behave more close to the 2-pK concept. More elaborated models as MUSIC and CD-MUSIC are advantageous since they take into account different mechanisms and the surface heterogeneity. Regarding the traditional terminology, one may say that the terms "1-pK" and "2-pK" are not the best choices. In fact, the term "1-pK"

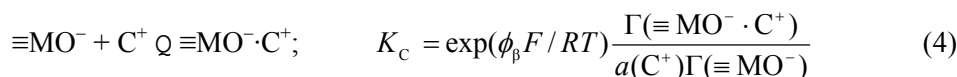
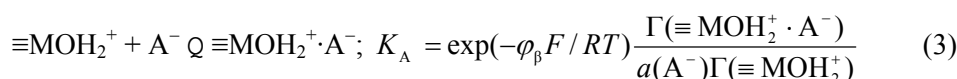
means that one reaction mechanism, characterized by one equilibrium constant, is responsible for charging of the interface. Similar applies to "2-pK model" which considers the amphoteric behaviour of the surface sites that can be either protonated or deprotonated. However, the terminology is not subject of this article and is of minor importance. For the sake of simplicity, further discussion will be based on the traditional "2-pK" model ("Amphoteric Model").

According to 2-pK mechanism amphoteric surface sites ($\equiv\text{MOH}$) on metal oxide surface, developed by hydration, undergo charging by protonation and deprotonation, with extents depending on the pH of aqueous solution



where Γ denotes equilibrium surface concentration, ϕ_0 the potential in 0-plane affecting the state of charged surface species, K_p and K_d are thermodynamic surface equilibrium constants, a is activity in the bulk of solution, while F , R and T have their usual meaning.

Counterions (anions A^- and cations C^+) from the solution associate with charged surface sites according to



Traditionally, for the equilibrium constants, as defined above, the term "intrinsic" equilibrium constant was used. The origin of this term is the original treatment according to which particular surface reaction was split into two steps. For example, in the protonation reaction, the first step is transport of the H^+ ion from the bulk of solution to the "intrinsic state" and the second step is binding of H^+ ion from the "intrinsic state" to the surface site. First step was described by the Boltzmann function, while the second one by the "intrinsic" equilibrium constant. The same exponential term in the expression for the equilibrium constant could be obtained by introducing the activity coefficients of surface species, and it could be shown that "intrinsic" equilibrium constant is in fact the thermodynamic equilibrium constant of a given surface reaction [27]. The

exponential term could be also considered as an electrostatic correction term for the equilibrium constant. In any case, the use of the exponential term, with electrostatic potential affecting the state of charged surface species, implies that species of the same kind are exposed to the same potential. Moreover, the consequence of such approach is that $\equiv\text{MOH}_2^+$ and $\equiv\text{MO}^-$ surface species are assumed to be exposed to the same ϕ_0 potential. It is clear that electrostatic potentials affecting the states of these charged surface groups are closely related so that it may be concluded that such a practice would not lead to disagreements with experimental finding, but would rather affect the obtained values of equilibrium constants. In the case of counterion association, the situation is somehow less complicated since in the "positive region" association of anions takes place, while in the "negative region" the associated counterions are cations. In the case of counterion association there is no region where both $\equiv\text{MOH}_2^+\cdot\text{A}^-$ and $\equiv\text{MO}^-\cdot\text{C}^+$ are present at the interface, as it is in the case of $\equiv\text{MOH}_2^+$ and $\equiv\text{MO}^-$ groups. However, as it is known from the solution studies, electrostatic ion pairs are not characterized by just one separation distance, but rather distributed in the association space between two limits (distance of closest approach and the Bjerrum critical separation distance). Consequently, the associated counterions are not exposed to the same and constant ϕ_b -potential. This problem was solved by introducing the Bjerrum concept to surface association, but the resulting equations are somehow too complicated for use in the regression analysis commonly applied in the data interpretation [28,29].

Electrostatic Interfacial Layer. In the interpretation of the interfacial equilibrium one cannot avoid to use the relationships between surface charge densities and electrostatic potentials at certain assumed planes. At first one should assume certain structure of the electrical interfacial layer (EIL). In the literature one is able to find different models of EIL [3]. It is clear that the simple Helmholtz and Gouy-Chapman models cannot explain the experimental findings. However, the combination of these two opposite extremes (Stern model) was found to be applicable. Several different combinations were proposed. Our early work was influenced by the F. Krempel [30] approach according to whom the significant potential drop occurs in a layer between the plane in which centers of associated counterions are located and the electrokinetic slipping plane. Properties of this layer depend on the type of solvent. In electrophoresis, this layer moves together with the particle so that outer plane of this layer is the electrokinetic slipping plane, while in the inner plane the centers of associated counterions are located. As it will be shown, Leckie [14-16] assumed that slipping plane is identical to the onset of diffuse layer, while we have assumed that slipping plane is located within the diffuse layer. By analyzing the common practice, we have concluded that all variations

of the Helmholtz-Gouy-Chapman-Stern model could be covered by the general model 4-layer model (Figure 1), which could be easily simplified into two different types of 3-layer models (Figures 2 and 3).

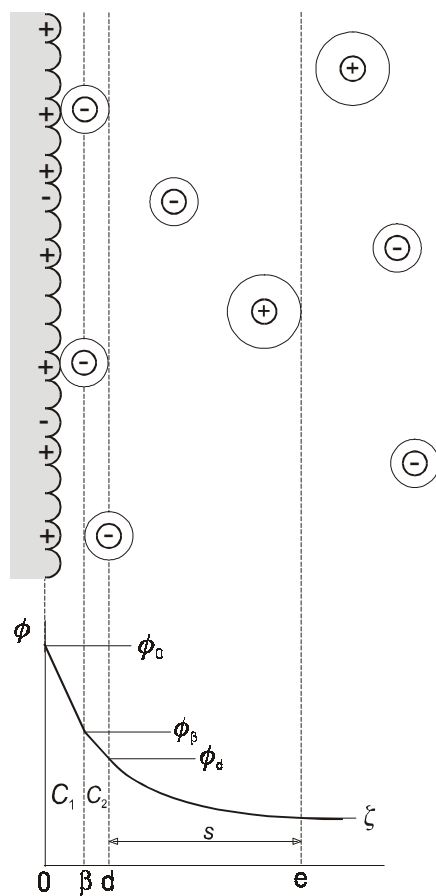


Fig. 1. Schematic presentation of the general 4-layer model of the electrical interfacial layer. Reproduced with permission from Croatica Chemica Acta [2]

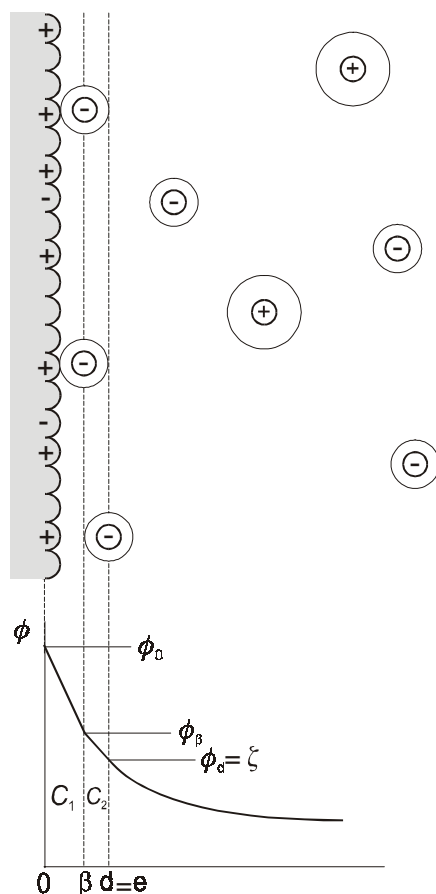


Fig. 2. Schematic presentation of the 3-layer model of the electrical interfacial layer as proposed by Davis, James and Leckie [14-16], with assumption $\phi_d = \zeta$. Reproduced with permission from Croatica Chemica Acta [2]

The first choice (Figure 2), introduced by Leckie and coworkers [14-16], assumes the potential drop between β -plane and the onset of the diffuse layer, the potential of which corresponds to the electrokinetic potential. The second choice, preferred by us, (Figure 3) assumes that β -potential is equal to the potential at the onset of diffuse layer, but introduces the concept of the slipping plane separation, so that electrokinetic potential becomes lower in magnitude with respect to the potential at the onset of diffuse layer. This problem will be discussed in more details later.

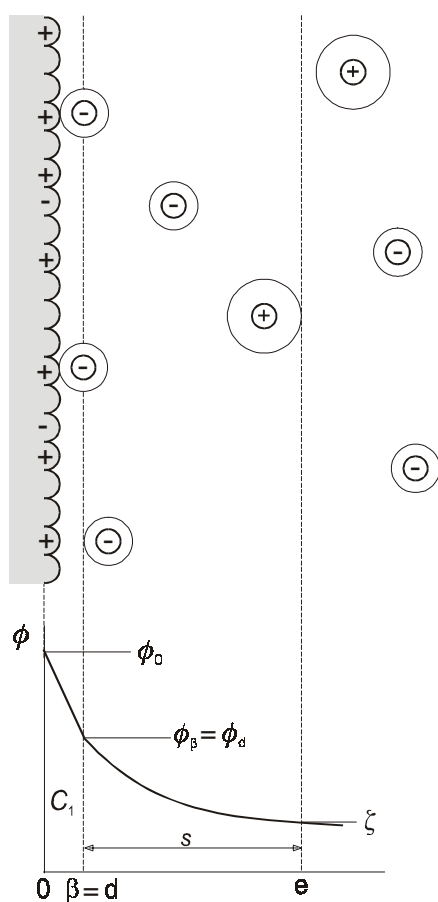


Fig. 3. Schematic presentation of the 3-layer model of the electrical interfacial layer, with assumption $\phi_{\beta} = \phi_d$. Reproduced with permission from Croatica Chemica Acta [2]

Surface Charge Densities. Within the EIL model one may define surface concentrations and the surface charge densities in the following way.

The total surface concentration (Γ_{tot}) of active surface sites is

$$\Gamma_{\text{tot}} = \Gamma(\equiv\text{MOH}) + \Gamma(\equiv\text{MOH}_2^+) + \Gamma(\equiv\text{MO}^-) + \Gamma(\equiv\text{MO}^- \cdot \text{C}^+) + \Gamma(\equiv\text{MOH}_2^+ \cdot \text{A}^-) \quad (5)$$

Surface charge density in 0-plane (σ_0), where the charges produced by interaction with potential determining ions are located, is

$$\sigma_0 = F(\Gamma(\equiv\text{MOH}_2^+) + \Gamma(\equiv\text{MOH}_2^+ \cdot \text{A}^-) - \Gamma(\equiv\text{MO}^-) - \Gamma(\equiv\text{MO}^- \cdot \text{C}^+)) \quad (6)$$

while surface charge density in β -plane (σ_β), where associated counterions are located, is

$$\sigma_\beta = F(I(\equiv\text{MO}^- \cdot \text{C}^+) - I(\equiv\text{MOH}_2^+ \cdot \text{A}^-)) \quad (7)$$

The net surface charge density (σ_s) is neutralized by the charge in diffuse layer (σ_d)

$$\sigma_s = -\sigma_d = \sigma_0 + \sigma_\beta = F(I(\equiv\text{MOH}_2^+) - I(\equiv\text{MO}^-)) \quad (8)$$

Surface Potentials. The important problem in quantitative description of the EIL is the relationships between surface charge densities and corresponding electrostatic potentials. The potential drop between the 0-plane and the β -plane is commonly described by the constant capacitance (C_1) of the inner Helmholtz layer

$$C_1 = \frac{\sigma_0}{\phi_0 - \phi_\beta} \quad (9)$$

while the potential drop between β -plane and the onset of diffuse layer (d-plane) depends on the capacitance of the outer Helmholtz layer (C_2).

$$C_2 = \frac{\sigma_\beta}{\phi_\beta - \phi_d} \quad (10)$$

The Leckie 3-layer model, presented on Figure 2, is characterized by the potential drop between β - and d-planes that correspond to $C_2 < \infty$. Such an assumption was necessary due to the statement that $\phi_d = \zeta$. The main reason for such a choice is that experiments require $|\phi_0| > |\phi_\beta| > |\zeta|$. If one assumes slipping plane separation, then the above requirement is satisfied also if β - and d-planes are taken as identical ($\phi_\beta = \phi_d$; $C_2 \rightarrow \infty$). These two different simplifications of the general model could be described quantitatively by

$$|\phi_0| > |\phi_\beta| > |\phi_d = \zeta|; C_2 \rightarrow \infty$$

and

$$|\phi_0| > |\phi_\beta = \phi_d| > |\zeta|; C_2 < \infty$$

Apart from the problems related to the choice between these two different simplifications of the general EIL, the introduction of the constant capacitance concept, as commonly accepted, remains unjustified. Let us consider the first capacitor C_1 . The question is why σ_0 is introduced in relationship but not σ_β . The simple electrostatics, considering parallel capacitors, would suggest the second choice, and not the first one as commonly accepted.

The additional problem is the equilibrium in the diffuse part of EIL for which the Gouy-Chapman theory is used. According to this theory surface charge density in the diffuse layer (σ_d) is related to ϕ_d by

$$\sigma_d = -\sqrt{8RT\varepsilon I_c} \sinh \frac{\phi_d F}{2RT} \quad (11)$$

where ε is medium permittivity and I_c ionic strength. In addition to the already known problems related to the approximations implied in the Gouy-Chapman theory, the use of the above equation requires the representative and exact values of the surface charge density. Let us imagine the surface that is rough on the nanometer scale. In such a case, one should consider that the surface area corresponding to σ_d is smaller than the surface area related to σ_0 and σ_β . By ignoring this fact, the relationships between potentials of different planes in the EIL become questionable.

According to the Gouy-Chapman theory, the ϕ_d -potential is related to the electrostatic potential (ϕ_x) at the distance x from the onset of the diffuse layer by

$$\phi_d = 2RTF^{-1} \ln \left[\frac{\exp(-x\kappa) + \tanh(F\phi_x/4RT)}{\exp(-x\kappa) - \tanh(F\phi_x/4RT)} \right] \quad (12)$$

where reciprocal Debye-Hückel length κ is given by

$$\kappa = \sqrt{\frac{2I_c F^2}{\varepsilon RT}} \quad (13)$$

The pH-dependency of surface potential ϕ_0 can be derived from Eqs. (1,2) as

$$\begin{aligned} \phi_0 &= \frac{RT}{2F} \ln \frac{K_p}{K_d} - \frac{RT}{2F} \ln \frac{\Gamma(\equiv \text{MOH}_2^+)}{\Gamma(\equiv \text{MO}^-)} + \frac{RT}{F} \ln a(\text{H}^+) = \\ &= \frac{RT \ln 10}{F} (\text{pH}_{\text{pzc}} - \text{pH}) - \frac{RT \ln 10}{2F} \log \frac{\Gamma(\equiv \text{MOH}_2^+)}{\Gamma(\equiv \text{MO}^-)} \end{aligned} \quad (14)$$

In certain pH range surface potential ϕ_0 is approximately linear with respect to pH, with the slope lower than $RTF^{-1} \ln 10$. The deviation from ideality could be expressed by factor α as

$$\phi_0 = \alpha \frac{-RT \ln 10}{F} (\text{pH} - \text{pH}_{\text{pzc}}) \quad (15)$$

Measurements of the surface potential ϕ_0 are not popular. Penners and Lyklema measured the potential of the platinum electrode covered by the hematite [39]. The slope was found to be close to the Nernstian. Avena and coworkers obtained significantly lower slope with titania electrode [40]. These results suggested that measurements of the surface potential might help in understanding the interfacial equilibria at the solid liquid interface. However, the problem with metal oxide electrodes is that one cannot be sure that measured electrode potential is directly related to the surface potential. It is possible that porosity of oxide layer makes electrode to behave as the electrode of the second kind. To solve this problem we have constructed the ice electrode that is not porous. The slope of ice electrode was significantly lower than the Nernstian due to sodium ion association [41]. In addition, the comparison with the electrokinetic data enabled us also to estimate the equilibrium parameters for ice/water interface [11]. These kinds of measurements may help in characterization of other systems. For that purpose it might be advisable to use field effect transistors [42,43] and membrane electrodes with PVC carriers [44].

Zero Charge Condition. Zero charge condition at the surface is commonly described by two quantities, *i.e.* by the isoelectric point (*i.e.p.*) and by the point of zero charge (*p.z.c.*). Isoelectric point corresponds to the condition at which $\zeta = \phi_d = 0$, and consequently to the zero effective charge; $\sigma_s = -\sigma_d = 0$. The point of zero charge is defined through the consumption of potential determining ions from the bulk of the solution. In the case of metal oxides, the point of zero charge corresponds to pH at which



In the absence of specific adsorption, *p.z.c.* corresponds also to $\sigma_0 = 0$. The third zero charge condition is the point of zero potential (*p.z.p.*) defined by $\phi_0 = 0$.

In the absence of specific adsorption, and in the case of negligible ($I(\equiv\text{MOH}_2^+ \cdot \text{A}^-) = 0$, $I(\equiv\text{MO}^- \cdot \text{C}^+) = 0$) or symmetric ($I(\equiv\text{MOH}_2^+ \cdot \text{A}^-) = I(\equiv\text{MO}^- \cdot \text{C}^+)$) counterion association, at *i.e.p.* all interfacial potentials (ϕ_0 , ϕ_p , ϕ_d)

are zero, and also $\sigma_0 = 0$, $\sigma_s = 0$, $\Gamma(\equiv\text{MOH}_2^+) = \Gamma(\equiv\text{MO}^-)$ so that all three zero charge conditions coincide

$$\text{pH}_{\text{pzc}} = \text{pH}_{\text{iep}} = \text{pH}_{\text{pzp}} = \frac{1}{2} \cdot \log \frac{K_p}{K_d} \quad (17)$$

Point of zero charge and the isoelectric point are important characteristics of the system. They separate the region of the positively charged surface from the region where surface bears the negative charge. Such finding is useful for consideration of the coagulation and adhesion phenomena. Also, if these two points coincide one may conclude that no specific adsorption takes place. In the opposite case one may deduce the charge of species that are specifically adsorbed. In addition, the temperature dependency of the point of zero charge enables evaluation of the difference in standard enthalpies of protonation and deprotonation reactions [45,46]. For that purpose the "mass titration method" *i.e.* the measurements of temperature dependency of pH of concentrated suspension was found to be suitable [47,48]. Temperature dependency of pH_{pzc} yields standard enthalpy and entropy change, while calorimetric data are influenced by the electrostatic effects [49-51]. It should be noted here that values of thermodynamic quantities directly depend on the assumed mechanism, and also on the way how the stoichiometric reaction equation is written [52]. The isoelectric point of conductive metallic surfaces is also an important parameter, especially in considering adsorption and adhesion phenomena. Except for metallic colloid particles, the classical electrokinetic cannot be applied so that "adhesion method" was introduced showing that electrical properties of metallic surfaces are closely related to the corresponding metal oxides [53,54].

3. EFFECT OF ELECTROLYTES ON THE COLLOID STABILITY

Stability of colloids in aqueous electrolyte solutions is due to electrostatic interactions *i.e.* determined by the equilibrium at their interfacial layers. The increase of electrolyte concentration is followed by simultaneous increase of counterion concentration and consequently increase in the extent of their association at the surface. The net surface charge is reduced so that substantial drop of the φ_d potential occurs. This phenomenon reduces electrostatic repulsion and promotes the aggregation. The second reason for the instability is so called compression of the diffuse layer. In this paragraph we shall analyze the effect of association of counterions at the interface on the colloid stability. It will be shown that their specificity (Schulze-Hardy rule) is characterized by the surface association equilibrium constants (Eqs. 3,4).

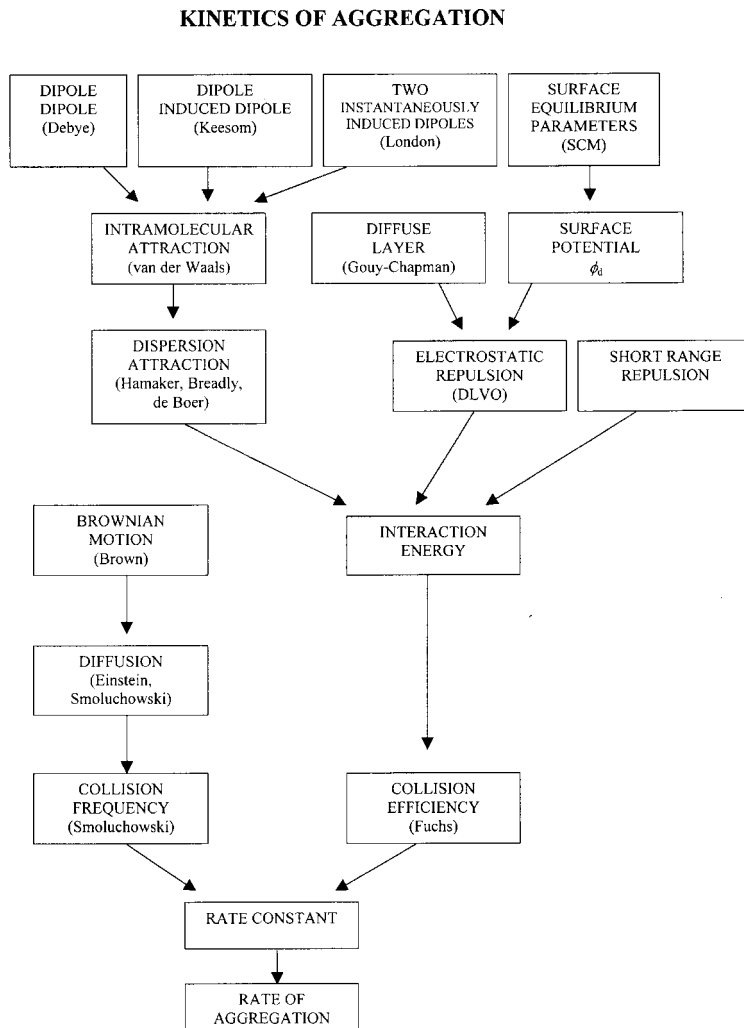


Fig. 4. Different theoretical contributions to the general theory of the colloid stability. Reproduced with permission from Croatica Chemica Acta [2]

The aggregation rate of colloid particles is determined by the collision frequency and collision efficiency (see Fig 4). The later quantity is reciprocal value of the commonly defined stability coefficient (W) and depends on the interaction energy barrier

$$W = 2r \int_0^{\infty} \frac{\exp(E/RT)}{x^2} dx \quad (18)$$

where r is radius of spherical particles and x is the separation distance between two interacting particles. Interpretation of the aggregation kinetics in the electrolyte solution requires the knowledge of the total interaction energy (E) which may be taken as a sum of the electrostatic repulsion between two particles (E_{el}), dispersion van der Waals attraction (E_{vdW}) and short range repulsion (E_r)

$$E = E_{el} + E_{vdW} + E_r \quad (19)$$

For the purpose of this study, we shall consider interaction of two identical spherical particles of radius r with the potential at the onset of diffuse layer ϕ_d . The Hogg, Healy, Fuerstenau (HHF) approximation [55] for electrostatic interaction energy between two charged particles separated by distance x with the same surface potentials ϕ_d yields

$$E_{el} = 2\pi\epsilon r\phi_d^2 \ln [1 + \exp(-\kappa x)] \quad (20)$$

For the same system, according to Hamaker [56], the attractive dispersion contribution E_{vdW} is given by

$$E_{vdW} = -A_H \frac{r}{12x} \quad (21)$$

where A_H is the Hamaker constant. Short-range repulsion (E_r) could be approximated by a "hard wall concept" ($E_r = 0$ at $x > x_{min}$ and $E_r = \infty$ at $x < x_{min}$).

Theoretical interpretation of the slow aggregation in the presence of the energy barrier is not straightforward. The problem lies in the Hamaker constant (Eq. 21), which is commonly accepted as adjustable parameter, but also in the unknown value of the surface potential determining the electrostatic repulsion.

According to the SCM, equilibrium at the metal oxide/liquid interface is characterized by several parameters. They are: total surface concentration of surface sites (Γ_{tot}), four equilibrium constants (K_p , K_d , K_A , K_C) and one or two capacitances (C_1 , C_2). The values of these parameters could be obtained by interpretation of adsorption measurements and electrokinetic data. For the aggregation kinetic, the potential at the onset of diffuse layer is essential (see Eq. 20). This potential can be easily calculated once the interfacial equilibrium parameters are known. Another possibility is to use Eq. (12) and calculate ϕ_d potential from measured ζ -potential.

According to the Eq. (17), the value of pH_{iep} is given by the ratio of protonation and deprotonation equilibrium constants. The dependency of the ϕ_d potential on pH for two metal oxides of the same pH_{iep} , but characterized with different K_p and K_d , values, is presented in Figure 5. It is obvious that low

values of K_p and K_d result in the broad region of low surface potential around the isoelectric point. Therefore, one may conclude that in such a case a broad instability region may be expected which is not a case if the values of K_p and K_d are enough high.

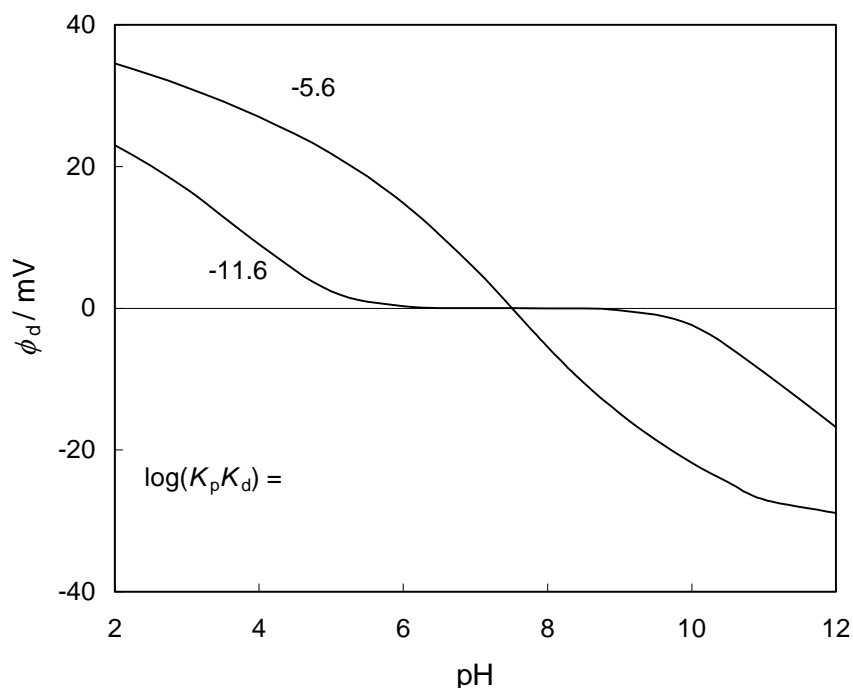


Fig. 5. Dependency of the ϕ_d potential on pH for two metal oxides of the same $\text{pH}_{\text{iep}} = \text{pH}_{\text{pzc}} = 7.5$, at 25°C and $I_c = 10^{-2} \text{ mol dm}^{-3}$. In the numerical simulation the following values of parameters were used: $r = 30 \text{ nm}$, $K_A = K_C = 1500$, $\Gamma_{\text{tot}} = 1.5 \times 10^{-5} \text{ mol dm}^{-3}$, $C_1 = 2 \text{ F m}^{-1}$;
 (a) $-\log(K_p K_d) = 5.6$ ($K_p = 5 \times 10^4$, $K_d = 5 \cdot 10^{-11}$)
 (b) $-\log(K_p K_d) = 5.6$ ($K_p = 50$; $K_d = 5 \times 10^{-14}$)

Figure 6 shows the $\phi_d(\text{pH})$ function calculated for the symmetric ($K_A = K_C$) and also for asymmetric ($K_A > K_C$) counterion association at different ionic strengths. The significant reduction in the magnitude of ϕ_d potential due to increase of the ionic strength was observed (full lines). In addition, the leveling of the $\phi_d(\text{pH})$ function is notable, especially at higher ionic strength. Since the rapid coagulation takes place at relatively high concentrations of 1:1 electrolytes, one may conclude that in the pH-region enough far (2-3 pH units) from pH_{iep} , the critical coagulation concentrations (c.c.c.) would not depend significantly on the pH. Such conclusion was supported experimentally [57]. In the case of higher association affinity of anions (with respect to cations) the

isoelectric point shifts towards lower pH-values (dashed line) changing the instability domain, respectively.

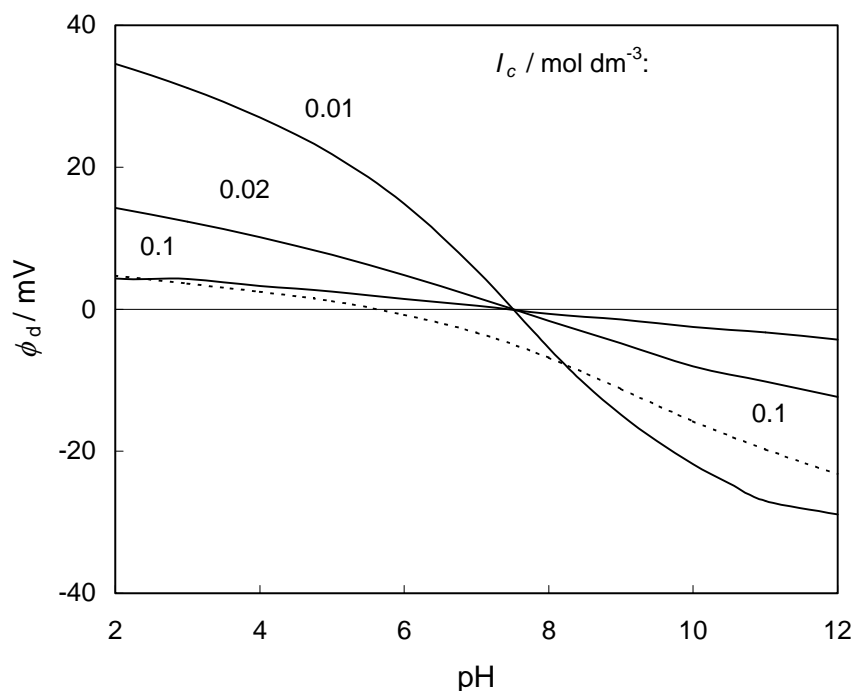


Fig. 6. Dependency of ϕ_d potential on pH calculated for the symmetric ($K_A = K_C = 1500$, full lines) and asymmetric ($K_A = 1500$; $K_C = 100$, dashed line) counterion association at 25 °C and different ionic strengths. In the numerical simulation the following values of parameters were used: $r = 30$ nm, $K_p = 5 \times 10^4$, $K_d = 5 \times 10^{-11}$, $\Gamma_{\text{tot}} = 1.5 \times 10^{-5}$, $C_1 = 2$ F m $^{-1}$

According to the HHF equation Eq. (20), the electrostatic repulsion decreases by electrolyte addition due to two reasons. At higher electrolyte concentration the κ value is higher and consequently the factor $\exp(-\kappa x)$ representing the "compression of the diffuse layer" decreases reducing the electrostatic repulsion. This effect is not specific; all 1:1 electrolytes will exhibit the same behaviour. The second effect, connected with decrease of the ϕ_d potential, is specific since it is determined mainly by the counterion association, *i.e.* by the association equilibrium constant (K_A in positive pH-region and K_C in the negative pH-region.).

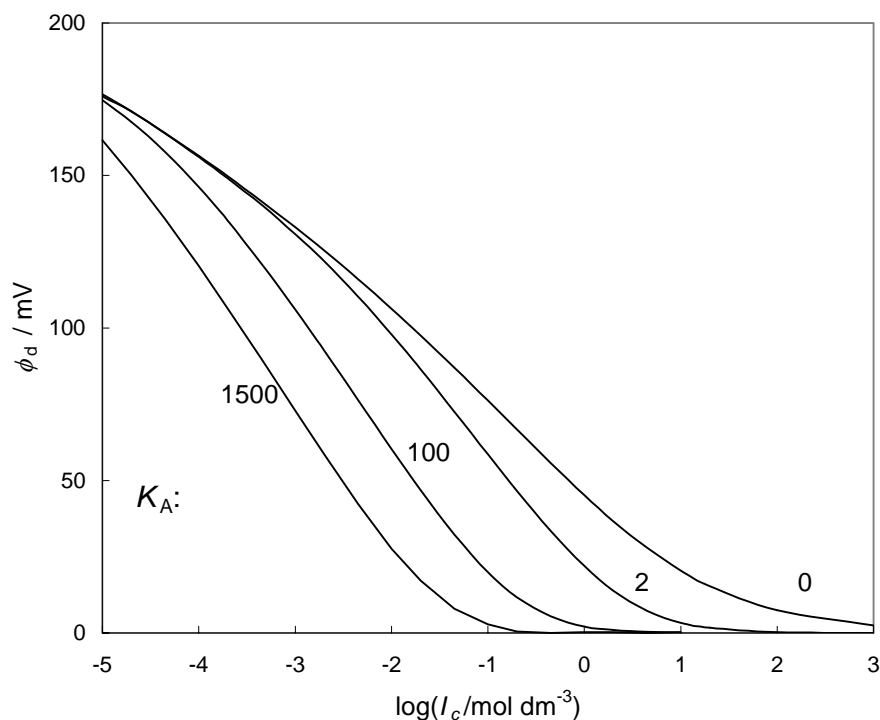


Fig. 7. Effect of counterion (anion) association constant K_A on the $\phi_d(\log I_c)$ function at pH = 4 and 25 °C. In the numerical simulation the following values of parameters were used: $r = 30$ nm, $K_p = 5 \times 10^4$, $K_d = 5 \times 10^{-11}$, $K_C = 100$, $\Gamma_{\text{tot}} = 1.5 \times 10^{-5}$, $C_1 = 2$ F m $^{-1}$

Figure 7 shows the effect of electrolytes on the potential at the onset of diffuse layer ϕ_d . Calculations were performed using different values of counterion association equilibrium constants; from 0 to 1500. It is clear that ϕ_d potential decreases (almost) to zero value at extremely high electrolyte concentrations. However, the concentrations of electrolyte, required for $\phi_d = 0$ (or *e.g.* 25 mV) conditions, is significantly decreased for counterions with higher association affinity. Figure 7 demonstrates that counterion association plays essential role in the aggregation kinetics but also that even in the absence of counterion association ϕ_d drops to zero at (extremely) high electrolyte concentrations.

Figure 8 displays effect of ionic strength on the total interaction energy, E_{max} , at the maximum of the $E(x)$ function. The electrolyte concentrations at which E_{max} is reduced to zero may be taken as critical coagulation concentration (c.c.c.). It is obvious that c.c.c. highly depends on the value of counterion association equilibrium constant, which explains the well known observation of

the lyotropic series effects in the coagulation phenomena (Schulze-Hardy rule) [58].

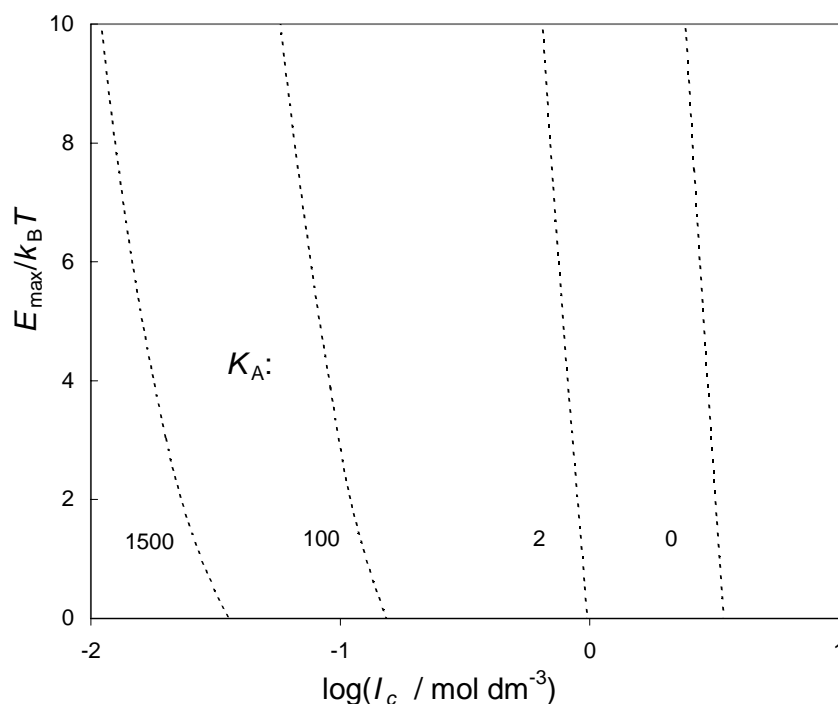


Fig. 8. Dependency of the total interaction energy E_{\max} at the maximum of the $E(x)$ function on the ionic strength at pH = 4 and 25 °C calculated for four counterion association constants: $K_A = 1500; 100; 2; 0$. In the numerical simulation the following values of parameters were used: $r = 30$ nm, $K_p = 5 \times 10^4$, $K_d = 5 \times 10^{-11}$, $K_C = 100$, $\Gamma_{\text{tot}} = 1.5 \times 10^{-5}$, $C_1 = 2$ F m $^{-1}$

REFERENCES

- [1] Kallay N. and Žalac S., *J. Colloid Interface Sci.* 230, 1 (2000).
- [2] Kallay N. and Žalac S., *Croat. Chem. Acta* 74, 479 (2001).
- [3] Kallay N., Kovačević D. and Čop A., *Interpretation of Interfacial Equilibria on the Basis of Adsorption and Electrokinetic Data in Interfacial Dynamics*, (Kallay N., Ed.), Marcel Dekker Inc., New York, 2000.
- [4] Kovačević D., Čop A. and Kallay N., *Evaluation and Usage of Electrostatic Potentials in the Interfacial Layer in Interfacial Electrokinetics and Electrophoresis*, (Delgado A., Ed.), Marcel Dekker Inc., New York, 2002.
- [5] Kovačević D., Kobal I. and Kallay N., *Croat. Chem. Acta* 71, 1139 (1998).
- [6] Kallay N., Kovačević D. and Kobal I., *Stud. Surf. Sci. Catal.* 132, 279 (2001).
- [7] Kovačević D., Čop A., Bradetić A., Kallay N., Pohlmeier A., Narres H.-D. and Lewandowski H., *Progr. Colloid&Polym. Sci.* 117, 32 (2001).

- [8] Kovačević D., Pohlmeier A., Özbas G., Narres H.-D. and Kallay N. *Progr. Colloid&Polym. Sci.* 112, 183 (1999).
- [9] Kovačević D., Pohlmeier A., Özbas G., Narres H.-D., Schwuger M. J. and Kallay N. *Colloids Surf.* 166, 225 (2000).
- [10] Čop A., Kovačević D., Dragić T. and Kallay N., *Colloids Surf.*, submitted.
- [11] Kallay N., Čop A., Chibowski E. and Holysz L., *J. Colloid Interface Sci.*, submitted.
- [12] Schindler P. and Kamber H. R., *Helvetica Chimica Acta* 51 1781 (1968).
- [13] Yates D. E., Levine S. and Healy T. W., *J. Chem. Soc. Faraday Trans 1* 70 1807 (1974).
- [14] Davis J. A., James R. O. and Leckie J. O., *J. Colloid Interface Sci.* 63, 480 (1978).
- [15] Davis J. A. and Leckie J. O., *J. Colloid Interface Sci.* 67, 90 (1978).
- [16] Davis J. A., James R. O. and Leckie J. O., *J. Colloid Interface Sci.* 74, 32 (1980).
- [17] Kallay N., *Croat. Chem. Acta* 48, 271 (1976).
- [18] Fišer I., Kallay N., Kramberger-Živković M. and Krznarić I., *Kem. ind. (Zagreb)* 26, 67 (1977).
- [19] Kallay N., *Croat. Chem. Acta* 50, 209 (1977).
- [20] Bolt G. H. and van Riemsdijk W. H., in *Soil Chemistry, B. Physico-chemical Models*, Bolt G. H. Ed., Elsevier, Amsterdam, 1982.
- [21] Parks G. A., *Chem. Rev.* 65 177; (1965).
- [22] Hiemstra T., van Riemsdijk W. H. and Bolt G. H., *J. Colloid Interface Sci.* 133, 91 (1989).
- [23] Hiemstra T., de Wit J. C. M. and van Riemsdijk W. H., *J. Colloid Interface Sci.* 133, 105 (1989).
- [24] Hiemstra T. and van Riemsdijk W. H., *Colloids Surf.* 59, 7 (1991).
- [25] Hiemstra T. and van Riemsdijk W. H., *J. Colloid Interface Sci.* 179, 488 (1996).
- [26] Venema P., Hiemstra T. and van Riemsdijk W. H., *J. Colloid Interface Sci.* 183, 515 (1996).
- [27] Kallay N., Sprycha R., Tomić M., Žalac S. and Torbić Ž., *Croat. Chem. Acta* 63, 467 (1990).
- [28] Kallay N. and Tomić M., *Langmuir* 4, 559 (1988).
- [29] Tomić M. and Kallay N., *Langmuir* 4, 565 (1988).
- [30] Krempler F., *Notes*, private communication, Zagreb, 1967.
- [31] Torres R., Kallay N. and Matijević E., *Langmuir* 4, 706 (1988).
- [32] Eversole W. G. and Lahr P. H., *J. Chem. Phys.* 9, 530 (1941).
- [33] Eversole W. G. and Boardman W. W., *J. Chem. Phys.* 9, 798 (1941).
- [34] Torres R., Kallay N. and Matijević E., *Langmuir* 4, 706 (1988).
- [35] Hesleitner P., Kallay N. and Matijević E., *Langmuir*, 7, 178 (1991).
- [36] Healy T. W. and White L. R., *Adv. Colloid Interface Sci.* 9, 303 (1978).
- [37] Sprycha R. and Matijević E., *Langmuir* 5, 479 (1989).
- [38] Harding I. H. and Healy T. W., *J. Colloid Interface Sci.* 107, 382 (1985).
- [39] Penners N. H. G., Koopal L. K. and Lyklema J., *Colloids Surf.* 21, 457 (1986).
- [40] Avena M. J., Camara O. R. and De Pauli C. P., *Colloids Surf.* 69, 217 (1993).
- [41] Kallay, N. and Čakara, D., *J. Colloid Interface Sci.* 232, 81 (2000).
- [42] Chicos C. and Geidel Th., *Colloid Polym. Sci.* 261, 947 (1983).
- [43] Bousse L., de Rooij N. F. and Bergveld P., *Surf. Sci.* 135, 479 (1983).
- [44] Matešić-Puač R., Stojanović M., Sak-Bosnar M., Hasenay D. and Šeruga M., *Tenside. Surf. Det.* 4, 37 (2000).
- [45] Kallay N., Preočanin T. and Žalac S., *Enthalpy of Surface Charging in Interfacial Dynamics*, (Kallay N., Ed.), Marcel Dekker Inc., New York, 2000.
- [46] Kallay N., Žalac S. and Štefanić G., *Langmuir* 9, 3457 (1993).
- [47] Žalac S. and Kallay N., *J. Colloid Interface Sci.* 149, 233 (1992).
- [48] Preočanin T., Krehula S. and Kallay N., *Applied Surface Sci.* 196, 392 (2002).
- [49] Kallay N., Preočanin T., Žalac S., Lewandowski H. and Narres H.-D., *J. Colloid Interface Sci.* 211, 401 (1999).

- [50] Rudzinski W., Panas G., Charnas R., Kallay N., Preočanin T., Piasecki W., *J. Phys. Chem. B* 104, 11912 (2000).
- [51] Rudzinski W., Panas G., Charnas R., Kallay N., Preočanin T. and Piasecki W., *J. Phys. Chem. B* 104, 11923 (2000).
- [52] Kallay N. and Žalac S., *Croat. Chem. Acta* 67, 467 (1994).
- [53] Kovačević D. and Kallay N., *Isoelectric Point of Metals in Aqueous Media* in *Encyclopedia of Colloid and Surface Science*, Hubbard A. Ed., Marcel Dekker, 2002. pp. 2917-2923.
- [54] Kallay N., Torbić Ž., Barouch E. and Jednačak J., *J. Colloid Interface Sci.* 118, 431 (1987).
- [55] Hogg R., Healy T. W. and Fuerstenau D. W., *Trans. Faraday Soc.* 62, 1638 (1966).
- [56] Hamaker H. C., *Physica* 4, 1058 (1937).
- [57] Kallay N. and Krznarić I., *Indian J. Chem.* 14A, 396 (1978).
- [58] Čolić M., Fuerstenau D. W., Kallay N. and Matijević E., *Colloid Surf.* 59, 69 (1991).

CURRICULA VITAE



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

at present he is Chairman of the Department of Chemistry (2001-). As Research Fellow, he spent academic year 1980/81 at Clarkson University (Potsdam, NY, U.S.A.), and later as visiting professor 3 months each year (1983-90). In addition, he is associated with Jozef Stefan Institute (Ljubljana, Slovenija), Institute for Applied Physical Chemistry, Forschungszentrum-Jülich (Jülich, Germany) and Faculty of Environmental Sciences (Nova Gorica, Slovenia), where he is visiting professor. He also collaborates with members of Maria Curie Skłodowska University (Lublin, Poland). He was/is member of numerous national and international organizations: Croatian Chemical Society (1973- ; member of the Board 1976-78, 1996-98) president 1994-96), International Union of Pure and Applied Chemistry, Commission on Physicochemical Symbols, Terminology and Units (titular member 1977-85; secretary 1983-85; associate member 1985-89); IDCNS 1985-89), International Union of Pure and Applied Physics, Commission on Symbols Units Nomenclature, Atomic Masses and Fundamental Constants (1985-89), Comité Consultatif des Unités, BIPM, Sèvres (1985-89), ISO/TC-12 (1985-89), American Chemical Society (1980-), International Association of Colloid and Interface Scientists (1984-), Kolloid Gesellschaft (1994-), International Symposium on Surfactants (Advisory Committee 1986-), International Symposium on Electrokinetic Phenomena (Advisory Board 1996-), Institute of Colloid and Surface Science, Clarkson University, Potsdam, NY, USA (1980-), Jozef Stefan Institute, Ljubljana, Slovenia (associate member 1990-), Journal of Colloid and

Interface Science (Advisory Board 1990-92), *Croatica Chemica Acta* (Editorial Board 1994-) etc. He is teaching Physical Chemistry, Colloid and Interface Chemistry and Laboratory courses in Physical Chemistry for graduate and undergraduate students. He is active in chemical education, and wrote several textbooks for high schools. Within International Union of Pure and Applied Chemistry he initiated work, and is co-author, of the most famous IUPAC Green Book (Quantities, Units and Symbols in Physical Chemistry), which was first published in 1988, and later had several editions and translations. His research is devoted to physical chemistry of colloids and surfaces, i.e. to development of experimental methods and theoretical interpretations. He was dealing with coagulation, adhesion, preparation, kinetics of crystal growth and dissolution, surface complexation (mechanism, equilibrium and enthalpy), electrical interfacial layer, dissolution of surfactants, micellization, microemulsions, effect of electromagnetic radiation and magnetic field etc. Recently, he solved the problems related to determination of enthalpy of interfacial processes (standard reaction enthalpy and electrostatic contribution), introduced electrokinetic potential in the interpretation of interfacial equilibria ("umbrella effect"), constructed ice-electrode (surface potential, interfacial equilibrium), developed theory for aggregation of nanoparticles (complete overlap of electrical interfacial layer), considered counterion association with micelles, etc. His future projects are related to determination and use of surface potentials, effects of electromagnetic radiation on interfaces, nanocoagulation, application of the van't Hoff equation to ionic reactions in dielectric media, etc. His approach is demonstrated in the Feature article published in *Journal Colloid Interface Science* (2000) and in the review article published in *Croatica Chemica Acta* (2001). He concluded that further scientific progress in the interfacial chemistry requires new experimental techniques combined with new theoretical concepts. Another route is to choose one sample, to standardize the treatment - purification, to measure properties of such uniform samples with all available techniques, and to critically test and refine present theoretical concepts. For that purpose the extensive international cooperation is necessity. He published over ten books (textbooks, recommendations on quantities and units, chapters in monographs) and is editor (and co-author) of *Interfacial Dynamics*, (1999). He is author of more than hundred scientific articles in prestigious international journals, and over thirty other professional articles. For his scientific achievements he received "Ruđer Bošković" award of the State of Croatia (1992), award from Croatian Academy of Sciences and Arts (1999), and award of the City of Zagreb (2000).

<http://www.chem.pmf.hr/~nkallay/>



Ana Čop was born in Šibenik, Croatia in 1973. She graduated from the Faculty of Science, University of Zagreb with a B. Sc. degree in 1997, and in 2001 she received M. Sc. degree in Chemistry from the same University. At present she works as assistant in the Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University Zagreb. On several occasions she spent few months at the Institute for Applied Physical Chemistry, Forschungszentrum-Jülich (Jülich, Germany). She is member of the Croatian Chemical Society. Main field of her scientific interest is physical

chemistry of colloids and interfaces (electrical interfacial layer, interfacial equilibria, measurement of surface potentials, electrokinetics, *etc.*). She is co-author of several scientific publications and some book chapters.



Davor Kovačević was born in Zagreb in 1965. He graduated from the Faculty of Science, University of Zagreb with B. Sc. degree in 1993. In 1996 he received M. Sc. degree, and in 2000. Ph.D. degree in Chemistry from the same University. At present he is employed as assistant in the Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University Zagreb. On several occasions he spent few months at the Institute for Applied Physical Chemistry, Forschungszentrum-Jülich (Jülich, Germany), and in 2001 one year as a post-doc in the Laboratory of Physical Chemistry and Colloid Science, Wageningen University, The Netherlands. He is member

of the Croatian Chemical Society. Main field of his scientific interest is physical chemistry of colloids and interfaces (electrical interfacial layer, interfacial equilibria, adsorption, electrokinetics, adhesion, *etc.*), as well as physical chemistry of macromolecules (polyelectrolyte multilayers, polyelectrolyte complexes, *etc.*). He is co-author of several scientific publications and some book chapters. In 1999 he was awarded by Society of University Scholars as a best young researcher at the University.



Kazimir Majorinc was born in Zagreb in 1962. He graduated in mathematics at Faculty of Science, University of Zagreb, Croatia in 1994, where he works as professional collaborator in Laboratory of Physical Chemistry. He is author or co-author of about twenty professional or scientific articles, high school textbook and few computer programs.

Tajana Preočanin was born in Zagreb in 1972. She graduated from the Faculty of Science, University of Zagreb with B. Sc. degree in 1995. In 1999 she received M. Sc. degree, and in 2001 Ph.D. degree in Chemistry from the same University. At present she is employed as assistant in the Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University Zagreb. On several occasions she spent few months at the Institute for Applied Physical Chemistry, Forschungszentrum-Jülich (Jülich, Germany). She is member of the Croatian Chemical Society. Main field of her scientific interest is physical chemistry of colloids and interfaces (electrical interfacial



layer, interfacial equilibria, thermodynamic of surface reactions, calorimetric and mass titration measurements, *etc.*) She is co-author of several scientific publications and one book chapter. In 2001 she was awarded by Society of University Scholars as a best young researcher at the University.



Suzana Žalac was born in Zagreb in 1965. She graduated from the Faculty of Science, University of Zagreb with a B. Sc. degree in 1988. In 1991 she received a M.Sc. degree and in 1994. a Ph.D. degree in Chemistry from the same University. During period 1989-1996 she was involved as an assistant in the Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb. At present she is working in pharmaceutical industry PLIVA d.d., Zagreb. She is member of Croatian Chemical Society. Main field of her scientific interest is physical chemistry of colloids and interfaces (electrical interfacial layer and thermodynamics of interfacial equilibria *etc.*). She is a co-author of several scientific publications and some book chapters. In 1995 she was awarded by the Croatian Chemical Society, as a young researcher, for her scientific achievements in the field of colloid chemistry.