Inner Layer Capacitor at the Solid/Liquid Interface*

Nikola Kallay,[a,] Davor Kovačević,[a] Ana Čop,[a] and Martina Medvidović[b]**

[a]*Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science,
University of Zagreb, Marulićev trg 19, P. O. Box 163, 10002 Zagreb, Croatia*

[b]*Department of Pure and Applied Chemistry, Faculty of Food Technology, University of J. J. Strossmayer,
Kuhačeva 18, 31000 Osijek, Croatia*

Key words
surface charge
electrical interfacial layer
capacitor
capacitance

Interpretation of the interfacial equilibrium at the solid/liquid interface based on the Surface Complexation Model requires introduction of the concept of the constant capacitance capacitor in the inner part of the electrical interfacial layer (EIL). There are two possible variations of this concept. The common approach is to define capacitance by the surface charge density in the inner part of the layer (σ_0). This concept is related to the simplified scheme of the serially connected capacitors within EIL. Another possibility was examined in this article. If one assumes that capacitors are connected parallel, the surface charge density of the plane in which associated counterions are located (σ_β) should be introduced into the definition of capacitance. The problem was analyzed on the basis of experimental findings as well as by numerical simulation. As assumed, it was found that both concepts provide almost the same result if the degree of counterion association is high. In the case of a low degree of counterion association, at a low electrolyte concentration, no pronounced discrepancy in surface charge density and surface potential was obtained by using these two different concepts. This unexpected result could be explained by considering the mutual dependency of the parameters determining the equilibrium in EIL. It was concluded that it is very difficult to distinguish between these two concepts experimentally, so both of them are still equally applicable.

INTRODUCTION

Solid/liquid interfaces are common in nature, as well as in numerous technological applications. Probably, the most extensively investigated interfaces are metal oxide aqueous systems. Charging of a metal oxide surface in contact with aqueous solution is due to specific interactions with ions from the bulk of the solution. Quantitative interpretation of the ionic interfacial equilibria considers specific interfacial reactions, accompanied with definitions of equilibrium constants taking into account the effect of electrostatic potentials on the charged species. The commonly accepted approach is the Surface Complexation Model (SCM).[1] Consequently, it is necessary to introduce relationships between surface charge

---

* This article is dedicated to Professor Nenad Trinajstić on the occasion of his 65th birthday for his outstanding contribution to science. It happened so that the critical equation in this article, which is analyzed here, bears the number 13 and is connected to the meaning of the surname Trinajstić, which is a diminutive of the word thirteen (thirteen is *trinajst* in čakavian dialect of the Croatian language).

** Author to whom correspondence should be addressed. (E-mail: nkallay@prelog.chem.pmf.hr)

densities and the corresponding electrostatic potentials. For this purpose, a certain structure of electrical interfacial layer (EIL) including several characteristic planes should be assumed. There are several variations of both SCM and EIL models, and the proper choice cannot be easily made on the basis of experimental data. Despite this shortcoming, however, the general behavior of the metal oxide aqueous interfaces is fairly well understood. This article will focus on examining the concept of constant capacitance of the inner layer within EIL.

Equilibria of Surface Reactions

The mechanism of surface reactions and equilibrium constants will be treated here in the traditional way, *i.e.,* by the 2-pK concept of the Surface Complexation Model, as originally introduced by Parks[2] in the 1960's. This model assumes the presence of amphoteric surface MOH groups that undergo protonation (p) and deprotonation (d) according to:

$$MOH + H^+ \rightarrow MOH_2^+$$

$$K_p = \exp(\phi_0 F/RT) \frac{\Gamma_{(MOH_2^+)}}{a_{(H^+)} \Gamma_{(MOH)}} \qquad (1)$$

$$MOH \rightarrow MO^- + H^+$$

$$K_d = \exp(-\phi_0 F/RT) \frac{a_{(H^+)} \Gamma_{(MO^-)}}{\Gamma_{(MOH)}} \qquad (2)$$
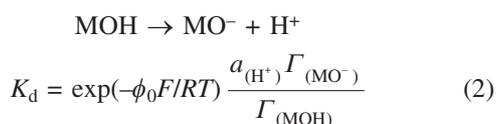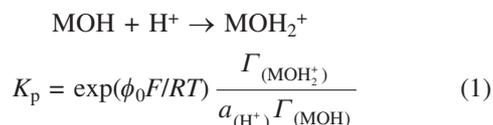
where M denotes the metal atom at the surface, Γ is the surface concentration of the surface species, K_p and K_d are the corresponding (thermodynamic) equilibrium constants, ϕ_0 is the potential in 0-plane that affects the state of charged surface species, a is activity in the bulk of solution, while F, R and T have their usual meanings. These two reactions involve potential determining ions (H$^+$ and OH$^-$) and are responsible for the charging of the inner plane of the inner layer within EIL.

Association of counterions with charged surface groups is also treated as a surface reaction with surface sites:

$$MOH_2^+ + A^- \rightarrow MOH_2^+ \cdot A^-$$

$$K_A = \exp(-\phi_\beta F/RT) \frac{\Gamma_{(MOH_2^+ \cdot A^-)}}{a_{(A^-)} \Gamma_{(MOH_2^+)}} \qquad (3)$$

$$MO^- + C^+ \rightarrow MO^- \cdot C^+$$

$$K_C = \exp(\phi_\beta F/RT) \frac{\Gamma_{(MO^- \cdot C^+)}}{a_{(C^+)} \Gamma_{(MO^-)}} \qquad (4)$$
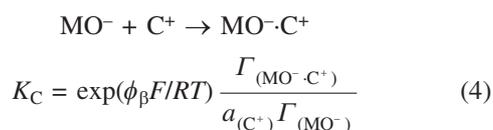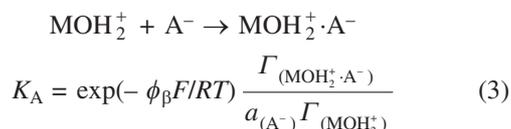
where A$^-$ and C$^+$ denote anions and cations, respectively, and K_A and K_C are respective (thermodynamic) equilibrium constants. The state of associated counterions is affected by electrostatic potential ϕ_β corresponding to the β-plane, *i.e.,* to the outer plane of the inner layer.

Surface charge densities corresponding to the postulated planes within EIL are according to the 2-pK model:

$$\sigma_0 = F(\Gamma_{(MOH_2^+)} + \Gamma_{(MOH_2^+ \cdot A^-)} - (\Gamma_{(MO^-)} - \Gamma_{(MO^- \cdot C^+)})) \qquad (5)$$

$$\sigma_\beta = F(\Gamma_{(MO^- \cdot C^+)} - \Gamma_{(MOH_2^+ \cdot A^-)}) \qquad (6)$$

The net surface charge density σ_s is opposite in sign to that of the diffuse layer and is equal to:

$$\sigma_s = -\sigma_d = \sigma_0 + \sigma_\beta = F(\Gamma_{(MOH_2^+)} - \Gamma_{(MO^-)}) \qquad (7)$$

Capacitors within the Electrical Interfacial Layer

In addition to the equilibrium and mass balance equations, solution of the equilibrium situation at the interface requires the relationships between surface charge densities and the corresponding electrostatic potentials. The problem will be discussed on the basis of the relatively simple Gouy-Chapman-Stern model. This model defines two layers and three planes. The inner layer (often called the Helmholtz layer) consists of an inner 0-plane and outer β-plane. Inner 0-plane is located at the solid surface, and in this plane the charges developed by interactions with potential determining ions are located. Therefore, the charged surface groups MOH$_2^+$ and MO$^-$ are exposed to the electrostatic potential ϕ_0. Centers of associated counterions are located in the outer β-plane, so they are exposed to the electrostatic potential ϕ_β. The second layer is a diffuse layer (often called the Gouy-Chapman layer). The onset or inner boundary of the diffuse layer is d-plane characterized by the electrostatic potential ϕ_d. Theoretically, this layer extends to infinity. However, there are two characteristic planes within the diffuse layer. The first is the electrokinetic slipping or shear plane (e-plane) characterized by the electrokinetic ζ-potential. The second plane characterizing the extension of the diffuse layer is the »thickness of the diffuse layer« κ^{-1} depending on the ionic strength I_c, temperature T and permittivity ε as:

$$\kappa = \sqrt{\frac{2F^2 I_c}{\varepsilon RT}} \qquad (8)$$

Three capacitors can be defined within the electrical interfacial layer. For the sake of simplicity, we shall discuss the simplified structure of EIL as shown in Figure 1.

The simplification with respect to the general scheme[3,4] of EIL lies in the assumption that the onset of the diffuse layer (d-plane) is identical to the plane in which associated counterions are located (β-plane). The
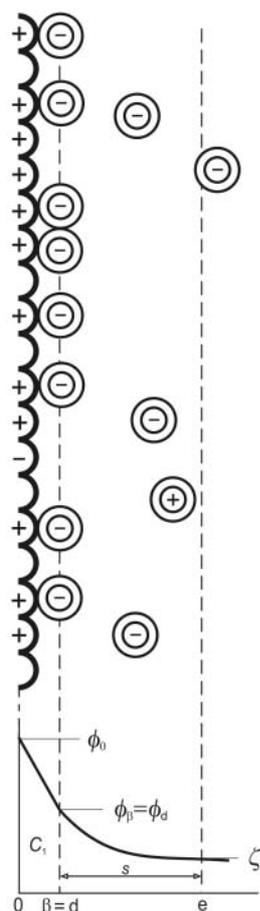
Figure 1. Schematic presentation of the electrical interfacial layer, at the assumption $\phi_\beta = \phi_d$.

consequence of this assumption is that the corresponding potentials equal:

$$\phi_\beta = \phi_d \tag{9}$$

and that we need to consider only two capacitors, *i.e.,* the outer or diffuse layer capacitor and the inner layer capacitor. The outer layer capacitor is commonly considered by the Gouy-Chapman theory. This theory gives the relationship between the potential at the onset of the diffuse layer and the corresponding surface charge density:

$$\sigma_s = -\sigma_d = \frac{4FI_c}{\kappa} \sinh \frac{\phi_d F}{2RT};$$

$$\phi_d = \frac{2RT}{F} \text{arsinh} \frac{\sigma_s \kappa}{4FI_c} \tag{10}$$

According to (10), the »effective capacity« of the diffuse layer is:

$$C_{dif} = \frac{\sigma_s}{\phi_d} \tag{11}$$

Analysis of above equations shows that even at constant κ, the value of C_{dif} depends on the potential, so this capacitor cannot be considered as the »constant capacitance capacitor«.
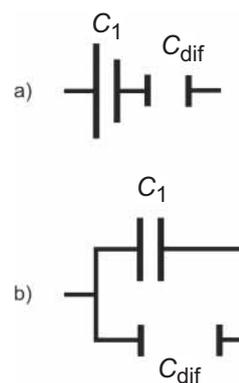
Figure 2. Schematic presentation of the concepts of serially (a) and parallel (b) connected capacitors.

According to the simplified structure of EIL (Figure 1), the inner layer Helmholtz capacitor has two planes: 0-plane and β(= d)-plane. These two planes are assumed to be divided by the space of permittivity ε. Since the distances between the planes are determined by the effective sizes of the ionic species in close contact, the capacity of this capacitor C_1 (divided by the surface area) is assumed to be constant and is commonly defined as:

$$C_{1,ser} = \frac{\sigma_0}{\phi_0 - \phi_d} \tag{12}$$

Index $_{ser}$ is related to the approximation that this capacitor acts as being in the serial connection with the diffuse layer capacitor and, consequently, to introduction of the surface charge density of the 0-plane into Eq. (12). The problem of the above definition lies in the fact that charges located in the 0-plane and β-plane are not equal in magnitude. To analyze this situation, we shall consider also the EIL as being composed of two parallel connected capacitors. These two approximations are demonstrated schematically in Figure 2.

According to the approximation based on the concept of parallel connected capacitors, the charges divided in the inner layer capacitor are $-\sigma_\beta$ and σ_β, but not σ_0 as in the case of the first commonly accepted concept, so that the second approximation leads to:

$$C_{1,par} = \frac{-\sigma_\beta}{\phi_0 - \phi_d} \tag{13}$$

Since the concept of the inner layer capacitor of constant capacitance is an approximation of the reality, it is hard to distinguish between the two variations, *i.e.,* between the serial and parallel connection of capacitors as defined by Eqs. (12) and (13), respectively. In the case of a relatively high degree of association ($-\sigma_\beta/\sigma_0 \rightarrow 1$), there is no significant difference between these two concepts. On the other hand, if the degree of counterion association is low, a pronounced difference is expected. The aim of this study is to analyze the consequences of these two opposite assumptions for the measurable characteristics of the solid/liquid interfaces.

EXPERIMENTAL FINDINGS

In order to discuss the difference of the applicability of Eqs. (12) and (13), the behavior of an ordinary colloidal system was examined. Figure 3 displays the dependency of σ_0, σ_β and σ_s for the alumina aqueous NaNO$_3$ electrolyte interface ($I_c = 1 \cdot 10^{-3}$ mol dm^{-3}). The surface charge density in the 0-plane was determined by the standard potentiometric titration while the net surface charge density σ_s was calculated from ζ-potentials *via* the Gouy-Chapman theory using the slipping plane separation[5] of 20 Å. Regardless of the approximations employed in data evaluation, it is clear that σ_0 does not significantly differ from $-\sigma_\beta$ (the degree of counterion association is ~92 %), so both Eqs. (12) and (13) lead essentially to the same results. The situation is similar in most of the examined systems; the net surface charge density is markedly lower than the surface charge density in the inner layer σ_0 so that both concepts, serial and parallel connections of the capacitors within EIL, are practically equivalent.

In addition to the evaluation of surface charge densities from potentiometric and electrokinetic measurements, useful information on the counterion association and applicability of the examined concepts can be obtained from direct measurements of counterion adsorption data. Janusz and co-workers[6] studied the adsorption of Na$^+$ and Cl$^-$ ions at the hematite-electrolyte interface. From their experiments at $I_c = 10^{-3}$ mol dm^{-3} the degree of counterion association can be calculated as ~87 % for Cl$^-$ and ~74 % for Na$^+$ association. Breeuwsma and Lyklema[7] studied the adsorption of ions on hematite and compared the charge ionic components in the electrical interfacial layer. The degree of counterion associa-

tion obtained by them for Ca^{2+}, K$^+$, Cl$^-$ and SO$_4^{2-}$ at $I_c = 10^{-3}$ mol dm^{-3} was also found to be close to 100 %.
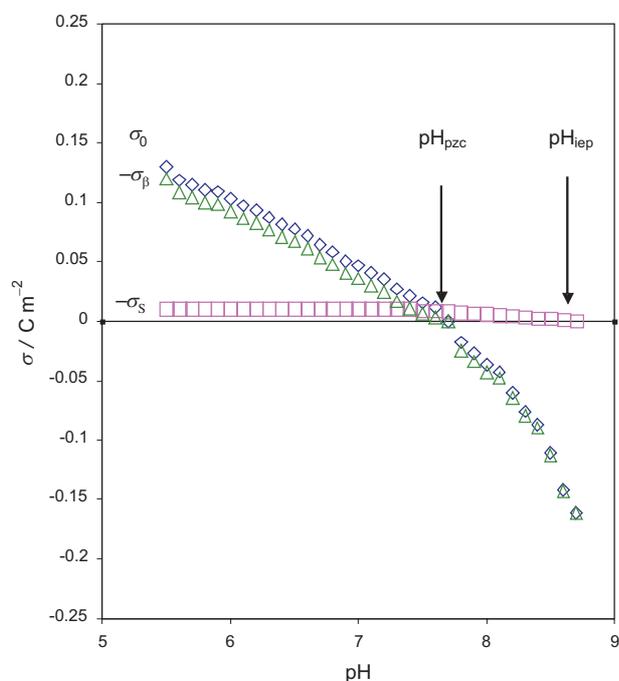
Another issue that should be discussed is the fact that the inner layer capacitance is not constant but significantly depends on the electrolyte concentration and pH. Several attempts at analyses of the capacitance constancy can be found in the literature. Trimbos and Stein[8] examined the ZnO aqueous electrolyte interface by measuring σ_0 and ζ-potentials. Applying the assumption $\zeta = \phi_d$, the C_1 values were calculated on the basis of Eq. (12). It was shown that C_1 values were not independent of pH, *i.e.*, C_1 values depend on the surface potential ϕ_0 as calculated on the basis of the Nernst approximation.[9,10] Sprycha[11] examined the anatase/aqueous electrolyte interface in the same manner and showed the dependency of C_1, as defined by (12), on both pH and the ionic strength. These findings do not mean that the concept of the inner layer capacitor of constant capacitance is in principle incorrect. The variation in capacitance may be due to other assumptions used in data evaluation, *e.g.*, due to the assumption that ϕ_0 potential obeys the Nernst equation.

Numerical Simulations

To analyze the difference between the concepts of parallel (12) and serially (13) connected capacitors, numerical simulations were performed. In all calculations, equilibrium parameters were kept constant and were as follows: $\varepsilon_r = 78.54$, $T = 298$ K, $C_1 = 1$ F m^{-2}, log $K_p = 3.1$,
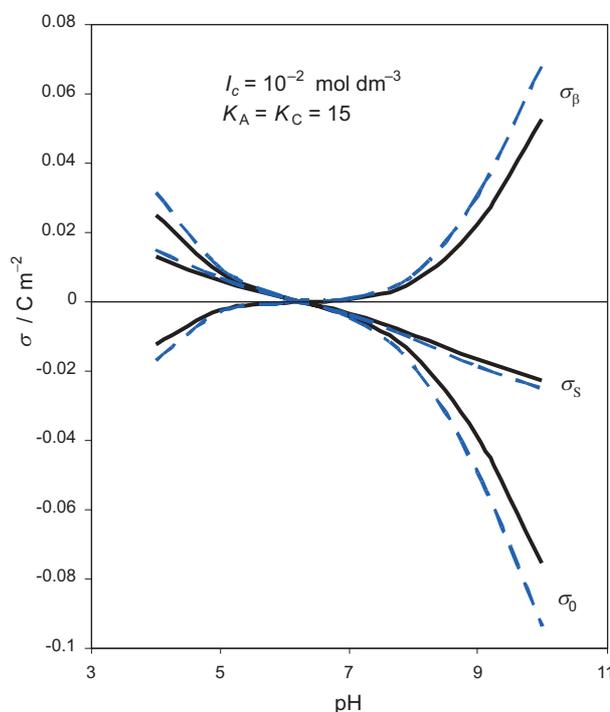
Figure 4. The pH dependency of surface charge for the metal oxide/aqueous solution interface obtained by numerical simulations for $I_c = 10^{-2}$ mol dm^{-3}. Calculations were performed with: $\varepsilon_r = 78.54$, $T = 298$ K, $C_1 = 1$ F m^{-2}, log $K_p = 3.1$, log $K_d = -9.4$, pH$_{pzc} = 6.3$, $K_A = K_C = 15$. Full lines represent calculations based on the concept described by Eq. (12), while dashed lines represent calculations based on the concept described by Eq. (13).

Figure 3. Dependency of σ_0, σ_β and σ_d values on pH calculated for the alumina aqueous interface at 25 °C in the presence of NaNO$_3$ at $I_c = 1 \cdot 10^{-3}$ mol dm^{-3} on the basis of potentiometric and electrokinetic measurements. The slipping plane separation of $s = 20$ Å was used in the calculation.
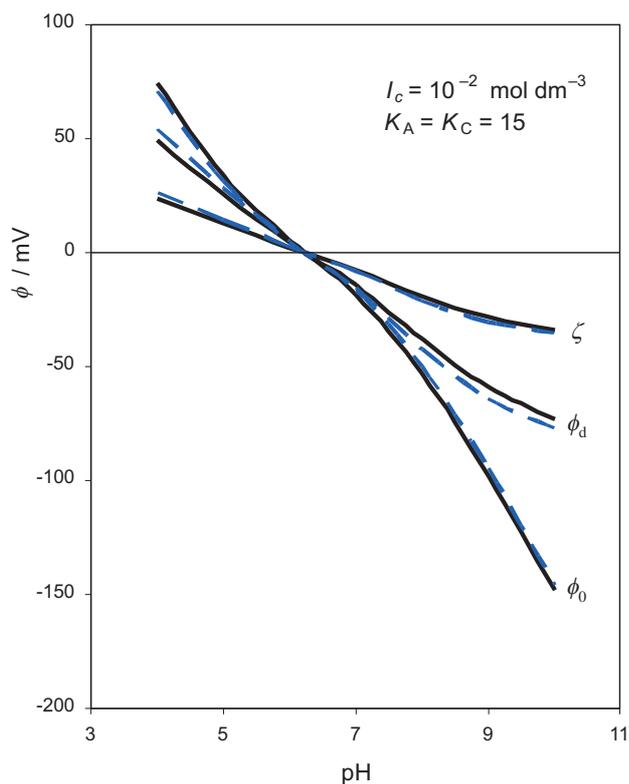
Figure 5. The pH dependency of surface potentials within EIL for the metal oxide/aqueous solution interface obtained by numerical simulations for $I_c = 10^{-2}$ mol dm^{-3}. In calculations, the same set of parameters was used as in Figure 4. Full lines represent calculations based on the concept described by Eq. (12), while dashed lines represent calculations based on the concept described by Eq. (13).

Figure 6. The pH dependency of surface charge for the metal oxide/aqueous solution interface obtained by numerical simulations for $I_c = 10^{-4}$ mol dm^{-3}. In calculations, the same set of parameters was used as in Figure 4. Full lines represent calculations based on the concept described by Eq. (12), while dashed lines represent calculations based on the concept described by Eq. (13).

$\log K_d = -9.4$, pH$_{pzc} = 6.3$. The values of these parameters were chosen to apply to an ordinary metal oxide system[12–16] such as *e.g.* Fe$_2$O$_3$, ZrO$_2$, Al$_2$O$_3$. Particularly, the above values describe approximately the titania[17] aqueous interface. The counterion association equilibrium constants were chosen to be equal for anions and cations. As expected, for a high degree of counterion association (~100 %), achieved by high association equilibrium constants $K_A = K_C = 1500$, no significant difference between the two concepts was observed even at ionic strengths as low as 10^{-4} mol dm^{-3}.

However, in the case of a low degree of counterion association, *i.e.*, a low value of association equilibrium constant, the situation is somehow different. The results are displayed in Figures 4 – 7.

In all figures, full lines represent calculations based on the »serial« concept described by Eq. (12), while dashed lines represent calculations based on the »parallel« concept described by Eq. (13). To achieve a low degree of association, the counterion association equilibrium constants were chosen as $K_A = K_C = 15$. Figures 4 and 5 describe the case of a higher electrolyte concentration ($I_c = 10^{-2}$ mol dm^{-3}) when about 70 % of the charge developed in the 0-plane is compensated by associated counterions. The surface charge

densities calculated by Eq. (12) are by about 25 % higher in magnitude compared to those calculated by Eq. (13). Surface potentials ϕ_0, ϕ_d and ζ are practically equal (Figure 5). A significantly more pronounced discrepancy was expected at low electrolyte concentrations ($I_c = 10^{-4}$ mol dm^{-3}) when the degree of counterion association is markedly lower (Figures 6 and 7). At an electrolyte concentration of 10^{-4} mol dm^{-3}, only about 35 % of the charge in the 0-plane is compensated by associated counterions, *i.e.*, σ_0 is approximately three times higher in magnitude than σ_β. Accordingly, one would expect a markedly pronounced difference when Eq. (13) is used instead of (12). Contrary to the expectations, the resulting difference does not exceed 20 %. The calculated surface potentials (Figure 7) show even lower discrepancy. These unexpected results could be understood if one considered the mutual effect of several parameters governing equilibrium in the electrical interfacial layer.

CONCLUSION

The results of this study suggest that the choice between the concepts of serially connected capacitors (Eq. 12) and parallel connected capacitors (Eq. 13) cannot be made unambiguously on the basis of experimental findings, even for the systems in which the counterion association is low. Therefore, taking into account experimental accuracy, it may be concluded that these two ex-

$$I_c = 10^{-4} \text{ mol dm}^{-3}$$
$$K_A = K_C = 15$$

Figure 7. The pH dependency of the potential in EIL for the metal oxide/aqueous solution interface obtained by numerical simulations for $I_c = 10^{-4}$ mol dm^{-3}. In calculations, the same set of parameters was used as in Figure 4. Full lines represent calculations based on the concept described by Eq. (12), while dashed lines represent calculations based on the concept described by Eq. (13).

that in the limiting case, in the absence of counterion association, ϕ_β approaches the ϕ_0 value. This result is in accordance with the fact that electrostatic potential does not change with the distance from the infinite planar charged plate if no charge compensation takes place.

The question that remains unsolved is the assumed constancy of the capacitance of the assumed capacitors. The observed dependency of C_1 could be attributed *e.g.* to the effect of the surface potential on the permittivity in the interfacial region.

REFERENCES

1. D. E. Yates, S. Levine, and T. W. Healy, *J. Chem. Soc., Faraday Trans I*, **70** (1974) 1807–1818.
2. G. A. Parks, *Chem. Rev.* **65** (1965) 177–198.
3. 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, 1999, pp. 249–271.
4. N. Kallay, A. Čop, D. Kovačević, K. Majorinc, T. Preočanin, and S. Žalac, *Annales Universitatis Mariae Curie-Sklodowska*, Vol. LVII, Lublin, 2000, pp. 226–248.
5. D. Kovačević, N. Kallay, I. Antol, A. Pohlmeier, H. Lewandowski, and H.-D. Narres, *Colloids Surf.* **140** (1998) 261–267.
6. W. Janusz, A. Sworska, and J. Szczypa, *Colloids Surf.* **149** (1999) 421–426.
7. A. Breeuwsma and J. Lyklema, *J. Colloid Interface Sci.* **43** (1973) 437–448.
8. H. F. A. Trimbos and H. N. Stein, *J. Colloid Interface Sci.* **77** (1980) 386–396.
9. M. A. Blesa and N. Kallay, *Adv. Colloid Interface Sci.* **28** (1988) 111–134.
10. N. Kallay and S. Žalac, *J. Colloid Interface Sci.* **230** (2000) 1–11.
11. R. Sprycha, *J. Colloid Interface Sci.* **102** (1984) 173–185.
12. J. Jablonski, W. Janusz, M. Reszka, R. Sprycha, and J. Szczypa, *Polish J. Chem.* **74** (2000) 1399–1409.
13. J. A. Davis, R. O. James, and J. O. Leckie, *J. Colloid Interface Sci.* **63** (1977) 480–499.
14. P. Hesleitner, D. Babić, N. Kallay, and E. Matijević, Langmuir **3** (1987) 815–820.
15. D. Lumsdon and L. J. Evans, *J. Colloid Interface Sci.* **164** (1994) 119–125.
16. R. Sprycha and J. Szczypa, *J. Colloid Interface Sci.* **102** (1984) 288–291.
17. W. Janusz, *Adsorpt. Sci. Technol.* **18** (2000) 117–134.

tremes may equally well describe the experimental findings. However, if one considers the effect of the degree of counterion association on the β-plane potential, it is possible to conclude that the concept of parallel connected capacitors is closer to the reality. The reason for such a speculation is as follows. Let us imagine a decrease in counterion concentration followed by a decrease in the degree of counterion association at constant σ_0. According to the classical concept of serially connected capacitors, the potential drop in the inner layer remains constant. Even if the degree of association approaches zero, this potential drop will be the same. The concept of parallel connected capacitors suggests that the decrease of counterion association will cause a reduction in potential drop in the inner layer, suggesting

SAŽETAK

Kondenzator unutrašnjega dijela međusloja čvrsto/tekuće

Nikola Kallay, Davor Kovačević, Ana Čop i Martina Medvidović

Interpretacija površinske ravnoteže na međupovršini čvrsto/tekuće, zasnovana na modelu površinskih reakcija (SCM), zahtijeva uvođenje koncepcije konstantnoga kapaciteta unutrašnjega dijela električkoga međupovršinskoga sloja (EIL). Postoje dvije mogućnosti. Uobičajeni pristup je definiranje kapaciteta rabeći površinsku gustoću naboja unutrašnjega dijela sloja (σ_0). Ovaj je pristup povezan s pojednostavljenom shemom serijski spojenih kondenzatora u električkome međupovršinskome sloju. U ovom radu ispituje se druga mogućnost. Ako se pretpostavi da su kondenzatori spojeni paralelno, potrebno je u definiciju kapaciteta uvesti površinsku gustoću naboja plohe na kojoj se nalaze asocirani protuioni (σ_β). Problem je analiziran na temelju eksperimentalnih nalaza, kao i numeričkim simulacijama. Kao što je i pretpostavljeno za slučaj visokoga stupnja asocijacije protuiona obje koncepcije daju gotovo jednake rezultate. U slučaju niskoga stupnja asocijacije protuiona, pri niskoj koncentraciji elektrolita, također nije uočeno naglašeno odstupanje u površinskim gustoćama naboja i površinskim potencijalima prilikom uporabe navedenih dviju koncepcija. Ovaj neočekivani rezultat može se objasniti uzevši u obzir višestruku ovisnost parametara koji određuju ravnotežu u električkome međupovršinskome sloju. Moguće je zaključiti da se navedene dvije koncepcije vrlo teško mogu eksperimentalno razlučiti te su stoga obje jednako primjenjive.