# Some Controversies in the Understanding of Equilibria in Electrical Interfacial Layer*

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This review discusses several controversies connected to the measurements and interpretation of equilibria in the electrical interfacial layer at the solid/solution interfaces. The discussion concerns equilibria of amphoteric reactions and counterion association at the surface. The applicability of the intrinsic equilibrium constant concept for counterion association is compared to a model where associated counterions are not located in a plane but distributed in the vicinity of central surface charged groups. Measurements indicating the adsorption of counterions in the region of the point of zero charge reveal insufficiencies of the common models based on the Gouy-Chapman theory. These results are explained in terms of the effect of the discreteness of surface charge. The differences in the double layer model and the triple layer model are discussed. Numerical simulation of interfacial layer equilibria shows that the isoelectric point can be close to the common intersection point despite the significant specific adsorption. This finding suggests that these values should be determined with high accuracy if they are used as the point of zero charge. It is demonstrated that mass titration method for p.z.c. determination is applicable only for pure samples. The contamination of samples by acid or base results in significant errors in p.z.c. and thus in experimental surface charge densities. The adhesion method for determination of the isoelectric point of metallic surfaces is presented.

## I. INTRODUCTION

The present state in the understanding of equilibria in the interfacial layer of metal oxide/aqueous electrolyte systems is still afflicted with some controversies.

These controversies are, in part, related to several problems with the measuring of surface charge by potentiometric technique, such as the accuracy

of data, the dissolution of the solid phase, and the determination of the zero of the absolute charge scale (defined as the point of zero charge, p.z.c.)[1] The latter quantity could be, in principle, evaluated from the common intersection point (c.i.p.), electrokinetic isoelectric point (i.e.p.) and also by adhesion[2] and mass titration[3,4] methods. Those methods are the subject of debate and will be one of the topics of this article.

Proposed models for the interpretation of equilibria in the electrical interfacial layer are another point of discussion. In discussing this issue, there are two problems to be considered. First of all, several surface reactions have been assumed, with the definitions of their equilibrium constants. Furthermore, the structure of the interfacial layer has been modeled by relationships between electrostatic potentials and relevant surface charge densities[5].
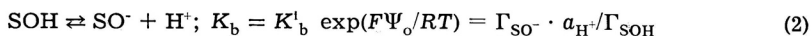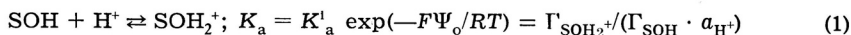
For simple systems, such as a suspension of metal oxide particles in the aqueous solution of simple 1:1 neutral electrolytes, one can satisfactorily interpret experimental data of surface charge dependency on pH by using several different models[5-22]. This situation requires either improvement of experimental accuracy or simultaneous use of several experimental techniques providing the evidence of more than one parameter. One example would be the simultaneous interpretation of surface charge data (potentiometric titration), counterion adsorption isotherm (radioactive tracers), and zeta potentials (electrokinetics) dependence on pH. Such an interpretation would involve less adjustable parameters than, for example, exclusive utilization of potentiometric data.

In addition to problems of interpretation, there seems to be serious experimental evidence which contradicts the proposed models. Although potentiometric data can be interpreted by several models, based on the surface complexation (site binding) approach, there is experimental evidence which contradicts the predictions of any of those models. All of the existing models predict negligible counterion adsorption around p.z.c. but there are experiments with radiotracers which show significant adsorption in this region.
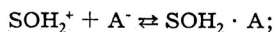
## II. SURFACE REACTIONS

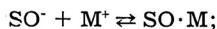It is commonly[1,5-20] accepted that a surface becomes charged due to the following surface reactions:

Amphoteric equilibria at the surface are

$$SOH + H^+ \rightleftharpoons SOH_2^+; \quad K_a = K'_a \exp(-F\Psi_0/RT) = \Gamma_{SOH_2^+}/(\Gamma_{SOH} \cdot a_{H^+}) \quad (1)$$

$$SOH \rightleftharpoons SO^- + H^+; \quad K_b = K'_b \exp(F\Psi_0/RT) = \Gamma_{SO^-} \cdot a_{H^+}/\Gamma_{SOH} \quad (2)$$

Association of counterions ($M^+$ and $A^-$) with surface charged groups is represented by

$$SOH_2^+ + A^- \rightleftharpoons SOH_2 \cdot A;$$

$$K_{ass}(A^-) = K'_{ass}(A^-) \exp(F\Psi_\beta/RT) = \Gamma_{SOH_2 \cdot A}/(\Gamma_{SOH_2^+} \cdot a_{A^-}) \quad (3)$$

$$SO^- + M^+ \rightleftharpoons SO \cdot M;$$

$$K_{ass}(M^+) = K'_{ass}(M^+) \exp(-F\Psi_\beta/RT) = \Gamma_{SO \cdot M}/(\Gamma_{SO^-} \cdot a_{M^+}) \quad (4)$$

$K$ denotes the total equilibrium constant (quotient) while $K^i$ is a real equilibrium constant and is often called the »intrinsic constant«. $\Gamma$ is the surface concentration, $\Psi$ denotes the electrostatic potential, and subscripts o and $\beta$ designate the properties at 0- and $\beta$-planes where surface charged groups and associated counterions are located, respectively.

Surface charge densities in the 0- and $\beta$-planes are given by

$$\sigma_o = F(\Gamma_{SOH_2^+} + \Gamma_{SOH_2 \cdot A} - \Gamma_{SO^-} - \Gamma_{SO \cdot M}) \tag{5}$$

$$\sigma_\beta = F(\Gamma_{SO \cdot M} - \Gamma_{SOH_2 \cdot A}) \tag{6}$$

The »net« (effective) surface charge density due to charges fixed to the surface $\sigma_s$ is equal in magnitude to the charge density in the diffuse layer $\sigma_d$

$$\sigma_s = \sigma_d = F(\Gamma_{SOH_2^+} - \Gamma_{SO^-}) \tag{7}$$

Bolt and Van Riemsdijk[21] developed a different approach (»the one-pK-model«) according to which the charge in the 0-plane is due to the following reaction, instead of reactions (1) and (2):

$$SOH^{1/2^-} + H^+ \rightleftarrows SOH_2^{1/2^+} \tag{8}$$
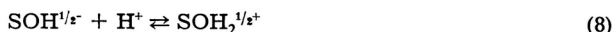
There is no experimental evidence which can be used to prove each of the afore mentioned hypotheses[17]. This problem is not a concern of this article but deserves special attention. The discussion presented here is based on the common approach as formulated by reactions (1) and (2).

The introduction of the equilibrium constants in (1—4) is based on the so called »intrinsic approach«. The potential affecting the energy state of surface charge groups $SOH_2^+$ and $SO^-$ is taken to be different from the potential affecting the associated counterions located in the $\beta$-plane. It is reasonable to assume that $SOH_2^+$ and $SO^-$ groups are located in one plane and are exposed to the same (average) potential, but the situation is more complicated for the associated counterions. It may be assumed that associated counterions are statistically distributed around surface charges rather than located at the fixed plane. This problem is discussed in the following section (III).

### III. COUNTERION ASSOCIATION EQUILIBRIUM

The common approach to the counterion association equilibrium is based on the intrinsic equilibrium constants as defined by Eqs (3,4) and takes into account the electrostatic potential at the $\beta$-plane where interaction occurs. In contrast to the fixed association plane concept, a different model was developed[22,23] which defines an interaction volume for associated counterions. This analysis is based on the Boltzmann distribution function and it assumes the total (effective) electrostatic potential as a sum of two contributions: the Coulombic potential of the central fixed surface charge and potential due to the overall surface charge. The probability function obtained in this manner shows a minimum at a certain (center-to-center) distance which is, according to Bjerrum[24], the critical distance; ions that are closer to the central surface charge than the critical distance are considered to be associated and those

that are further from the critical distance are free. The critical distance increases with the surface potential ($\Psi$) and, at the planar surface, is dependent on the orientation. Figure 1 gives a schematic presentation of cross-sections of critical boundaries (boundary of association space) for different surface potentials. Circle denoted by 0 represents the critical boundary calculated for $\Psi' = 0$ (i.e.p.). This boundary, obviously, corresponds to the critical distance in the bulk of a solution. The other curves denote critical boundaries obtained for higher values of $\Psi$ ($0 < \Psi_1 < \Psi_2 < \Psi_3$). If the minimum separation between centers of counterion and a surface charge group (dashed line
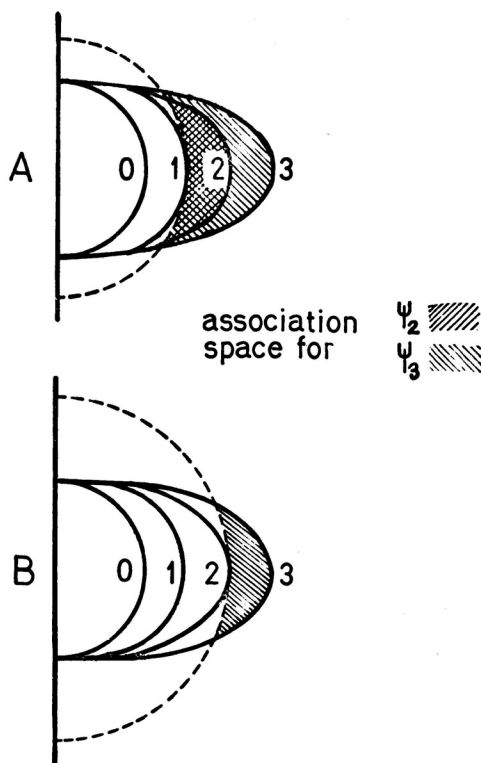


Figure 1. Schematic presentation of critical boundaries of counterion association space around a fixed central surface charged group for gradually increasing surface potentials $\psi_0 = 0 < \psi_1 < \psi_2 < \psi_3$ (solid lines). Dashed lines are minimum distances between centers of central ion and counterion for relatively small (A) and large (B) counterions[22,23]. The association space is limited by the critical boundary (outer limit) and the minimum separation (inner limit).

on Figure 1) is smaller than the critical distance, their association (according to Bjerrum[24]) does not occur. For relatively small counterions (part A of Figure 1) association takes place only when $\Psi > \Psi_1$, while the larger counterions (part B) require higher values of surface potential ($\Psi > \Psi_2$). For the latter case association is less pronounced. Such an approach, based on associations space (AS model), explains the counterion specific effect (other

than charge) on the equilibria at the interface. In the »intrinsic« approach this specific effect is characterized in an implicit way through the intrinsic association constant and/or the inner layer capacitance.

The advantage of the AS model is in the possibility of calculating the total equilibrium »constant« from a given surface potential, size parameter (minimum center-to-center distance), and ionic strength. In the original publication[22,23] the potential drop in the interfacial region was approximated by the Gouy-Chapman function so that one cannot expect the values of the equilibrium constant to be accurate. However, this model explains the influence of effective counterion size and suggests that association does not occur in the vicinity of the point of zero charge. Counterions have a characteristic pH, above which they associate at the surface; this pH corresponds to the critical potential. For positive counterions of larger size, the magnitude of critical potential is higher than that of smaller ions and, consequently, characteristic pH is higher.
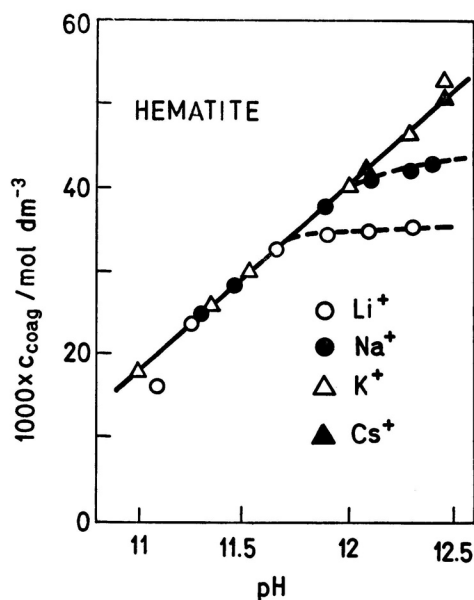


Figure 2. The effect of pH on the critical coagulation concentration of different alkaline chlorides for hematite dispersion. Data are taken from reference 25.

Application of the AS concept to the equilibrium in the inner part of the interfacial region is supported by coagulation experiments[25]. Figure 2 schematically presents the critical coagulation concentration of several 1:1 electrolytes for hematite as a function of pH. At pH < 11.7 the c.c.c. values coincide for all counterions, indicating that counterions are distributed in the diffuse part of the interfacial layer without being directly bound to the surface charged groups. For pH > 11.7 the potential is high enough to allow association of $Li^+$ ions. Consequently, their c.c.c. is lowered with respect to the c.c.c. of larger counterions ($Na^+$, $K^+$ and $Cs^+$). $Na^+$ ions, which are larger

than Li+ ions, show this abrupt slope decrease at a higher value of surface potential *i.e.* at pH = 12. It could be concluded that ions behave similarly close to p.z.c. region where they are present in the diffuse layer only, but at relatively high potentials their association affinities are different and therefore their coagulation abilities differ. In contrast, the »intrinsic« concept would predict association in the whole pH region. The extent of association would depend on the values of the intrinsic equilibrium constant and thus each counterion will have different association properties. Therefore, according to »intrinsic« concept one would expect different c.c.c. values for different electrolytes, for entire pH range; a prediction which is contradicted by experimental evidence, as show in Figure 2.

### IV. CHARGE-POTENTIAL RELATIONSHIPS

The interpretation of experimental data requires the knowledge of the relationship between surface charge densities and relevant potentials. Potentials in the 0-and the β-planes are related to the charge density in the 0-plane by postulating the inner layer constant capacity $C_1$:

$$C_1 = \sigma_o/(\Psi_o - \Psi_\beta) \tag{9}$$

The potential at the origin (onset) of diffuse layer $\Psi_d$ is usually related to the relevant surface charge densities by the Gouy-Chapman theory:

$$\sigma_s = -\sigma_d = (8RT\varepsilon I_c)^{1/2} \sinh(F\Psi_d/2RT) \tag{10}$$

The relationship between $\Psi_\beta$ and $\Psi_d$ is controversial (see Fig. 3) The simple approach,[15] (Stern-Gouy-Chapman, DL model) would be to take

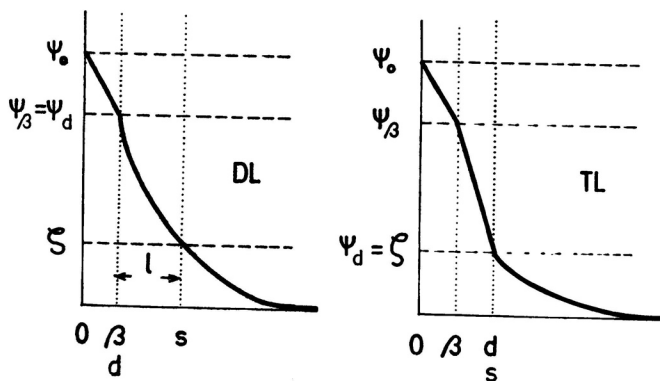$$\Psi_\beta = \Psi_d; \text{ DL} \tag{11}$$



Figure 3. Schematic presentation of electrostatic potential profile in the interfacial region according to the double layer (DL) and the triple layer (TL) models. The slipping plane is denoted by s and its separation from the onset of diffuse layer (d) is *l*. The centers of surface charged groups are in 0-plane while associated counterions are located in the β-plane.

while the triple layer model[7] (TL model) considers the potential drop from $\beta$ to d-plane. Consequently, the second capacitor, with the constant capacity $C_2$, was introduced by the TL model:

$$C_2 = \sigma_s/(\Psi_\beta - \Psi_d); \; TL \tag{12}$$

The use of the TL model is convenient because it allows simultaneous interpretation of electrokinetic data. It is assumed[7,26] that the electrokinetic potential $\zeta$ may be taken as equal to $\Psi_d$. This substitution is compatible with the interpretation of experimental data which requires $\Psi_d$ values significantly higher than $\zeta$; accordingly, in the TL approximation $\Psi_o$ should be higher than $\Psi_d$, as given by Equation (12). The difference in $\zeta$ — potential and $\Psi_d$ may be also accounted for in the DL model. In this approach, instead of $C_2$, there is another parameter to be introduced: the slipping plane separation ($l$). The relation between $\Psi_d$ and $\zeta$ is given by the Gouy-Chapman theory:

$$\Psi_d = 2RTF^{-1} \ln \left[ \frac{\exp(-l\varkappa) + \tanh(F\zeta/4RT)}{\exp(-l\varkappa) - \tanh(F\zeta/4RT)} \right] \tag{13}$$

where $l$ is the separation of the slipping plane from the d-plane and $\varkappa$ is the Debye-Hückel inverse length given by

$$\varkappa = (2F^2 I_c/\varepsilon RT)^{1/2} \tag{14}$$

$\varepsilon$ is the permittivity and $I_c$ is the ionic strength due to the presence of 1:1 electrolyte.

Equation (13) indicates that $\Psi_d$ is higher in magnitude than $\zeta$ so that $\Psi_d$ could be equal to $\Psi_\beta$ as used in the DL approach (Eq. 11).

Recent electrokinetic data[27-31] showed that the electrokinetic slipping plane is separated by several ångstroms from the solid surface. Since two layers (inner and diffuse layer) in the DL model may satisfactorily explain present experimental observations[5,32], it seems that there is no necessity of introducing third layer into the description of the structure of the electric interfacial layer. The evaluation of the slipping plane separation is discussed in Section IX.

### V. POTENTIOMETRIC TITRATION

The most common tool in studying equilibrium at the solid/solution interface is the potentiometric titration method. In the case of metal oxides, the surface charge density in the 0-plane, due to amphoteric equilibrium, can be calculated from[1,5];

$$\sigma_o = F \{ n_o(HNO_3) + v(HNO_3) \, [HNO_3] - v(KOH) \, [KOH] +$$
$$+ Vc^o(yK^o_w/a_{H^+} - a_{H^+}/y) \}/A_s \tag{15}$$

$n_o(HNO_3)$ is the initial amount of acid, $A_s$ is the surface area, $V$ is the total volume of the system, $K_w^o$ is the equilibrium constant of water dissociation, and $v$ is the volume of added acid or base. The standard value of concentration is as usual $c^o = 1 \; mol \; dm^{-3}$. Note that activity $(a)$ is a dimensionless quantity defined by $a = yc/c^o$. The activity coefficient, $y$, depends on ionic strength ($I_c$).

Equation (15) applies to a general case where acidic suspension of inso-luble metal oxide is titrated with base (KOH) and/or (re)titrated with acid (HNO₃). The activites of H⁺ ions are measured by a glass electrode which should be calibrated either by buffers or by blank titration. The main pro-blem is the initial amount of acid in the system. This amount is known only if pure solid powder is dispersed in the acid of known concentration ("dry sample method"). However, the purity of the sample is always under ques-tion. Even in the case of repeated washing, the sample may contain a signifi-cant portion of acid or base impurities. In practice, one calculates relative values of the charge density in the 0-plane by

$$\sigma_0(\text{rel}) = F \{ \Gamma_{H^+} - \Gamma_{OH^-} - n_0(\text{HNO}_3)/A_s \} =$$

$$= F \{ v(\text{HNO}_3) [\text{HNO}_3] - v(\text{KOH}) [\text{KOH}] + (Vc^\circ/y) (K^\circ_w/a_{H^+} - a_{H^+}) \}/A_s \qquad (16)$$

The absolute values of $\sigma_0$ can be evaluated by setting the zero on the charge density scale at the point of zero charge (p.z.c.) which should be de-termined separately. The evaluation of p.z.c. deserves special attention and will be discused in more detail.

### VI. RELATIONSHIP BETWEEN C.I.P., I.E.P. AND P.Z.C.

Most of the published data are based on the assumption that the com-mon intersection point (c.i.p.) corresponds to the point of zero charge. The common intersection point can be obtained by plotting the relative values of $\sigma_0$ as a function of the pH at different ionic strengths. It has been demonstra-ted[33,34] that such an assumption holds true for systems where there is no spe-cific adsorption, i.e. when the binding of ions, other than potential determi-ning ions, directly to the surface can be neglected. Specific adsorption moves p.z.c. and i.e.p. in opposite directions with respect to the original p.z.c. and i.e.p. In such a case one may still obtain c.i.p. but it does not corre-spond to p.z.c. In the absence of specific adsorption c.i.p., i.e.p. and p.z.c. coin-cide. Accordingly, the proper procedure for obtaining p.z.c. in this case would be to determine both c.i.p. and i.e.p. by potentiometric titration and electroki-netic method, respectively. If the value of i.e.p. is independent of ionic strength and coincides with c.i.p., one can assume the absence of specific adsorption, and therefore, c.i.p. (or i.e.p.) can be taken to be equal to p.z.c.

In order to investigate this problem in more detail, the numerical simu-lations for different situations are performed on the basis of the triple layer model[7].

Figure 4. demonstrates the results of calculations of the specific adsorp-tion of ions X⁻ ([X⁻] = 10⁻⁵ mol/dm³) and for the system where there is no specific adsorption of "neutral electrolyte" (the one that is responsible for ionic strength). These calculations were performed for three different values of ionic strength. In the calculation procedure the following reaction was assumed together with reactions (1—4):

$$S + X^- \rightleftarrows SX^-; \quad K_x = K^i_x \exp(F\Psi_0/RT) = \Gamma_{SX^-}/(\Gamma_S \, a_{X^-}) \qquad (17)$$
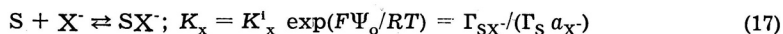
It was assumed that specifically adsorbed X⁻ ions are located in the 0-pla-ne and that specific adsorption does not compete for active surface sites in-
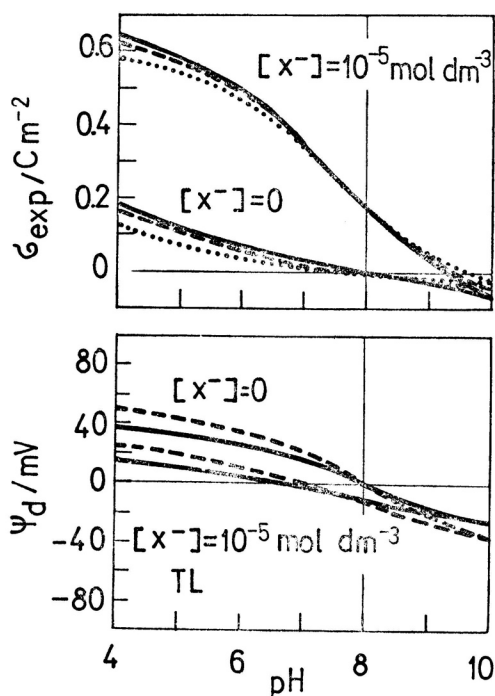
Figure 4. Calculated values os $\sigma_{exp}$ (upper part) and $\psi_d$ (lower part) as a function of pH according to the TL modal in the presence and in the absence of specifically adsorbable ions (X⁻). The calculations are performed for three ionic strengths controlled by a neutral 1 : 1 electrolyte [MA] : $10^{-3}$ mol/dm³ (dotted line), $5 \cdot 10^{-3}$ mol/dm³ (dashed line), and $10^{-2}$ mol/dm³ (solid line). The following values of parameters are used: $K_a^1 = 10^7$, $K_b^1 = 10^{-9}$, $K_{ass}^1$ (M⁺) = $K_{ass}^1$ (A⁻) = 10, $K_x^1 = 10^7$, $C_1 = 1.5$ F/m², $C_2 = 0.2$ F/m², $T = 298$ K, $\varepsilon_r = 78.5$. The total surface concentration of amphotheric sites is $10^{-5}$ mol/m² and the total surface concentration of sites to which X⁻ binds is $10^{-5}$ mol/m². The vertical line at pH = 8 denotes p.z.c. in the absence of specific adsorption.

volved in amphotheric equilibria. In this case the experimental surface charge density, as obtained by potentiometric titration is:

$$\sigma_{exp} = F (\Gamma_{SOH2^+} + \Gamma_{SOH2 \cdot A} - \Gamma_{SO^-} - \Gamma_{SO \cdot M}) \qquad (18)$$

while the surface charge in the 0-plane is:

$$\sigma_o = \sigma_{exp} - F\Gamma_{X^-} \qquad (19)$$

The aforementioned assumptions did not influence the conclusions since the trends in i.e.p., c.i.p. and p.z.c. were found to be generally the same, regardless of the model used in calculations. It is clear from Figure 4 that, in the absence of specific adsorption, c.i.p. and i.e.p. coincide and correspond to $\sigma_{exp} = \sigma_o = 0$ i.e. to the p.z.c. In the case of specific adsorption the c.i.p. was obtained at $\sigma_{exp} = 0.2$ C/m² but not at 0. Note that in this case p.z.c. is defined by $\sigma_{exp} = 0$ while i.e.p. corresponds to $\Psi_d = 0$ i.e. to $\sigma_s = 0$. The di-

screpancy between the c.i.p. and i.e.p. value can hardly be observed (pH difference of 0.2). Both values are close to the original p.z.c. and i.e.p. as obtained in the absence of specific adsorption. Therefore, it is very likely that one would neglect this discrepancy and use c.i.p. as the p.z.c. The real p.z.c. for the specific adsorption (where $\sigma_{exp} = 0$), however, is between pH 9.3 and 9.7. Consequently, the error in absolute $\sigma_{exp}$ values of the surface charge density will be about 0.2 C/m². This finding indicates the necessity for extremely high accuracy of potentiometric and electrokinetic data.
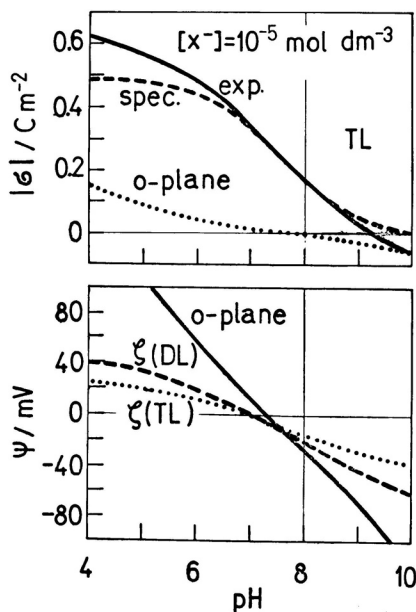


Figure 5. Calculated absolute values of different contributions to the surface charge density (upper part). The line denoted by »spec« describes $F\Gamma_{x}$- function i.e. the absolute value of surface charge density due to specific adsorption of X⁻ ions. Lower part: electrostatic potentials at the different planes as function of pH according to the TL model. Electrokinetic ζ-potential is also calculated by the DL model by assuming $l = 6$ Å. The ionic strength (MA) was taken to be $5 \cdot 10^{-3}$ mol/dm³, while other parameters are the same as in Figure 4.

Figure 5 (upper part) presents the contribution of the specific adsorption to the total surface charge. The charge in the 0-plane is the sum of the charge due to amphoteric equilibria (reactions 1,2) and specific adsorption (Equation 19). For the chosen conditions, the charge in the 0-plane was significantly lower than the charge obtained by potentiometric titration. The adsorption of negative X⁻ ions (presented in terms of absolute value of surface charge density) markedly reduces the positive charge of the surface. The lower part of Figure 5 presents calculated potential in the 0-plane. The function is almost linear with the slope of 43 mV which is, as expected[5,35], lower than the Nerstian one. Electrokinetic potentials for the TL model was taken as equal to $\Psi_{d}$, while in the case of the DL model (Stern-Gouy-Chapman) the ζ-po-

tential was calculated by means of Eq. (13) by taking $l = 6\text{Å}$. It is obvious that the zero value of the $\zeta$-potential (i.e.p.), which is at pH $= 7$, does not correspond to the p.z.c. which is in the pH range from 9 to 10.

The effect of the concentration of specifically adsorbable $X^-$ ions on the electrokinetic properties is displayed on Figure 6. The upper part of the figure presents the $\Psi_d$-potential which is, according to the TL model equal to the $\zeta$-potential. The lowering in the values of $\Psi_d$, causes a shift in the i.e.p. The calculations were performed for the ionic strength of $10^{-3}$ mol/dm$^3$. The lower part of Figure 6 presents the effect of the ionic strength on the i.e.p. dependency on the $X^-$ concentration. Acccording to this finding the examinations of the i.e.p. as dependent on the ionic strength may be suggested as a sensitive test for specific adsorption.
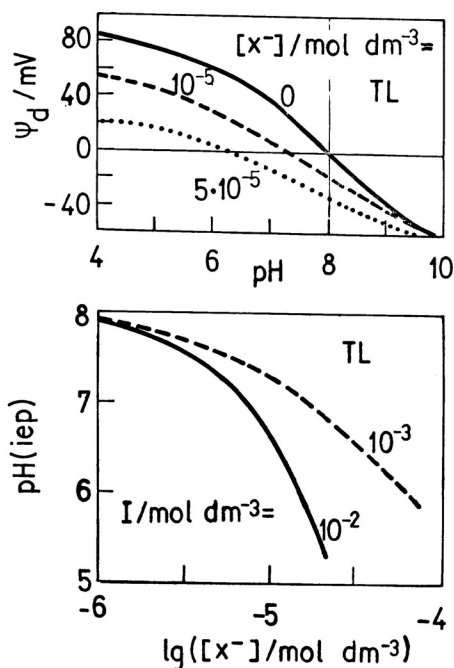


Figure 6. The effect of the concentration of specifically adsorbable ions $X^-$ on the potential at the onset of the diffuse layer (upper part) and on the isoelectric point (lower part) as calculated by the TL model for ionic strength of $5 \cdot 10^{-3}$ mol/dm$^3$. Note that in the TL model $\psi_d = \zeta$. The parameters used in calculations are the same as in Fig. 4.

In the case of a system in which the specific adsorption takes place, it is recommended that one at first performs the experiments with the simple electrolytes for which p.z.c. corresponds to c.i.p. and i.e.p. In such a case one determines the initial amount of acid (or base) by Eq. (15). Once this initial amount is known, one can use the sample of the same composition (same initial amount of acid), introduce the electrolyte causing the specific adsorption, and calculate the absolute surface charge density directly by Eq. (15).
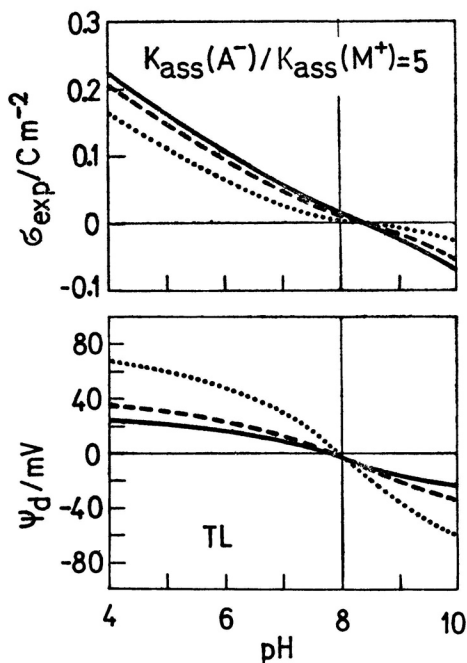
Figure 7. The pH dependency of the experimental surface charge density (upper part) and $\psi_d$ (lower part) as calculated by the TL model for three diferent ionic strengths: [MA] = $10^{-3}$ mol/dm³ (dotted line), $5 \cdot 10^{-3}$ mol/dm³ (dashed line), and $10^{-2}$ mol/dm³ (solid line). The parameters used in calculations are the same as in Fig. 4, except the intrinsic constants for associations of counterions: $K_{ass}^{1}$ (A⁻) = 50, $K_{ass}^{1}$ (M⁺) = 10.

This absolute charge is equal to $\sigma_{exp}$ as defined by Eq. (18). The p.z.c. is then simply available since it corresponds to the zero value of the $\sigma_{exp}$.

Specific adsorption is not the only cause for discrepancies between p.z.c., c.i.p. and i.e.p. Such a finding may be due to uneven association of positive and negative counterions. This is demonstrated on Figure 7. The i.e.p. and p.z.c., in the absence of specific adsorption, is at pH = 8 (see Fig. 4). If the intrinsic constant for anion association is 5 times higher than that for cations, the i.e.p. will be still close the original value. The p.z.c. value, however, will be shifted to pH = 8.4 and one would still obtain the common intersection point (c.i.p.).

This section demonstrates the main problems related to p.z.c. determination. This value is reliable only when the i.e.p. coincides with the c.i.p. Small deviations, which cannot always be accurately determined, can be accompanied with significant specific adsorption and erroneous values of p.z.c.

### VII. ADDITIONAL METHODS FOR DETERMINATION OF P.Z.C. AND I.E.P

There are several methods for the determination of p.z.c. and i.e.p. The so called »mass titration« method was proposed[3,4] for the determination of p.z.c. When using this method, the solid is added to the solution; the pH

changes as the concentration of solid increases, and it assimptoticaly reaches the constant value (pH$_\infty$ It was claimed that, for pure samples, this limiting pH value corresponds to the p.z.c. Our calculations showed that pH always approaches a limiting value at high solid contents. This finding was obtained for a pure sample and also for samples contaminated with acid or base. However, the limiting pH value corresponds to the p.z.c. only for the pure sample. The samples contaminated with base resulted in a pH$_\infty$ significantly higher than the p.z.c., while acid contamination produced a final pH lower than the p.z.c. Figure 8 displays the results of calculations based on the DL model (similar results were obtained by the TL assumptions). The values of the parameters were chosen so that the p.z.c. was at pH = 6. If
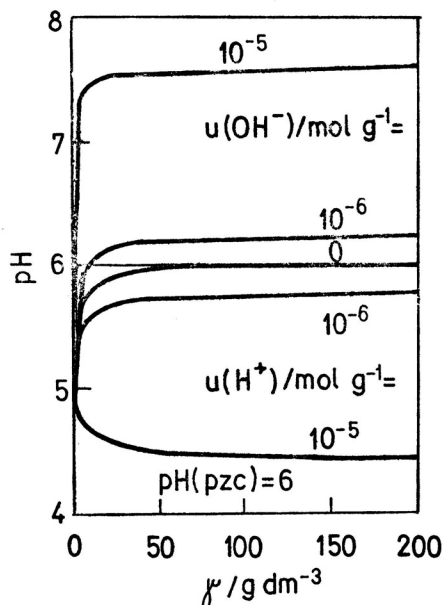


Figure 8. The dependency of pH on the mass concentration of solid powder ($\gamma$) as calculated by the DL model for different portions ($u$) of acidic or basic impurities. The specific surface area of the powder was taken to be 100 m$^2$/g, ionic strength is 10$^{-3}$ mol/dm$^3$ and $C$ = 1.5F/m$^2$. The values of $K_a^1$ and $K_b^1$ are chosen to be 10$^7$ and 10$^{-5}$, respectively, so that p.z.c. is at pH = 6. Other parameters are the same as in Fig. 4.

the system was taken as contaminated with 10$^{-5}$ moles of base per one gram of solid the final (limiting) pH value was found to be 7.6. The same portion of acid ($u$) resulted in the pH$_\infty$ = 4.4. Ten times lower contamination ($u$ = 10$^{-6}$ mol/g) produced a diference in the p.z.c. of 0.26. This finding suggests that the mass titration method may result in serious errors in the p.z.c.

The isoelectric point corresponds to the zero value of $\Psi_d$ and consequently to $\zeta$ = 0. The most common methods for determining the isoelectric point are electrokinetic techniques: electrophoresis, electroosmosis, streaming potential, streaming currrent, and rarely sedimentation potential measurements. In addition, the isoelectric point may be observed by coagulation measurements.

At the i.e.p., where $\zeta = \Psi_d = 0$, the potential barrier disappears and rapid coagulation takes place. To increase the sensitivity of the method these experiments should be performed at low ionic strengths.
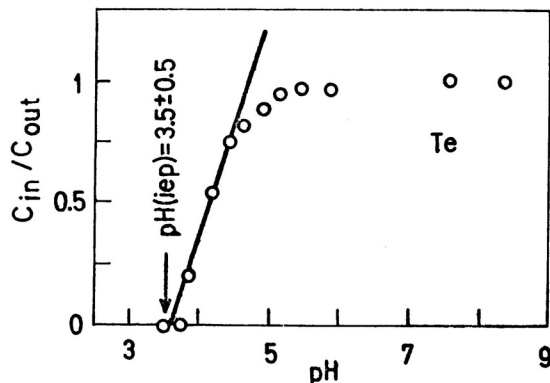


Figure 9. The determination of the isoelectric point of tellurium by adhesion method[2]. Dilute suspension of negatively charged particles were passed through the column packed with beads of Te ($r = 60$ μm). The ratio of inlet to outlet particle number concentration ($C_{in}/C_{out}$) corresponds to reciprocal rate of deposition. The isoelectric point for tellurium (aqueous systems at 25 °C) is obtained by extrapolation at pH = 3.5.

Similar reasoning, as applied to the coagulation, can be related to adhesion. The adhesion of particles (at low ionic strength) is fast if the surface bears an opposite charge with respect to the charge of the depositing particles[36,37]. For example, if one measures the deposition of hematite particles ($pH_{iep} = 7.3$)[20] on glass beads ($pH_{iep} < 3$) in a packed column and changes the pH from 10 to 4 the abrupt increase in the adhesion rate will be noted at the i.e.p. of hematite[38]. This method is useful for metallic surfaces[2,39], since classical methods applied to these surfaces cause serious problems due to their conductivity. In such a case one uses metal as a collector and colloid particles as sensors. It is convenient to use latex particles because their sign of charge is constant in a broad pH range.

Figure 9 presents results of the i.e.p determination of tellurium by the adhesion method. The negative latex dispersion was passed through the column packed with Te beads. To minimize the accumulation of particles at the surface, the starting condition was chosen to be basic (both surfaces were negative). The ratio of outlet to inlet particle concentration corresponds to reciprocal value of the adhesion rate. The pH was decreased by acid addition and the adhesion rate increased to the conditions of fast deposition at pH = 3.5. This pH value may be taken to be the isoelectric point of tellurium.

VIII. COUNTERION ADSORPTION

According to the present theories describing the equilibria in the electric interfacial layer[5-20], one would not expect a significant accumulation of counterions at the surface in the p.z.c. region. We shall consider a metal oxide dispersion in aqueous solution of a neutral electrolyte, the ions of which do

not adsorb directly to the surface. At the isoelectric point, which is equal to the point of zero charge, the net charge of the surface is zero *i.e.* the amount of $SOH_2^+$ groups is equal to the amount of $SO^-$ groups. The $\Psi'_o$ potential is zero and consequently $\Psi_\beta = 0$. As a consequence, the association of counterions should be zero or negligible (see Eqs 3,4). The value of $\Psi_\beta = 0$ produces $\Psi_d = 0$ and according to the Gouy-Chapman theory, the excess concentration of counterions and co-ions in the diffuse layer is also zero. If this conclusion is true, one would not observe the decrease in the ionic concentrations in the bulk of the liquid medium. Contrary to such an expectation, the numerous adsorption data obtained by radiotracer technique showed appreciable adsorption at the p.z.c. The adsorption of ions of neutral (inert) electrolytes was observed in the p.z.c. region by Li and de Bruyn[40] for $SiO_2/NaCl$ system, Smit *et al*[41-43] ($SiO_2/NaCl$ and $Al_2O_3/NaBr$), Foissy and coworkers[44,45] ($Tio_2/NaCl$), Sprycha[46,47] ($TiO_2$ and $Al_2O_3$/different electrolytes), Janusz[48] ($ZrO_2/NaCl$), Shiao and Mayer[49] ($Al_2O_3/NaBr$) and Chibowski[50-52] ($Tio_2$ and $Fe_2O_3/CsCl$). Smit *et al*[41-43] did not determine adsorption by measuring the concentration decrease in the bulk of solution, but they measured the amount of ions adsorbed on the
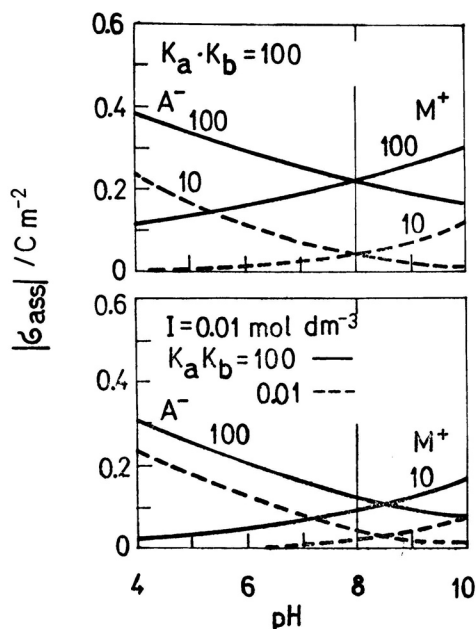


Figure 10. Absolute values of the surface charge density due to association (adsorption) of counterions ($M^+$ and $A^-$) as a function of pH calculated by the TL model.

$$\sigma_{ass} = F\Gamma_{SOH_2 \cdot A} \text{ or } \sigma_{ass} = F\Gamma_{SO \cdot M}$$

Upper part: effect of intrinsic constants for ionic association (values are demoted on diagrams) for $K_a' K_b' = 100$).

Lower part: effect of amphoteric intrinsic constants: $K_a' K_b' = 100$ (solid line), and $K_a' K'_b = 0.01$ (dashed line). The intrinsinc constants for counterion association are $K_{ass}'$ ($A^-$) = 100 and $K_{ass}'$ ($M^+$) = 10, as denoted on lines.

The ratio $K_a'/K_b'$ is always $10^{16}$ so that p.z.c. in the absence of the counterion association effect would be 8. The values of other parameters were the same as in **Figure 4.**

crystal surface using a special procedure of washing the crystals. Such a method violates the equilibrium state at the interface. The same technique was applied by Foissy et al[45] for powdered $TiO_2$; again the adsorbed amount may be considered to be lower than in the equilibrium state. The above problems were discussed by Sprycha and Golkiewicz[53] who also considered the application of ion-sensitive electrodes. The disadvantage of the techniques which are based on concentration change in the bulk of solution lies in required high solid content. Under such condition the overlapping of interfacial layers may affect the experimental data. At the present time the results of counterion adsorption in the p.z.c. region are sometimes considered as nonconvincing[18]. The reason for such an opinion may be the disagreement between expectations (theory) and results (experiments).

Figure 10 demonstrates the calculated adsorption of »indifferent« ions at the p.z.c. To obtain appreciable adsorption, high values of intrinsic equilibrium constants for both amphoteric and counterion association equilibria are necessary. However, high values of the association constants would cause such a high counterion association in the region far from i.e.p. that the surface concentration of free surface charge groups and, consequently, potentials in 0-, $\beta$- and d-planes would be lower than those expected from electrokinetic data.

Therefore, if counterion adsorption data are accepted, one should find a reason for the discrepancy between theoretical expectations and experimental data. A possible explanation is based on the inhomogeneous structure of the surface charge, which has been ignored in the Gouy-Chapman model. At the isoelectric point, despite the zero of overall charge, there are (in same amounts) fixed point charges of $SOH_2^+$ and $SO^-$ groups. The electrostatic (Coluombic) field around these charges attracts counterions. For example, nitrate ions will be attracted by $SOH_2^+$ groups and sodium ions will tend to be located closer to $SO^-$ groups. The equilibrium distribution could be described by the Debye-Hückel theory in a similar way as used by Mirnik[54] or Manning[55]. As a consequence the uptake of cations from the solution will be equivalent to the amount of surface $SO^-$ groups. Analogously, the amount of surface $SOH_2^+$ groups will correspond to the adsorption of anions. This assuption may be used to estimate the values of $\Gamma_{SOH_2^+}$ and $\Gamma_{SO^-}$ at the i.e.p. Such information will be extremely useful, because it may enable direct evaluation of single values of $K_a^i$ and $K_b^i$. The ratio of these two constants can be readily obtained from the p.z.c., but the commonly accepted method for evaluation of single values of of $K_a^i$ and $K_b^i$ is not accurate and depends highly on the assumed model of the electrical interfacial layer.

## IX. SLIPPING PLANE SEPARATION

The determination of the electrokinetic slipping plane separation from the solid surface is based on the assumption that $\zeta$-potential corresponds to the imaginary shear plane in the electric interfacial layer. The knowledge of the value of the separation distance of the slipping plane ($l$) would be important because it enables the calculation of the $\Psi_d$ potential from the electrokinetic data (Eq. 13).

It is often assumed[26] that the slipping plane is so close to the surface and that potential drop in this region could be neglected so that $\zeta = \Psi_d$. However, there are indications that this separation is large enough[27-31] to cause a significant error if neglected. Some adsorption studies suggested that this separation is between 16 and 20 ångstroms[28-30]. Recent electrokinetic data on »hairless« latex particles[27] lead to conclusion that $l = 6$ Å.

Eversole and coworkers[56,57] introduced a method to obtain the slipping plane separation based on the Gouy-Chapman theory. The Gouy-Chapman function (13) can be rewriten as

$$\ln[\tanh(F\zeta/4RT)] = \ln[\tanh(F\Psi_d/4RT)] - \varkappa l \tag{20}$$

In the original work the l.h.s. of Eq. (20) was plotted vs $\varkappa$ and the slope was taken to be the value of the slipping plane separation. Such a procedure assumes that $\Psi_d$ is independent of $\varkappa$ (i.e. of the ionic strength) as long as the activity of potential determining ions (pH for metal oxides) is kept constant. This assumption would be true only if $\Psi_d$ shows the Nerstian behavior. However, according to surface complexation model, the value of $\Psi_d$ decreases as ionic strength increases so that the slope is always higher than $l$. Consequently, the values of $l$, as obtained by the original Eversole's method[56,57], are too high. Moreover, the plot of $\ln[\tanh(F\zeta/4RT)]$ vs $\varkappa$ is not linear. Therefore, the only information available by this method is the maximum possible value of $l$ from the minimum value of the slope. Figure 11
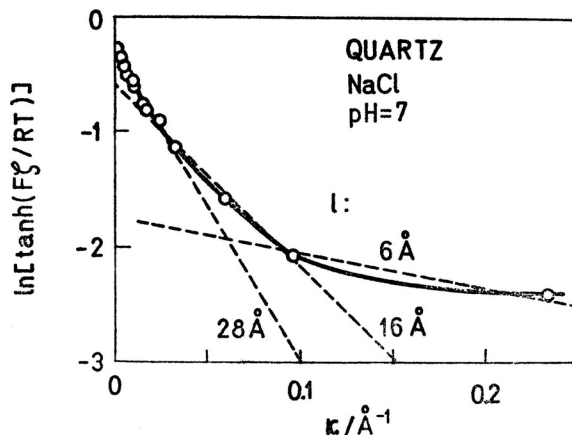


Figure 11. The determination of the slipping plane separation (l) for quartz in aqueous solution of NaCl as suggested by Eversole and coworkers[58]. The plot is according to Eq. (20). Dashed lines correspond to different values of $l$ as denoted on the diagram. The experimental data were taken from reference 58.

presents the electrokinetic data for quartz as obtained by Gaudin and Fuerstenau[56]. The dashed lines denote slopes corresponding to three different values of the slipping plane separation. The lowest slope indicates that $l < 6$ Å, which does not contradict recent data for latex particles[27]. Our recent data[30] on hematite resulted in $l \approx 8$ Å. This value was obtained by the simultaneous interpretation of electrokinetic and potentiometric data for hematite dispersion in water and in water/alcohol mixtures.

## X. MEASUREMENTS OF SURFACE POTENTIALS

There are several attempts to directly measure surface potentials[59-61]. The major problem is to assign measured values to corresponding electrostatic potentials at certain planes postulated by certain model. For example, the potential of platinum electrode covered with sintered hematite showed the Nernstian behavior[59], i.e. the slope of electrode potential vs pH was 59 milivolts. If measured values corresponded to $\Psi_0$ one would expect deviations from the Nernstian slope at high ionic strengths[23]. Unfortunately, the experiments were performed at low ionic strength so that one cannot use these data for such a discussion. In order to clarify this problem the experiments with several »glass electrodes« were performed in different media[61]. In the first experiment hydrochloric acid from a commercial glass electrode (Iskra, Kranj) was discharged. After drying, the electrode was filled with mercury.
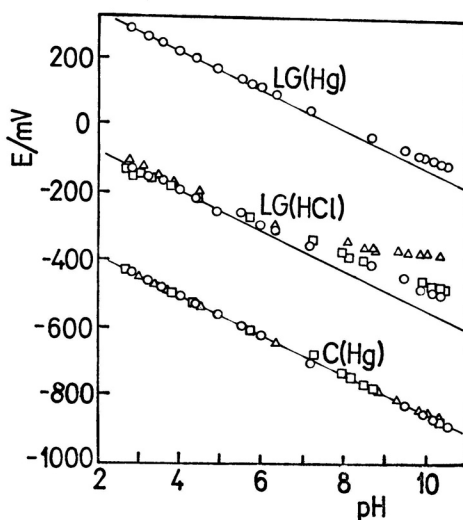


Figure 12. The dependency of electrode potential (vs N.H.E.) on pH at 25 °C. Data were taken from reference 61.
    Electrodes are as follows. Comertial glass electrode filled with mercury: C(Hg); glass electrode made from ordinary laboratory glass filled with HCl: LG(HCL); and electrode made from the same glass and filled with mercury: LG(Hg). Media: [KNO₃] = 0.1 mol/dm³ (O), [KNO₃] = 1 mol/dm³ (□), [NaNO₃] = 1 mol/dm³ (Δ).
    Solid lines denote the Nernstian slope of 59.2 millivolts.

The contact was realized by means of a platinum wire. The data obtained with this electrode are denoted by C(Hg) in Fig. 12. The response of this electrode was Nerstian in entire pH range (2.5 ... 10.5) for all examined electrolyte media (see Fig. 12). This result suggests that potential difference is created at the solid/solution interface and that signal is transferred through the glass and glass/mercury interface regularly; there is no need for another (inside) glass/solution interface. Such electrode is directly comparable with platinum/hematite electrode used by Penners, Koopal and Lyklema[59]. Additional experi-

ments were performed with glass electrodes made from ordinary laboratory glass tubes. Electrode denoted by LG(HCl) was filled with hydrochloric acid, and an Ag/AgCl electrode was used to transfer the signal. This electrode showed significant deviation from the Nernstian slope in the alkaline region, esspecially at high concentrations of NaNO₃. This effect, known as »sodium error«, can be explained in terms of sodium (counterion) association with negatively charged surface groups. The isoelectric point of glass is low[62] (pH below 3). In this region the counterion association is negligible. However, at high pH values the surface becomes negative which promotes association of counterions and thus, according to the surface complexation model, the potential at the surface ($\Psi_o$) should be lowered. The (laboratory) glass electrode was also filled with mercury (LG(HG)) and showed similar behavior as the electrode prepared from same glass when filled with HCl.

## CONCLUSION

This article discusses several theoretical approaches to the interpretation of the results of ionic equilibria at the solid/liquid interfaces. The purpose of a theory is twofold. First of all, it enables the understanding of a process or a state, and may relate a specific behavior to a few general principles. On the other hand, from a practical point of view, the theory serves for the interpretation of experimental results and characterizes the behavior of the system with few physically meaningful parameters. The values of those parameters can be used to predict the behavior of the system at different conditions. For example, the equilibrium constant of acetic acid dissociation could be obtained by measuring pH of a sample of known concentration. Afterwards it can be used to predict pH for any concentration, even in mixtures.

The present state of the art in surface chemistry has not reached such a level of refinement. The commonly accepted theories enable only understanding of main reasons for a certain behavior of a system, and some semiquantitative predictions. Therefore, one may conclude that new experimental techniques are necessary to understand better the ionic processes at the interface. Some more recent approaches use spectroscopy[63], calorimetry[64,65], new electrodes[59] etc. On the other hand, modern numerical techniques enable the exact solutions of the problems so that commonly used approximations are no longer necessary.

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## SAŽETAK

### Neke proturječnosti u razumijevanju ravnoteža u električnom dvosloju

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U ovom pregledu se razmatraju neke proturječnosti povezane s mjerenjima i interpretacijom ravnoteže u električnom međupovršinskom sloju na granici čvrsto/tekuće. Diskutiraju se ravnoteže amfoteričkih reakcija i asocijacija protuiona pri površini. Uspoređuje se primjenjivost koncepta intrinzičke konstante ravnoteže za asocijaciju protuiona s modelom u kojem asocirani protuioni nisu smješteni u ravnini, nego su raspoređeni oko nabijenih površinskih grupa. Mjerenja adsorpcije protuiona oko točke nule naboja ukazuju na nedostatke uobičajenih modela zasnovanih na teoriji Gouy-Chapman. Ovi rezultati su objašnjeni efektom diskretnosti površinskog naboja. Razmatraju se razlike između modela dvostrukog i trostrukog sloja. Numerička simulacija ravnoteža u međupovršinskom sloju pokazuje da izoelektrička točka može biti bliska zajedničkom sjecištu titracijskih krivulja, unatoč značajnoj specifičnoj adsorpciji. To ukazuje na potrebu za visokom točnošću u određivanju ovih točaka. Pokazuje se da se točka nula naboja može odrediti pomoću masene titracije samo ako su uzorci čisti. Kontaminacija uzorka kiselinom ili bazom dovodi do značajnih grešaka u točki nula naboja i eksperimentalnoj površinskoj gustoći naboja. Opisana je adhezijska metoda za određivanje izoelektričke točke metalnih površina.