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Formal Mathematical Analysis of the Existence of the Common Intersection Point in Relation to Determining the Parameters Describing Ion Adsorption at the Oxide/Electrolyte Interface: Comparison of the Triple and Four-Layer Models

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Abstract. For most oxide/electrolyte systems potentiometric titration curves measured for different ionic strengths have a Common Intersection Point (CIP) which corresponds to the Point of Zero Charge (PZC). However, there are systems where a CIP exists but the surface charge at this point does not equal zero (PZC $\neq$ CIP). In this paper theoretical analysis of the systems in which the PZC and CIP do not coincide is presented. It is based on the well-known 2-pK surface charging approach and Triple Layer Model (TLM) as well as the Four Layer Model (FLM) of the electric double layer. The appropriate mathematical criterion for CIP existence was applied with detailed derivations, both for TLM and FLM. Having determined in this manner the parameter values, one can draw proper conclusions about the features of oxide/electrolyte adsorption systems, in which PZC and CIP do not coincide. The values of adsorption parameters are found by fitting simultaneously the obtained theoretical expressions to both of the experimental titration isotherms, and to the individual isotherms of electrolyte cation adsorption measured using radiometric methods.

Keywords: oxide/electrolyte interface, ion adsorption, double layer modeling

Introduction

Metal (hydr)oxides in aqueous solution most frequently have electric charge on their surfaces, which plays important role in stabilizing colloids suspensions and is crucial for ion adsorption on oxide surfaces. In principle the amount of surface charge depends on the pH of solution, because protons are potential determining ions in the case of metal oxides. The pH at which surface charge equals zero is defined as point of zero charge (PZC). Sometimes the pristine point of zero charge (PPZC) is also defined as

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PZC determined in the absence of strongly adsorbing species in solution. Additionally, the isoelectric point (IEP) is commonly used. This point is defined as the pH at which the electrokinetic potential equals zero. Detailed and clear discussion of the above mentioned quantities could be found, for example, in Kosmulski (2001).

Except for the rare cases, the experimental potentiometric titration curves (surface charge isotherms—δ_0 (pH)) for the oxide/electrolyte adsorption systems, measured in different inert electrolyte (1:1) concentrations have a common intersection point (CIP) at PZC (Lyklema, 1984). Some authors instead of CIP use the term point of zero salt effect (PZSE) (Sposito, 1992). In the case of the lack of specific adsorption it has been believed that the coincidence of PZC and CIP is a common feature of these adsorption systems. However, the lack of such coincidence in experimental data for such systems has already been published (Block and De Bruyn, 1970; Breeuwsma and Lyklema, 1971; Yates and Healy, 1980; Kokarev et al., 1982; Penners et al., 1986; Persin et al., 1992; Kosmulski, 1997; Mustafa et al., 1998; Janusz et al., 1997). Figure 1 presents two systems: in the first one the coincidence of PZC and CIP is shown and in the second one discrepancy between PZC and CIP is visible.

It has been done very little on theoretical interpretation of the systems which show discrepancy between PZC and CIP—only certain assumptions have been expressed or some qualitative conclusions drawn. Just recently, two our papers have been published concerning this problem. In the first one, the temperature dependence of surface charge isotherms (Mustafa et al., 1998) in the systems where PZC and CIP do not coincide was subjected to a quantitative theoretical-numerical analysis (Rudzinski et al., 2000). The second one (Rudzinski et al., 2001) concerned the theoretical analysis not only experimental titration curves, but also individual isotherms of ion adsorption of inert electrolyte, measured by using radiometric methods (Janusz et al., 1997). In both cases the theoretical modeling was performed according to 2-pK charging mechanism and triple layer model (TLM) based on the surface reactions suggested by Davis and Leckie (1978) and Davis et al. (1978).

We applied 2-pK charging mechanism due to its popularity and cohesion of obtained thermodynamic parameters. As it has been recently demonstrated by Sverjensky the proper definition of standard states for activities of mineral surface sites and species enables us to obtain unique set of parameters for given oxide and electrolyte solution from the data obtained by various authors for different samples of the same oxide (Sverjensky, 2003).

We did not use the multi site complexation (MUSIC) model of surface charging (Hiemstra et al., 1996) because of its mineral sample specificity. Namely, MUSIC model makes possible to calculate the proton affinity of individual surface groups on the basis of the undersaturation of the surface oxygen valence, which can be determined from crystal structure. However, the type and number of surface groups depends on assumed ratios of different crystal faces in the investigated oxide sample, which should be well-crystallized solid. As we see the MUSIC model is designed to describe specific, well-defined systems whereas the 2-pK approach

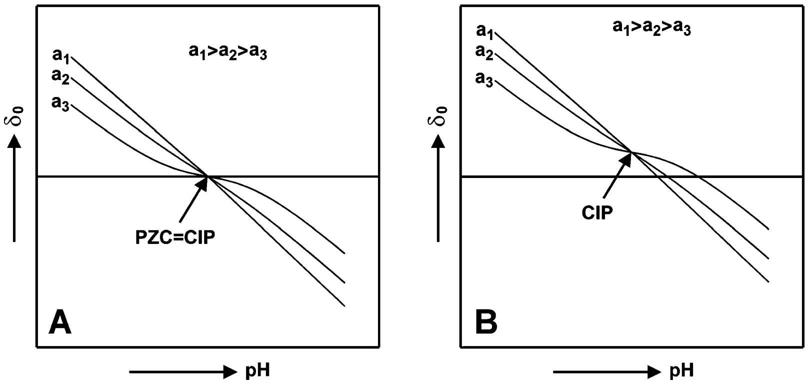

Figure 1. Schematic picture of the δ_0 (pH) plots depending on the concentration (activity) of electrolyte a_i $(i = 1, 2, 3)$. (A) The case of equality PZC = CIP, (B). The case of inequality PZC $\neq$ CIP.

is general framework describing oxide surface charging in solution.

It is well-known, that the experimental data can, almost equally well, be fitted by a variety of theoretical expressions, corresponding to various adsorption models, and high correlations are observed between certain best-fit parameters. Therefore, the problem of a fundamental importance is to decrease on some rational basis the number of best-fit parameters. Simplification of an adsorption model, is not the best solution of the problem. In a series of recently published papers, Rudzinski and co-workers have shown, that the existence of CIP may be applied for that purpose (Rudzinski et al., 1998, 1999a, 1999b, 1999c). The idea is very simple and was published before (Lyklema, 1984; Sposito, 1992) as the derivative: $(d\delta_0/da)_{\mathrm{pH=CIP}} = 0$ (where a is the activity of inert electrolyte). It allows for the investigated adsorption model to reduce the number of the best-fit parameters.

The refinement of the classical 2-pK TLM is the four layer model (FLM). Its idea was introduced to literature by Barrow et al. (1981). Bousse et al. (1983a) presented in their paper a diagram of FLM, in which anions and cations of the basic electrolyte are not located in the same layer (as in TLM), but in two separate ones. The first rigorous thermodynamic description based on that physical model, and providing theoretical expressions for all the experimentally measured physicochemical quantities, has been recently published by Charmas et al. (1995), Charmas and Piasecki (1996) and Charmas (1998, 1999).

In this paper, we are going to show how the existence of CIP may be explored in a quantitative analysis of adsorption in the oxide/electrolyte systems in which PZC and CIP do not coincide. For such a case, the mathematical criterion $(d\delta_0/da)_{\mathrm{pH=CIP}} = 0$ has been applied formally with detailed appropriate derivations, both for TLM and FLM models. Having determined properly the parameter values one can draw proper conclusions about the features of oxide/electrolyte adsorption systems, in which PZC and CIP do not coincide.

The symbols PZC and CIP used in the paper refer not only to the names of appropriate points but also to the values of pH at which $\delta_0 = 0$ and at which surface charge isotherms measured in different inert electrolyte concentrations have a common intersection point, respectively.

Theory

Brief Principles of Triple Layer Model

The potential determining ions H^+, cations C^+ and anions A^- of the basic electrolyte form, according to the 2-pK charging mechanism, the following surface complexes: SOH^0, SOH_2^+, SO^-C^+ $SOH_2^+A^-$, where S is the surface site. We consider the adsorption of ions as a result of the following surface reactions suggested by Davis, Leckie and other authors (Davis and Leckie, 1978, 1979, 1980; Davis et al., 1978; Yates and Healy, 1980):

$$SOH_2^+ \overset{K_{\mathrm{a1}}^{\mathrm{int}}}{\longleftrightarrow} SOH^0 + H^+ \tag{1a}$$

$$SOH^0 \overset{K_{\mathrm{a2}}^{\mathrm{int}}}{\longleftrightarrow} SO^- + H^+ \tag{1b}$$

$$SOH_2^+A^- \overset{{}^*K_{\mathrm{A}}^{\mathrm{int}}}{\longleftrightarrow} SOH^0 + H^+ + A^- \tag{1c}$$

$$SOH^0 + C^+ \overset{{}^*K_{\mathrm{C}}^{\mathrm{int}}}{\longleftrightarrow} SO^-C^+ + H^+ \tag{1d}$$

where SO^- denotes the outermost surface oxygens. The equilibrium constants $K_{\mathrm{a1}}^{\mathrm{int}}$, $K_{\mathrm{a2}}^{\mathrm{int}}$, ${}^*K_A^{\mathrm{int}}$, and ${}^*K_C^{\mathrm{int}}$ refer to reactions (1a)–(d).

Introducing the notation,

$$\begin{aligned}
\theta_0 &= [SOH^0]/N_s \quad \theta_+ = [SOH_2^+]/N_s \\
\theta_A &= [SOH_2^+A^-]/N_s \\
\theta_C &= [SO^-C^+]/N_s \\
\theta_- &= [SO^-]/N_s = 1 - \sum_i \theta_i \quad (\mathrm{i} = 0, +, \mathrm{A}, \mathrm{C}) \\
N_s &= [SO^-] + [SOH^0] + [SOH_2^+] \\
&\quad + [SO^-C^+] + [SOH_2^+A^-]
\end{aligned} \tag{2}$$

we can arrive, as shown in paper (Rudzinski et al., 1991) at the following set of Langmuir-like equations,

$$\theta_i = \frac{K_i f_i}{1 + \sum_i K_i f_i}, \quad i = 0, +, \mathrm{A}, \mathrm{C} \tag{3}$$

where the constants K_i are the following functions of common accepted intrinsic equilibrium constants of surface reactions (1a)–(d):

$$\begin{aligned}
&K_0 = \frac{1}{K_{a2}^{\mathrm{int}}} \quad K_+ = \frac{1}{K_{a1}^{\mathrm{int}} K_{a2}^{\mathrm{int}}} \quad K_{\mathrm{C}} = \frac{{}^*K_C^{\mathrm{int}}}{K_{a2}^{\mathrm{int}}} \\
&K_A = \frac{1}{K_{a2}^{\mathrm{int}} \cdot {}^*K_A^{\mathrm{int}}}
\end{aligned} \tag{4}$$

defined for the following surface reactions:

$$\mathrm{SO^- + H^+ \overset{K_0}{\longleftrightarrow} SOH^0} \tag{5a}$$

$$\mathrm{SO^- + 2H^+ \overset{K_+}{\longleftrightarrow} SOH_2^+} \tag{5b}$$

$$\mathrm{SO^- + 2H^+ + A^- \overset{K_A}{\longleftrightarrow} SOH_2^+A^-} \tag{5c}$$

$$\mathrm{SO^- + C^+ \overset{K_C}{\longleftrightarrow} SO^-C^+} \tag{5d}$$

and where

$$f_0 = \exp\left\{-\frac{e\psi_0}{kT} - 2.3\mathrm{pH}\right\}, \quad f_+ = f_0^2 \tag{6a}$$

$$f_C = a_C \exp\left\{-\frac{e\psi_0}{kT} + \frac{e\delta_0}{kTc_1}\right\} \tag{6b}$$

$$f_A = a_A \exp\left\{-\frac{e\psi_0}{kT} - \frac{e\delta_0}{kTc_1} - 4.6\mathrm{pH}\right\} \tag{6c}$$

where a_C and a_A are the activities of inert electrolyte cation and anion, respectively, ψ_0 is the surface potential, c_1 is the first integral capacitance, δ_0 is the monitored surface charge, defined as follows,

$$\delta_0 = B_s[\theta_+ + \theta_A - \theta_- - \theta_C], \qquad B_s = e \cdot N_s \tag{7}$$

and N_s is the surface density (sites/m^2).

To express ψ_0 (pH) dependence, which occurs in the equations for the individual adsorption isotherms θ_i's, and for the surface charge δ_0 (3), (6) and (7), we accepted in our papers (Rudzinski et al., 1991, 1992, 1998, 1999a, 1999b, 1999c) the relation used by Bousse et al. (1983b) and Van der Velkkert et al. (1988),

$$2.303(\text{PZC-pH}) = \frac{e\psi_0}{kT} + \sin\mathrm{h}^{-1}\left(\frac{e\psi_0}{\beta kT}\right) \tag{8}$$

where β is given by

$$\beta = \frac{2e^2N_s}{c_{\mathrm{DL}}kT}\left(\frac{K_{\mathrm{a2}}^{\mathrm{int}}}{K_{\mathrm{a1}}^{\mathrm{int}}}\right)^{1/2} \tag{9}$$

In Eq. (9) c_{DL} is the linearized double-layer capacitance which can be theoretically calculated (depending on the salt concentration in the solution), in the way described in Bousse's paper (1983b).

Taking into account Eq. (6), the non-linear equation system (3) can be transformed into the following, non-linear equation with respect to δ_0

$$\delta_0 = B\frac{K_+f_+ + K_Af_A - K_Cf_C - 1}{1 + \sum_i K_if_i} \qquad i = 0, +, \mathrm{A}, \mathrm{C} \tag{10}$$

This non-linear equation for δ_0 can be easily solved by means of an iteration method, to give the value of δ_0 for each pH value. Having calculated these values, one can evaluate easily the individual adsorption isotherms θ_i's from Eqs. (3).

Coincidence of PZC and CIP in TLM: TLM$_{PZC=CIP}$

The experimental studies show, that in the majority of the investigated systems, the value of the point of zero charge (PZC) does not practically depend upon the salt concentration in the equilibrium bulk solution. So, all the surface charge (titration) curves δ_0 (pH) have a common intersection point (CIP) at a certain pH value. It is shown in Fig. 1(A).

In the systems in which PZC = CIP, the independence of PZC of the salt concentration can be formally expressed as follows, when we assume that $a = a_C = a_A$,

$$\frac{\partial\delta_0}{\partial a} = -\frac{\partial G/\partial a}{\partial G/\partial\delta_0} = 0 \tag{11}$$

where G is obtained from Eq. (10):

$$G = \delta_0 - B\frac{K_+f_+ + K_Af_A - K_Cf_C - 1}{1 + \sum_i K_if_i} \tag{12}$$

To find the interrelation among the values of the equilibrium constants of the surface reactions (5a)–(d), only the following derivative should be calculated:

$$\frac{\partial G}{\partial a} = 0 \tag{13}$$

So, performing translations one can obtain the following general equation,

$$\begin{aligned} 2K_A\frac{\partial f_A}{\partial a} &+ K_0f_0\left[K_A\frac{\partial f_A}{\partial a} - K_C\frac{\partial f_C}{\partial a}\right] \\ &- 2K_+f_+K_C\frac{\partial f_C}{\partial a} - 2K_Af_AK_C\frac{\partial f_C}{\partial a} \\ &+ 2K_Cf_CK_A\frac{\partial f_A}{\partial a} = 0 \end{aligned} \tag{14}$$

For pH = PZC, i.e. $\delta_0 = 0$ and $\psi_0 = 0$ (in Eqs. (6)), Eq. (14) can be transformed then to the following form:

$$K_0H(K_AH^2 - K_C) - 2K_+K_CH^2 + 2K_AH^2 = 0 \tag{15}$$

$$H = 10^{-\mathrm{PZC}} \tag{15a}$$

On the other hand, taking into account Eq. (10) for pH = PZC we obtain

$$K_+H^2 + K_AH^2a - K_Ca - 1 = 0 \tag{16}$$

One can prove that for the set of Eqs. (15) and (16) we obtain the following interrelations between equilibrium constants:

$$K_AH^2 - K_C = 0 \tag{17a}$$

$$K_+H^2 = 1 \tag{17b}$$

what goes to the well known interrelations for the classical TLM model (Davis and Leckie, 1978; Davis et al., 1978; Rudzinski et al., 1991)

$$K_{a2}^{\text{int}} = \frac{H^2}{K_{a1}^{\text{int}}} \quad \text{and} \quad {}^*K_A^{\text{int}} = \frac{H^2}{{}^*K_C^{\text{int}}} \tag{18}$$

Relations (18) can be also written in another form,

$$\text{PZC} = \frac{1}{2}\left(\text{p}K_{a1}^{\text{int}} + \text{p}K_{a2}^{\text{int}}\right) \tag{19a}$$

$$\text{PZC} = \frac{1}{2}\left(\text{p}^*K_C^{\text{int}} + \text{p}^*K_A^{\text{int}}\right) \tag{19b}$$

where symbols: $\text{p}K = -\text{logK}$.

These two equations allow to reduce the number of unknown best-fit parameters (equilibrium constants) from four to two.

Lack of Coincidence of PZC and CIP in TLM: $TLM_{PZC\neq CIP}$

In the case when PZC ≠ CIP, as shown in Fig. 1(B), the surface charge curves for different inert ion concentrations have a common intersection point constant for a certain value δ_0. Using this we can solve the problem in another way. Let us consider a common intersection point CIP $(\partial\delta_0/\partial a)_{\text{pH=CIP}} = 0$ (i.e. PZC ≠ CIP) as independence of CIP of the salt concentration. It can be formally expressed as follows:

$$\frac{\partial\text{CIP}}{\partial a} = -\frac{\partial G/\partial a}{\partial G/\partial\text{CIP}} = 0 \tag{20}$$

Rewriting Eq. (10) in the following form:

$$\frac{\delta_0(\text{pH} = \text{CIP})}{B} = \frac{K_+f_+ + K_Af_A - K_Cf_C - 1}{1 + \sum_i K_if_i} \tag{21}$$

and remembering that now $\delta_0 \neq 0$, so substituting $E = \frac{\delta_0(\text{pH=CIP})}{B}$, the function G will have now the following form:

$$G = E\left(1 + \sum_i K_if_i\right) - K_+f_+ - K_Af_A + K_Cf_C + 1 \tag{22}$$

To find the interrelation between the equilibrium constants we can perform only the differentiation $\partial G/\partial a$ in Eq. (20). So, we obtain:

$$K_A\frac{\partial f_A}{\partial a}(1 - E) - K_C\frac{\partial f_C}{\partial a}(1 + E) = 0 \tag{23}$$

For pH = CIP the functions f_i in Eqs. (6) have the following forms:

$$f_0 = MP \quad f_+ = M^2P^2 \quad f_C = MDa \quad f_A = \frac{M}{D}P^2a \tag{24}$$

where

$$P = 10^{-\text{CIP}} \quad D = \exp\left\{\frac{e\delta_0(\text{CIP})}{kTc_1}\right\}$$

$$M = \exp\left\{-\frac{e\psi_0(\text{CIP})}{kT}\right\} \tag{25}$$

and where $\delta_0(\text{CIP})$ and $\psi_0(\text{CIP})$ are the values of surface charge and potential, respectively, in the point of pH = CIP.

Then, Eq. (23) can be written in the following form:

$$K_C = K_A\frac{P^2}{D^2} \cdot \frac{1 - E}{1 + E} \tag{26}$$

It can be observed that the value E occurring in the numerator and denominator of Eq. (26) is very small $E \ll 1$ so (26) can be presented in a simpler form which is a very good approximation

$$K_C = K_A\frac{P^2}{D^2} \tag{27}$$

The simplification of Eq. (26) is similar to the buffers problem and their capability, i.e. when we add small volume of strong acid or base, the pH of buffer almost does not change. In our case, similar, the value of K_C almost does not change because of small E value.

The next equation, which allows to reduce the number of equilibrium constants as the best-fit parameters, can be obtained from the condition that for each concentration titration curves have the "individual" PZC value . So, for pH = PZC the Eq. (24) have the following forms for $D = 1$, $M = 1$, $P = H : f_0 = H$, $f_+ = H^2$, $f_C = a$ and $f_A = aH^2$. Using Eq. (10) we obtain the interrelation (16).

Combining Eqs. (16) and (27) we obtain the following equation:

$$K_+H^2 + K_A a\left(H^2 - \frac{P^2}{D^2}\right) = 1 \tag{28}$$

which can be presented in the following form:

$$K_{a2}^{\text{int}} = \frac{H^2}{K_{a1}^{\text{int}}} + \frac{H^2 - P^2/D^2}{{}^*K_A^{\text{int}}}a \tag{29a}$$

However, Eq. (27) can be presented in the following form:

$${}^*K_C^{\text{int}} = \frac{P^2}{D^2 \cdot {}^*K_A^{\text{int}}} \tag{29b}$$

Equation set (29) corresponds to set (18) form the model PZC = CIP and allows to reduce the number of unknown best-fit parameters from four to two.

The Brief Principles of the Four Layer Model

The four layer model FLM is a refinement of the TLM. Its idea was introduced to literature by Barrow et al. (1981). A new layer (the fourth one as the name indicates, but situated as the second, next to the suface layer "0" where protons are adsorbed), was reserved first for the bivalent metal ions or anions of multiproton oxy-acids. Cations and anions of basic electrolyte were placed still in the same layer as in the TLM. Another kind of FLM was launched by Bousse et al. (1983a) who presented in their paper electrolyte and the potential determining ions H^+. They argued that anions and cations of the basic electrolyte are not located in the same layer (as in TLM), but in two separate ones. A rigorous thermodynamic description and expressions for all the experimentaly measured physicochemical quantities, has been recently published by Charmas et al. (1995), Charmas and Piasecki (1996), and Charmas (1998, 1999).

Here only the basic equations will be repeated to help the reader following the transformations corresponding to CIP consequences.

The basic definitions given by Eqs. (1)–(5) are the same in both TLM and FLM. Moreover, the functions f_0 and f_+ are the same in both complexation models and have the forms given by Eqs. (6a). The functions f_C and f_A are different what is connecting with the localization of cation and anion in different layers. Now, instead of Eqs. (6b) and (6c) they have the more complex forms (Charmas et al., 1995),

$$f_C = a_C \exp\left\{-\frac{e\psi_0}{kT} + \frac{e\delta_0}{kTC_+}\right\} \tag{30a}$$

$$f_A = a_A \exp\left\{-\frac{e\psi_0}{kT} - \frac{e\delta_0}{kTC_+} - \frac{e\delta^*}{kTC_+} + \frac{e\delta^*}{kTC_-} - 4.6\text{pH}\right\} \tag{30b}$$

where

$$\delta^* = B_S(\theta_- - \theta_+ - \theta_A) \tag{30c}$$

and where C_+ and C_- are the electrical capacitances constant in the regions between planes: surface—plane of cation adsorption and surface—plane of anion adsorption, respectively.

The way of solving non-linear Eq. (10) for FLM is more complex and was explained elsewhere (Charmas et al., 1995; Charmas and Piasecki, 1996).

Coincidation of PZC and CIP in FLM: FLM$_{PZC=CIP}$

The independence of PZC of the salt concentration can be formally expressed using the relation given by Eq. (10). The functions f_i for this model—Eqs. (6a), (30a) and (30b)—have now the following forms:

$$f_0 = H \quad f_+ = H^2 \quad f_C = a \quad f_A = a\,H^2\,P^* \tag{31}$$

where

$$P^* = \exp\left\{-\frac{eB}{kT}\cdot\frac{{}^*K_C^{\text{int}}a}{2K_{a2}^{\text{int}} + H + 2^*\,K_C^{\text{int}}a} \times \left(\frac{1}{C_-} - \frac{1}{C_+}\right)\right\} \tag{32}$$

So, the general Eq. (14) can be transform to the following one:

$$K_0H\,(K_A\,H^2\,X^* - K_C) - 2K_+K_C\,H^2 + 2K_AH^2\,X^* + 2K_C\,K_AH^2\,a^2\,\frac{\partial P^*}{\partial a} = 0 \tag{33}$$

where

$$\frac{\partial P^*}{\partial a} = P^* \ln P^* \left(\frac{1}{a} \cdot \frac{2K_{a2}^{\text{int}} + H}{2K_{a2}^{\text{int}} + H + 2^* K_C^{\text{int}} a} + \frac{d \ln\left(\frac{1}{C_-} - \frac{1}{C_+}\right)}{da} \right) \tag{34}$$

and

$$X^* = P^* + a \frac{\partial P^*}{\partial a} \tag{35}$$

On the other hand, taking into account Eq. (10) for pH = PZC we obtain for this model:

$$K_+ H^2 + K_A H^2 a P^* - K_C a - 1 = 0 \tag{36}$$

For the set of Eqs. (33) and (36) we obtain the following interrelations between equilibrium constants:

$$K_A H^2 X^* - K_C = 0 \tag{37a}$$

$$K_+ H^2 = Y^* \tag{37b}$$

where

$$Y^* = a \frac{\partial P^*}{\partial a} \cdot \frac{H^2}{K_{a2}^{\text{int}}\, {}^*K_A^{\text{int}}} + 1 \tag{38}$$

Then we can obtain the following interrelations:

$$K_{a1}^{\text{int}} = \frac{H^2}{K_{a2}^{\text{int}} Y^*} \quad \text{and} \quad {}^*K_A^{\text{int}} = \frac{H^2 X^*}{{}^*K_C^{\text{int}}} \tag{39}$$

Relations (39) can be also written in another form:

$$\text{PZC} = \frac{1}{2}\left(\text{p}K_{a1}^{\text{int}} + \text{p}K_{a2}^{\text{int}} - \log Y^*\right) \tag{40a}$$

$$\text{PZC} = \frac{1}{2}\left(\text{p}^* K_C^{\text{int}} + \text{p}^* K_A^{\text{int}} + \log X^*\right) \tag{40b}$$

So, we obtained also the set of two equation but determination of two equilibrium constants from Eqs. (40a) and (40b) for give values of two others is not as simple as in the case of TLM. For example, determination of K_{a1}^{int} and ${}^*K_A^{\text{int}}$ for given K_{a2}^{int} and ${}^*K_C^{\text{int}}$ is following: First the value of ${}^*K_A^{\text{int}}$, Eq. (40) is used next to calculate K_{a1}^{int} employing the fact that Y* depends on ${}^*K_A^{\text{int}}$. Of course, we can determine K_{a1}^{int} and ${}^*K_C^{\text{int}}$, or K_{a1}^{int} and ${}^*K_A^{\text{int}}$.

When we compare Eqs. (40a) and (40b) for FLM and (19a) and (b) for TLM we can see that when $X^* \to 1$ and $Y^* \to 1$, the reduction of FLM into TLM takes place. It occurs when $C_- = C_+$, then $P^* \to 1$ and $\partial P^*/da \to 0$.

Lack of Coincidation of PZC and CIP in FLM: FLM$_{PZC \neq CIP}$

In the case when PZC ≠ CIP, similar as was shown in Section 3 for TLM, the independence of CIP of the salt concentration can be formally expressed by Eq. (20) obtaining Eq. (23), which is also fulfilled in this case. Remembering, that now we have:

$$f_0 = MP \quad f_+ = M^2 P^2 \quad f_C = MDa$$
$$f_A = \frac{M}{D} P^2 a P^* \tag{41}$$

where now,

$$P = 10^{-\text{CIP}} \quad D = \exp\left\{\frac{e\delta_0(\text{CIP})}{kTC_+}\right\}$$
$$M = \exp\left\{-\frac{e\psi_0(\text{CIP})}{kT}\right\} \tag{42}$$

Then, Eq. (23) can be written in the following form:

$$K_C = K_A \frac{P^2}{D^2} X^* \frac{1-E}{1+E} \tag{43}$$

Because of small values of E we obtain the simpler form of Eq. (43),

$$K_C \cong K_A \frac{P^2}{D^2} X^* \quad \text{for } E \ll 1 \tag{44}$$

The next equation, which allows to reduce the number of equilibrium constants as the best-fit parameters, can be obtained from the condition that for each concentration titration curves have the "individual" PZC value . So, for pH = PZC the definitions in Eqs. (42) have the following forms for $D = 1$, $M = 1$, $P = H$: $f_0 = H$, $f_+ = H^2$, $f_C = a$ and $f_A = H^2 a P^*$. Using Eq. (10) we obtain the interrelation (36).

Combining Eqs. (36) and (44) we obtain the following equation:

$$K_+ H^2 + a K_A \left(H^2 P^* - \frac{P^2}{D^2} X^* \right) = 1 \tag{45}$$

which can be presented in the following form:

$$K_{a1}^{\text{int}} = \frac{H^2}{K_{a2}^{\text{int}}} + a\frac{H^2P^* - \frac{P^2}{D^2}X^*}{{}^*K_A^{\text{int}}} \tag{46a}$$

Also, Eq. (44) can be presented in the following form:

$${}^*K_A^{\text{int}} = \frac{P^2 \cdot X^*}{D^2 \ \cdot {}^*K_C^{\text{int}}} \tag{46b}$$

Equation set (46) allows for reduction the number of unknown best-fit parameters from four to two. But because X^* is the function of K_{a2}^{int} and ${}^*K_C^{\text{int}}$ we have to use equation set (46) to calculate the other two intrinsic equilibrium constants K_{a1}^{int} and ${}^*K_A^{\text{int}}$. So, firstly from Eq. (46b) we calculate value of ${}^*K_A^{\text{int}}$ and then form Eq. (46a) we can calculate value of K_{a1}^{int}.

One can find the equation set (46) as the most general one. So, for $X^* \to 1$ it reduces to the equivalent set (29) for the triple layer model (PZC $\neq$ CIP). For $D = 1$, $M = 1$ and $P = H$ (when PZC = CIP) it reduces to the set (39) for the four layer model ($\text{FLM}_{\text{PZC=CIP}}$).

Results and Disscusion

This paper is the continuation of our previous paper (Rudzinski et al., 2001). Its aim is to present the detailed derivations of the equations resulting from the formal mathematical application of the existence of the Common Intersection Point for two complexation models: TLM and FLM. Therefore, the same set of experimental data was used for verification of the theoretical results.

The detailed description of the experiment can be found in the paper published by Janusz et al. (1997). Titanium dioxide (anatase) and NaCl and CsCl solutions were used in those experiments. The surface charge of TiO_2 was determined by the potentiometric titrations in nitrogen atmosphere at 25°C. Sodium and cesium ion adsorption was determined by the radiotracer technique, measuring the decrease of activity in the supernatant. For labeling solutions ^{22}Na and ^{137}Cs isotopes were used. The surface charge isotherms for the system TiO_2/NaCl solution have a common intersection point at PZC = 6.25. In the case of TiO_2/CsCl system CIP is still observed but it is located at $\delta_0 = 2.0\,\mu\text{C/cm}^2$ and CIP = 5.2.

Due to earlier conclusions that titration curves are not sensitive for the choice of adsorption model (compensation effect) (Rudzinski et al., 1991, 1992), we did not expect to obtain much better fit of the experimental data using FLM than TLM. We expected to obtain somewhat different values of best-fit parameters for FLM, for which we have as good fit as for TLM presented in the previous paper (Rudzinski et al., 2001). Such values of best-fit parameters should be treated as more realistic ones.

There is a quite common belief that if the simpler model (with a smaller number of parameters) described a given type of the experiment, it is sufficient evidence for its superiority over the model possessing more realistic and precise assumptions (but more parameters), which is often a direct development of the simpler model. But we have to realize that if in both such models the definition of parameters are in agreement and we obtain their different values as the best-fit results, then the results obtained for the model with precise assumptions are more realistic. Of course, it should be taken into consideration if our results are good enough to justify application of a more complex model. Taking into account the assumptions of the models compared in this paper, it is obvious that the FLM is the more accurate. Moreover, the models include the same definitions of parameters: surface reaction equilibrium constants which make their comparison easy.

Table 1 collects the values of the parameters found by us for FLM while fitting simultaneously the titration isotherms, and the individual isotherms of cation adsorption measured radiometrically.

The two Figs. 2 and 3 show an agreement between experimental and theoretical titration isotherms, obtained by using the parameters collected in Table 1.

Also a good agreement can be seen in Fig. 5 between the experimentally measured and theoretically calculated individual isotherms of Cs^+ ion adsorption. The less impressive agreement for sodium ions Na^+,

Table 1. The values of the parameters and calculated values of intrinsic equilibrium constants found by using the interrelations (39) for $\text{FLM}_{\text{PZC=CIP}}$ and (46) for $\text{FLM}_{\text{PZC}\neq\text{CIP}}$.

	Parameters					Calculated values	
				C$_-$	C$_+$		
Concentration	PZC	pK_{a2}^{int}	p$^*K_C^{\text{int}}$	F/m^2	F/m^2	pK_{a1}^{int}	p$^*K_A^{\text{int}}$
0.1 M NaCl	6.25	8.75	7.75	0.60	0.90	3.71	4.84
0.01 M NaCl	6.25	8.75	6.80	0.60	0.80	3.72	5.77
0.001 M NaCl	6.25	8.75	6.05	0.55	0.75	3.74	6.50
0.1 M CsCl	5.80	8.40	6.60	0.90	0.85	3.81	4.55
0.01 M CsCl	5.99	9.05	6.00	0.80	0.70	3.88	5.27
0.001 M CsCl	6.43	10.90	6.05	0.80	0.65	3.78	5.35

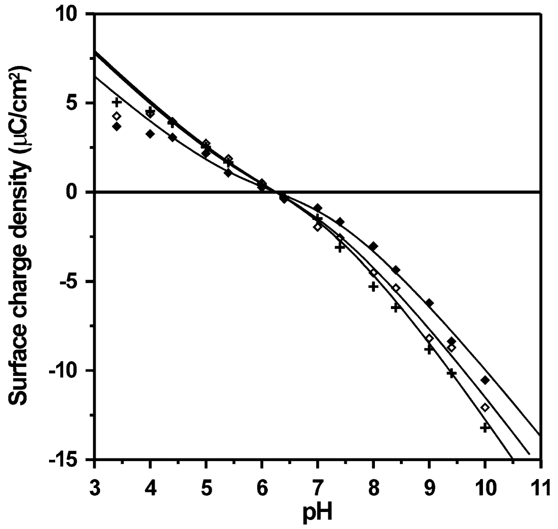

Figure 2. The comparison between the experimental titration isotherms in the system TiO_2/NaCl and the theoretical ones (——), calculated by using the parameters collected in Table 1. The experimental points are related to the following electrolyte concentrations: (+) 0.1 mol/dm^3, (◇) 0.01 mol/dm^3 and (◆) 0.001 mol/dm^3.

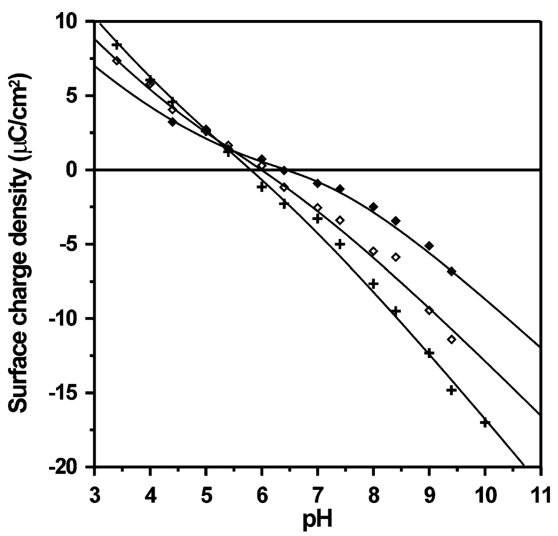

Figure 3. The comparison between the experimental titration isotherms in the system TiO_2/CsCl and the theoretical ones (——), calculated by using the parameters collected in Table 1. The experimental points are related to the following electrolyte concentrations: (+) 0.1 mol/dm^3, (◇) 0.01 mol/dm^3 and (◆) 0.001 mol/dm^3.

shown in Fig. 4, is due to scattering in the measured experimental data.

If we compare the best-fits obtaining using FLM with those presented in the previous paper (Rudzinski et al., 2001) for TLM, we will not notice

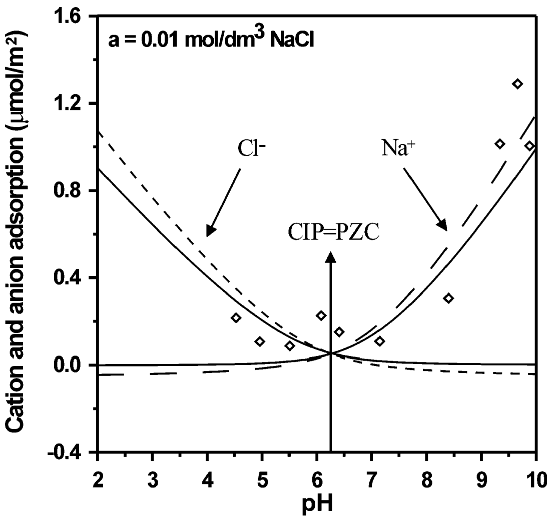

Figure 4. The comparison between the individual isotherms of Na^+ adsorption, measured radiometrically at the concentration 0.01 mol/dm^3 (◇), and the theoretically calculated ones using the parameters collected in Table 1. The solid lines (——) denote the calculated amounts of ions adsorbed in the β-plane, whereas the broken lines are the total amounts of anions (- - - - -) and cations (– – –) calculated by adding their amount adsorbed in the diffuse layer, calculated in the way described in the previous paper (Rudzinski et al., 2001).

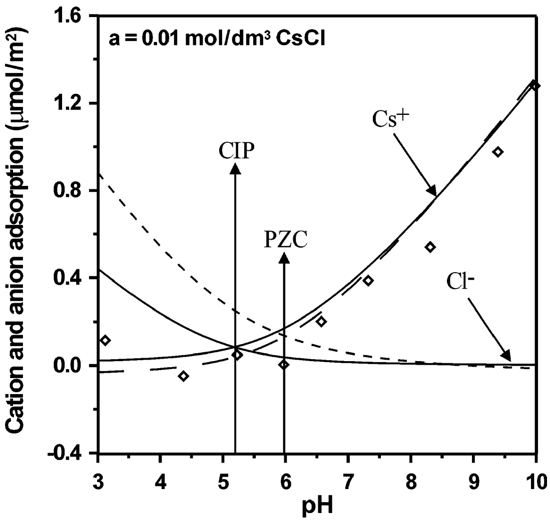

Figure 5. The comparison between the individual isotherms of Cs^+ adsorption, measured radiometrically at the concentration 0.01 mol/dm^3 (◇), and the theoretically calculated ones using the parameters collected in Table 1. The solid lines (——) denote the calculated amounts of ions adsorbed in the β-plane, whereas the broken lines are the total amounts of anions (- - - - -) and cations (– – –) calculated by adding their amount adsorbed in the diffuse layer, calculated in the way described in the previous paper (Rudzinski et al., 2001).

significant differences—best-fits are only slightly better. This is consistent with our expectation presented earlier. The differences between models manifest itself in the values of the parameters collected in Table 1, which values should be treated as more realistic ones.

Similar to the values of the parameters obtained for TLM (Rudzinski et al., 2001), we can see, that a good simultaneous fit of the titration isotherms and of the individual isotherms of cation adsorption, requires parameters somewhat different for different electrolyte concentrations. We launched hypotheses concerning the origin of these variations, which are still present, i.e. (i) these variations reflect real changes in the reaction equilibrium constants, induced by the changing environment caused by the changing electrolyte concentration—measurements for each concentration are treated as separate experimental system; (ii) the variations in the estimated values of the equilibrium (reaction) constants simulate effects which have not been taken into account, in the present mechanistic model, and the related theoretical approach; (iii) both the above mentioned hypotheses are true.

Similar to the results obtained for TLM (Rudzinski et al., 2001) for the system TiO_2/NaCl, in which PZC and CIP coincide, also for FLM the estimated values of the parameter pK_{a2}^{int} do not depend on the concentration of the inert electrolyte. On the contrary one can observe there an opposite variation in the estimated parameter $p^*K_C^{int}$, but these variations must be considered together with the variation in the estimated values of C_+ and C_- parameters. For the system TiO_2/CsCl, pK_{a2}^{int} increases significantly with the decreasing electrolyte concentration, whereas pK_{a1}^{int} remains almost constant. Like previously, $p^*K_A^{int}$ increases with the decreasing electrolyte concentration. The last feature would advocate for the hypothesis that the equilibrium constants are not much affected by the changing molecular environment induced by the changing electrolyte concentration. This is because the majority of the titration data in the system TiO_2/CsCl belongs to the range of pH values, where cation adsorption prevails. So, cation adsorption makes the features of the layer with cations pretty stable, and then it appears that $p^*K_C^{int}$ remains constant.

The results for the smallest electrolyte concentration (0.001 mol/dm^3) are similar to those presented in the previous paper (Rudzinski et al., 2001). Cation (Cs^+) adsorption strongly dominates over the anion (Cl^-) adsorption, that the features of the interface must be determinated practically only by the presence of one kind of ion (cation) adsorption. Also similar behaviour of the ratio θ_C/θ_A calculated for both TiO_2/NaCl and TiO_2/CsCl for various electrolyte concentrations can be obtained for FLM as well as for TLM (Fig. 9 in Rudzinski et al., 2001). For the system TiO_2/CsCl for the lowest electrolyte concentration the ratio θ_C/θ_A is the highest over a large region of pH values.

Drawing mathematical consequences of the existence of CIP is important for establishing two relations between the surface complexation constants. These two interrelation decrease by two the number of the best-fit parameters found by fitting experimental data by theoretical expressions. This increases substantially the reliability of the determined adsorption parameters. This is especially important in the case of the adsorption systems where PZC and CIP do not coincide. This is because in this case, the commonly applied graphical methods for determining the adsorption parameters fail, and only numerical methods can be applied.

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