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A Thermodynamic Analysis of Ion Adsorption in the Metal Oxide/Electrolyte Systems in which PZC and CIP do not Coincide

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Abstract. A theoretical-numerical analysis of two adsorption systems composed of the same kind of oxide- TiO_2, and of two different electrolytes, NaCl and CsCl is presented. For one kind of the electrolyte (NaCl), PZC and CIP coincide, whereas they are different for the other (CsCl) electrolyte. The analysis is carried out by applying the popular TLM model, and by drawing formal-mathematical consequences of CIP existence in both kinds of adsorption systems. The values of the adsorption parameters are found by fitting simultaneously the obtained theoretical expressions to both experimental titration isotherms, and to the individual isotherms of cation adsorption measured using radiometric methods. That theoretical-numerical analysis suggests, that the inequality PZC $\neq \frac{1}{2}(pK_{a1}^{\mathrm{int}} + pK_{a2}^{\mathrm{int}})$ may be a general feature of the oxide/electrolyte systems including the systems in which PZC and CIP coincide.

Keywords: ion adsorption, surface charge, oxide/electrolyte interface

Introduction

One very interesting feature of the oxide/electrolyte adsorption systems is, that the surface charge isotherms δ_0(pH) measured in different inert (1:1) electrolyte concentrations have a common intersection point (CIP) at a certain pH value (Lyklema, 1984). This point is also know as Point of Zero Salt Effect (p.z.s.e) and defined by Sposito (1992) as the pH value at which the net proton surface charge density is invariant under changes of ionic strength. In the case of the lack of specific adsorption it has been believed that the coincidence of PZC (Point of Zero Charge), and CIP is a common feature of these adsorption systems. The lack of such coincidence has been treated in this case as an interesting anomaly. Also, the lack of coincidence between PZC and IEP (Isoelectric Point) in such systems has been treated as another anomaly.

As the time passed, more and more papers reported on differences between PZC and IEP (Smit and Holten, 1980; Kallay et al., 1986; Wood et al., 1990; Thomas et al., 1989). Recently a theoretical paper (Charmas, 1998) have been published, suggesting that the lack of coincidence between PZC and IEP may

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be a fundamental feature of these systems, more or less clearly demonstrated. Also, a certain feeling is growing now, that the same may be true in the case of the lack of coincidence between PZC and CIP.

However, although a certain body of 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), very little has been done on their theoretical interpretation. Only certain assumptions have been expressed or some qualitative conclusions drawn.

One reason for that may be the fact that the popular graphical methods of estimating the values of equilibrium constants from the titration isotherms fail in the case of the systems in which PZC and CIP do not coincide. This has been shown recently by Mustafa et al. (1998) Here, we will show another example based on the data published by Janusz et al. (1997).

An alternative to graphical methods is numerical methods of fitting theoretical expressions to experimental data. They are based on the idea of finding a minimum of an error function of the best-fit parameters. The popularity of these methods is still growing, but certain risks related to their use are not sufficiently recognized.

First of all, a proper definition of an error function is a complicated theoretical problem, in general. So, several simple error functions are chosen at hoc, and their choice must affect the values of the determined parameters to some extent. Then, it is also well-known, an error function may have a variety of local minima, frequently happens in practice, that the absolute minimum is not found. Then, it is also well known that the growing number of best-fit parameters decreases quickly their reliable estimation. That problem is especially important for fitting experimental titration curves.

This is because, it is well-known, that these 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, Rudziński 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): $\left(\frac{d\delta_0}{dI}\right)_{\mathrm{pH=CIP}} = 0$ (where I is the ionic strength of inert electrolyte. So, it may only surprise one, that it has not been applied to the investigated adsorption models in order to reduce the number of the best fit parameters until very recently.

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. However, although several papers have already been published, reporting on such systems, only few of them are suitable for being used for that purpose.

These are the papers where, in addition to the experimental titration curves (net proton adsorption data), also other ion adsorption data were reported. A rare example of such papers is the paper by Janusz et al. (1997), who have reported not only titration curves measured at various electrolyte concentrations, but also individual isotherms of ion adsorption, measured by using radiometric methods. When these two kinds of experimental data, coming from two independent experiments, are fitted by the same set of parameters, then the risk of finding an improper set of parameters must substantially decrease. Having determined properly the parameter values one will allow to draw proper conclusions about the features of oxide/electrolyte adsorption systems, in which PZC and CIP do not coincide. This was the basic idea behind the calculations (analysis) presented in this paper.

Theory

We consider the adsorption of ions as a result of the following surface reactions suggested by Davis, Leckie and by other authors (Davis and Leckie, 1978, 1979, 1980; Davis et al., 1978; Yates and Healy, 1980).

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

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

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

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

where $\mathrm{SO^-}$ denotes the outermost surface oxygens, $\mathrm{H^+}$ is the proton, $\mathrm{A^-}$ and $\mathrm{C^+}$ denote the anion and cation of electrolyte, respectively. The equilibrium constants $K_{\mathrm{a1}}^{\mathrm{int}}$, $K_{\mathrm{a2}}^{\mathrm{int}}$, ${}^*K_{\mathrm{A}}^{\mathrm{int}}$, and ${}^*K_{\mathrm{C}}^{\mathrm{int}}$ concern reactions (1a)–(d).

Introducing the notation,

$$\begin{aligned}
&\theta_0 = [\mathrm{SOH}^0]/\mathrm{N_s} \qquad \theta_+ = [\mathrm{SOH}_2^+]/\mathrm{N_s}\\
&\theta_\mathrm{A} = [\mathrm{SOH}_2^+\mathrm{A}^-]/\mathrm{N_s}\\
&\theta_\mathrm{C} = [\mathrm{SO}^-\mathrm{C}^+]/\mathrm{N_s} \qquad \theta_- = [\mathrm{SO}^-]/\mathrm{N_s}\\
&\quad = 1 - \sum_i \theta_i \quad (i = 0, +, \mathrm{A}, \mathrm{C})\\
&\mathrm{N_s} = [\mathrm{SO}^-] + [\mathrm{SOH}^0] + [\mathrm{SOH}_2^+] + [\mathrm{SO}^-\mathrm{C}^+]\\
&\qquad + [\mathrm{SOH}_2^+\mathrm{A}^+]
\end{aligned} \tag{2}$$

we can arrive (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

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

and where

$$f_0 = \exp\left\{-\frac{e\psi_0}{kT} - 2.3\ \mathrm{pH}\right\}, \quad f_+ = f_0^2 \tag{5a}$$

$$f_\mathrm{C} = a_\mathrm{C} \exp\left\{-\frac{e\psi_0}{kT} + \frac{e\delta_0}{kTc_1}\right\} \tag{5b}$$

$$f_\mathrm{A} = a_\mathrm{A} \exp\left\{-\frac{e\psi_0}{kT} - \frac{e\delta_0}{kTc_1} - 4.6\mathrm{pH}\right\} \tag{5c}$$

where c_1 is the first integral capacitance, δ_0 is the monitored surface charge, defined as follows,

$$\delta_0 = B_\mathrm{s}[\theta_+ + \theta_\mathrm{A} - \theta_- - \theta_\mathrm{C}], \quad B_\mathrm{s} = \mathrm{e} \cdot \mathrm{N_s} \tag{6}$$

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 (3,5,6), we accepted in our works the relation used by Yates et al. (1974) and by Bousse et al. (1983), Van der Vlekkert et al. (1988).

$$2.303(\mathrm{PZC} - \mathrm{pH}) = \frac{e\psi_0}{kT} + \sinh^{-1}\left(\frac{e\psi_0}{\beta kT}\right) \tag{7}$$

where β is given by

$$\beta = \frac{2e^2 N_\mathrm{s}}{c_\mathrm{DL} kT}\left(\frac{K_\mathrm{a2}^\mathrm{int}}{K_\mathrm{a1}^\mathrm{int}}\right)^{1/2} \tag{8}$$

In Eq. (8) c_DL is the linearized double-layer capacitance. The value of c_DL can, theoretically, be calculated (depending on the salt concentration in the solution), in the way described in Bousse's work (1983):

$$\frac{1}{c_\mathrm{DL}} = \frac{2kT/e}{(8\varepsilon_\mathrm{r}\varepsilon_0 kTI)^{1/2}} + \frac{1}{c_\mathrm{Stern}} \tag{9}$$

where ε_r is the relative permittivity of solvent, ε_0 is the permittivity of free space and I is the ionic strength of solution (ions/m^3). The value of c_Stern is assumed to be 0.2 F/m^2.

Equation (7) was derived by applying TLM model and assuming that the adsorption of electrolyte ions does not affect the surface potential (Bousse et al., 1983). In order to obtain Eq. (7) one should assume that the difference between the equilibrium constants values $K_\mathrm{a1}^\mathrm{int}$ and $K_\mathrm{a2}^\mathrm{int}$ is high enough ($K_\mathrm{a2}^\mathrm{int}/K_\mathrm{a1}^\mathrm{int} \ll 1$) and the diffuse charge δ_d is small, i.e., the properties of the electric double layer are determined by the Stern layer. The latter is the case when the electrolyte concentration is not very low.

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

$$\delta_0 = \mathrm{B}\frac{K_+ f_+ + K_\mathrm{A} f_\mathrm{A} - K_\mathrm{C} f_\mathrm{C} - 1}{1 + \sum_i K_i f_i} \quad i = 0, +, \mathrm{A}, \mathrm{C} \tag{10}$$

This non-linear equation for δ_0 can easily be 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).

At the point of zero charge (PZC), we have:

$$\begin{aligned}
\mathrm{PZC} = &\frac{1}{2}\left(pK_\mathrm{a1}^\mathrm{int} + pK_\mathrm{a2}^\mathrm{int}\right)\\
&- \frac{1}{2}\log\frac{1 + \left({}^*K_\mathrm{C}^\mathrm{int}/K_\mathrm{a2}^\mathrm{int}\right)a_\mathrm{C}}{1 + \left(K_\mathrm{a1}^\mathrm{int}/{}^*K_\mathrm{A}^\mathrm{int}\right)a_\mathrm{A}}
\end{aligned} \tag{11}$$

For pH = PZC, $\delta_0 = 0$ and $\psi_0 = 0$, so Eq. (10) can be transformed then to the following form:

$$\delta_{0(\mathrm{pH=PZC})} = \frac{H^2}{K_{\mathrm{a1}}^{\mathrm{int}} K_{\mathrm{a2}}^{\mathrm{int}}} + \frac{H^2 a_{\mathrm{A}}}{K_{\mathrm{a2}}^{\mathrm{int}\,*}K_{\mathrm{A}}^{\mathrm{int}}} - \frac{{}^*K_{\mathrm{C}}^{\mathrm{int}} a_{\mathrm{C}}}{K_{\mathrm{a2}}^{\mathrm{int}}} - 1 = 0$$
$$\text{where } H = 10^{-\mathrm{PZC}} \qquad (12\mathrm{a})$$

or

$$K_+ H^2 + K_{\mathrm{A}} H^2 a_{\mathrm{A}} - K_{\mathrm{C}} a_{\mathrm{C}} - 1 = 0 \qquad (12\mathrm{b})$$

The experimental studies show that in the majority of the investigated systems, the value of the point of zero charge does not partically 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.

In the systems in which PZC = CIP, the independence of PZC of the salt concentration can formally be expressed as follows, when we assumed that $a = a_{\mathrm{C}} = a_{\mathrm{A}}$:

$$\left(\frac{\partial \delta_0}{\partial a}\right)_{(\mathrm{pH=PZC})} = \frac{H^2}{K_{\mathrm{a2}}^{\mathrm{int}\,*}K_{\mathrm{A}}^{\mathrm{int}}} - \frac{{}^*K_{\mathrm{C}}^{\mathrm{int}}}{K_{\mathrm{a2}}^{\mathrm{int}}} = 0 \qquad (13)$$

Solving the set of Eqs (12, 13) we obtain

$$K_{\mathrm{a2}}^{\mathrm{int}} = \frac{H^2}{K_{\mathrm{a1}}^{\mathrm{int}}} \quad \text{and} \quad {}^*K_{\mathrm{A}}^{\mathrm{int}} = \frac{H^2}{{}^*K_{\mathrm{C}}^{\mathrm{int}}} \qquad (14)$$

The relations (14) can be still written in another form,

$$\mathrm{PZC} = \frac{1}{2}\left(pK_{\mathrm{a1}}^{\mathrm{int}} + pK_{\mathrm{a2}}^{\mathrm{int}}\right) \qquad (15\mathrm{a})$$

$$\mathrm{PZC} = \frac{1}{2}\left(p^*K_{\mathrm{C}}^{\mathrm{int}} + p^*K_{\mathrm{A}}^{\mathrm{int}}\right) \qquad (15\mathrm{b})$$

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

Relation (15a) has already been discussed in literature. As for Eq. (15a), it can also be derived in another way, but only for the particular case of the triple layer model TLM considered here. The prerequisite is that the PZC and IEP (isolectric point) values were the same point or very close to each other. Let us remark for that purpose that the Langmuir-like isotherm for θ_+ can be rewritten to the following form

$$\frac{\theta_+}{\theta_-} = K_+ f_+ \qquad (16\mathrm{a})$$

or

$$4.6\mathrm{pH} = -2.3 \log\left(K_{\mathrm{a1}}^{\mathrm{int}} \cdot K_{\mathrm{a2}}^{\mathrm{int}}\right) - \frac{2e\psi_0}{kT} - \ln\frac{\theta_+}{\theta_-} \qquad (16\mathrm{b})$$

At pH = PZC, $\psi_0 = 0$ and $\theta_+ = \theta_-$. Thus, from Eq. (16) we arrive again at Eq. (15a).

However, more and more cases are reported in literature where PZC and IEP do not coincide (Smit and Holten, 1980; Kallay et al., 1986; Wood et al., 1990; Thomas et al., 1989). So, a certain feeling is also growing now, that the difference between PZC and IEP may be a case of these adsorption systems.

Now, let us consider the oxide/electrolyte adsorption systems in which PZC and CIP do not coincide. There are reports in literature (Charmas, 1998; 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) on both adsorption systems (1 : 1 inert electrolyte) in which δ_0 (CIP) > 0, and on the systems in which δ_0 (CIP) < 0. Trying to find interrelations reducing the number of the "free" equilibrium constants, which can be treated as the best-fit parameters, we will still use the condition δ_0 (PZC) = 0 as one of these interrelations. So, let us remark that also in the case when CIP ≠ PZC the condition δ_0 (PZC) = 0 leads again to Eq. (11).

The general condition for the existence of CIP takes now the form (Sposito, 1992),

$$\left[\frac{\partial \delta_0}{\partial a}\right]_{\mathrm{pH=CIP}} = 0 \qquad (17)$$

Solving above equation using Eq. (10) one can obtain the following relation, (remembering that Eq. (10) is implicit equation with respect to δ_0)

$$2K_{\mathrm{A}} \frac{\partial f_{\mathrm{A}}^{\mathrm{p}}}{\partial a} + K_0 f_0^{\mathrm{p}} \left[K_{\mathrm{A}} \frac{\partial f_{\mathrm{A}}^{\mathrm{p}}}{\partial a} - K_{\mathrm{C}} \frac{\partial f_{\mathrm{C}}^{\mathrm{p}}}{\partial a}\right]$$
$$- 2K_+ f_{\mathrm{C}}^{\mathrm{p}} K_{\mathrm{C}} \frac{\partial f_{\mathrm{C}}^{\mathrm{p}}}{\partial a} - 2K_{\mathrm{A}} f_{\mathrm{A}}^{\mathrm{p}} K_{\mathrm{C}} \frac{\partial f_{\mathrm{C}}^{\mathrm{p}}}{\partial a}$$
$$+ 2K_{\mathrm{C}} f_{\mathrm{c}}^{\mathrm{p}} K_{\mathrm{A}} \frac{\partial f_{\mathrm{A}}^{\mathrm{p}}}{\partial a} = 0 \qquad (18)$$

where

$$f_i^{\mathrm{P}} = f_i(\mathrm{pH = CIP}) \quad i = 0, +, \mathrm{A}, \mathrm{C} \qquad (18\mathrm{a})$$

It can be proved that Eq. (18) reduces with very good approximation to the following simplified explicit form,

$$K_A \frac{\partial f_A^P}{\partial a} - K_C \frac{\partial f_C^P}{\partial a} = 0 \tag{19}$$

After certain rearrangement and substitutions, Eq. (19) takes the form,

$$K_C = K_A \frac{P^2}{D^2} \tag{20a}$$

where

$$P = 10^{-\mathrm{CIP}}, \qquad D = \exp\left(\frac{e\delta_0}{kTc_1}\right) \tag{20b}$$

For our further purposes, we rewrite Eq. (20a) to the following form

$${}^{*}K_C^{\mathrm{int}} = \frac{P^2}{D^{2*} K_A^{\mathrm{int}}} \tag{21}$$

Now Eq. (20a) is combined with Eq. (12b) to give,

$$K_+ H^2 + K_A a\left(H^2 - \frac{P^2}{D^2}\right) = 1 \tag{22}$$

or considering Eq. (4),

$$K_{a2}^{\mathrm{int}} = \frac{H^2}{K_{a1}^{\mathrm{int}}} + \frac{\left(H^2 - \frac{P^2}{D^2}\right)\mathrm{a}}{{}^{*}K_A^{\mathrm{int}}} \tag{23}$$

where $H = 10^{-\mathrm{PZC}}$.

When CIP → PZC, the relations (21) and (23) reduce to the previously developed ones. The two interrelations (21) and (23) reduce from four to two the number of the free parameters-the equilibrium constants, found by fitting theoretical expressions to experimental data. This must increase the reliability of the estimated parameters to a great extent.

Then, according to the basic idea of this work, the reliability of the determined parameters will be further controlled by the requirement that they must lead to a simultaneous good fit of both experimental titration data isotherms, and of the experimentally monitored individual isotherms of ion adsorption.

These individual isotherms of ion adsorption were measured by Janusz et al. (1997) by using the radiotracer technique. In that way, the total amount of the ions adsorbed in the different layers was monitored. This total quantity is the sum of the ions adsorbed in the β-plane, and in the diffuse layer. The latter quantity is described by the following expressions (Lyklema, 1985)

$$\delta_d^+ = \frac{2c|z|F}{\kappa}\left[\exp\left(-\frac{|z|e\psi_d}{2kT}\right) - 1\right] \tag{24a}$$

$$\delta_d^- = \frac{2c|z|F}{\kappa}\left[1 - \exp\left(-\frac{|z|e\psi_d}{2kT}\right)\right] \tag{24b}$$

where: δ_d^+—is the cation component of the diffuse layer charge, δ_d^- -is the anion component of the diffuse layer charge, c—is the electrolyte concentration, F—the Faraday constant, κ^{-1}—the diffuse layer thickness, ψ_d-the diffuse layer potential, and z—is the charge of the ion. The potential ψ_d appearing in Eqs. (24) will be evaluated from the following equation (Kallay and Tomic, 1988; Tomic and Kallay, 1988):

$$\psi_d = \frac{2kT}{|z|e}\ln\left[\frac{-\delta_d}{\sqrt{8\varepsilon_0\varepsilon_r kTI}} + \sqrt{\frac{\delta_d^2}{8\varepsilon_0\varepsilon_r kTI} + 1}\right] \tag{25}$$

where

$$\delta_d = B_s[\theta_- - \theta_+] \tag{25a}$$

Summing up we can say that:

1. Classical 2-pK Triple Layer model is used to analyze experimental data.
2. To describe surface potential Eq. (7) is applied which is good approximation of real surface potential.
3. Every time on the basis of the definitions of PZC and CIP it is possible to obtain relationships between equilibrium constants, which reduce the number of these independent parameters from four to two.
4. When calculating the adsorption of electrolyte we also include the ions from diffuse layer.

Analysis and Disscusion of the Experimental Data

The detailed description of the experiment can be found in our previous paper published by Janusz et al. (1997). Here, for the reader's convenience, we repeat only some most essential information.

Titanium dioxide (anatase) and NaCl and CsCl solutions were used in our experiments. The oxide was washed with double-distilled water unitl the conductivity of the supernatant was the same as that of the double distilled water. The specific surface area of the TiO_2 determined by the BET method (nitrogen adsorption) was 9.3 m^2/g. All reagents were analytical grade, dissolved in double-distilled water.

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 supernantant. 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 $\mathrm{PZC} = 6.25$. In the case of TiO_2/CsCl system CIP is still observed but it is located at $\delta_0 = 2.0$ μC/cm^2 and CIP = 5.2. These two sets of net proton adsorption isotherms (titration curves) are shown in Fig. 1.

It should be noted that contrary to Figs. 1 and 2 in our previous publication (Janusz et al., 1997), the surface charge curves corresponding to the lowest concentration 10^{-4} mol/dm^3, are not shown here. Our present revised analysis of these experimental data has brought us to the conclusion, that this concentration was not possible to hold constant in the course of titration. So these data will be ignored in our present considerations. That revised analysis has shown also that the adsorption of Na$^+$ and Cs$^+$ ions was measured at somewhat different electrolyte concentrations from those given in our previous publication. These correctly determined electrolyte concentrations will be introduced into the present comparison between theory and experiment.

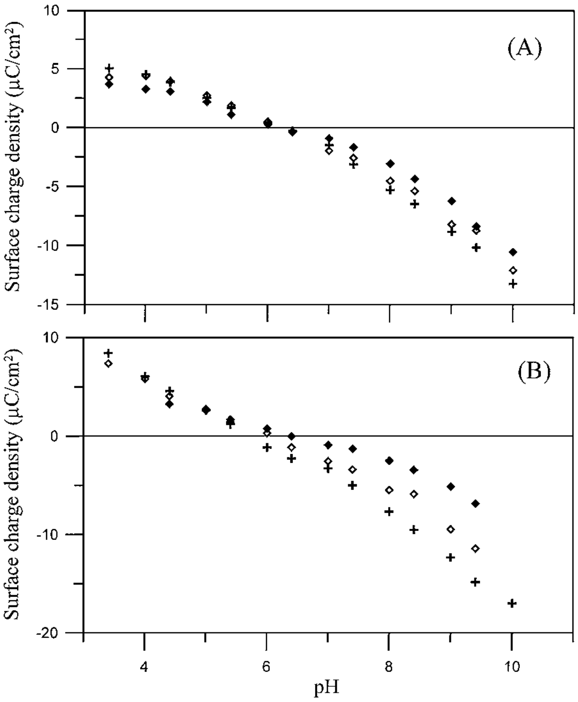

Figure 1. The surface charge isotherms measured at the three electrolyte concentrations: 0.1 mol/dm^3 (+++), 0.01 mol/dm^3 (◇◇◇), 0.001 mol/dm^3 (◆◆◆), for the system TiO_2/NaCl (A) and for the system TiO_2/CsCl (B).

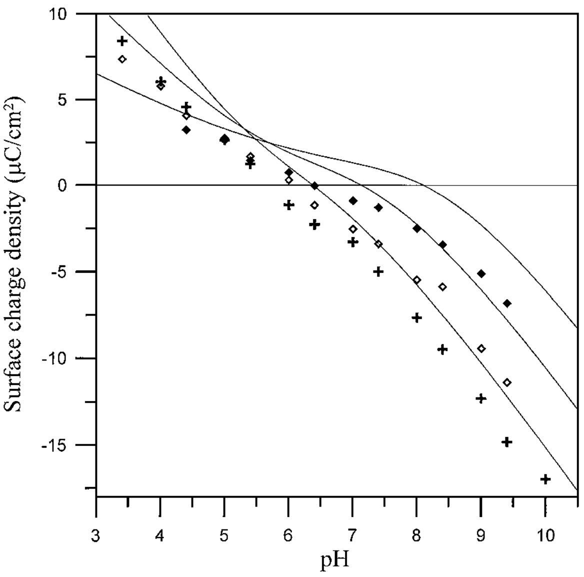

Figure 2. The comparison between the experimental titrations isotherms measured in the system TiO_2/CsCl, at the three electrolyte concentrations: 0.1 mol/dm^3 (+++), 0.01 mol/dm^3 (◇◇◇), 0.001 mol/dm^3 (◆◆◆), and the theoretical ones (——) calculated by using the Davies' parameters collected in Table 1, and assuming that $c_1^L = c_1^R = 1$.

While establishing the values of the equilibrium constants K_{a1}^{int}, K_{a2}^{int}, $^*K_A^{int}$, and $^*K_C^{int}$ in our previous publication, only surface charge isotherms were taken into consideration and two well-known methods were applied. This was the method by Davis et al. (1978) and the Schwarzenbach method (Janusz, 1991; Schwarzenbach and Ackerman, 1948). The equilibrium constants determined using these two methods are collected in Table 1.

Figures 2 and 3 show the fit of the experimental titration isotherms in the system TiO_2/CsCl, obtained by using the Davis' and Schwarzenbach's parameters collected in Table 1.

Table 1. Equilibrium constants of the TiO_2/NaCl and TiO_2/CsCl solutions obtained (Janusz et al., 1997) using Davis method (Davis et al., 1978) and Schwarzenbach method (Janusz, 1991; Schwarzenbach and Ackerman, 1948).

System	pK_{a1}^{int}	pK_{a2}^{int}	$p^*K_C^{int}$	$p^*K_A^{int}$
Davis et al. Method (Davis et al., 1978)				
TiO_2/NaCl	3.5 ± 0.2	9.1 ± 01	8.1 ± 01	4.0 ± 0.2
TiO_2/CsCl	3.9 ± 0.2	9.5 ± 0.3	7.4 ± 0.3	3.2 ± 0.3
Schwarzenbach method (Janusz, 1991; Schwarzenbach and Ackerman, 1948)				
TiO_2/NaCl	3.5 ± 0.1	9.2 ± 0.6	8.2 ± 1.1	5.1 ± 0.1
TiO_2/CsCl	3.9 ± 0.3	9.4 ± 0.4	7.2 ± 0.1	5.1 ± 0.9

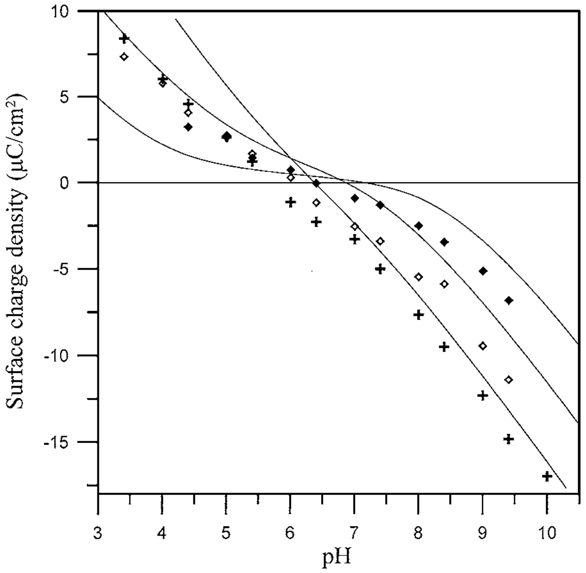

Figure 3. The comparison between the experimental titrations isotherms measured in the system TiO_2/CsCl, at the three electrolyte concentrations: 0.1 mol/dm^3(+++), 0.01 mol/dm^3 (◇◇◇), 0.001 mol/dm^3 (◆◆◆), and the theoretical ones (——) calculated by using the Schwarzenbach's parameters collected in Table 1, and assuming that $c_1^L = c_1^R = 1$.

One can conclude that Figs. 2 and 3 show poor agreement between theory and experiment, obtained by using either the Davies', or Schwarzenbach's parameters.

Performing our calculations we assumed, similar to Smit (1986), two values of capacitance c_1: one for the acidic c_1^L and the other for the alkaline c_1^R branch of the titration curve.

While drawing the theoretical titration isotherms very high, but still physically reasonable values of the parameter $c_1^L = c_1^R = 1$ F/m^2 were accepted. Taking still higher values of c_1 would result in slight improvement of the agreement between theory and experiment, but would also rise a serious question as to the physical meaning of such high values of c_1, in view of its typical values reported in literature. c_1 values smaller than unity, like these found by us, and collected in Tables 2 and 3 seen to be much more realistic. However, taking $c_1 < 1$ F/m^2 would result into further worsening of the agreement between theory and experiment.

Tables 2 and 3 collect the values of the parameters found by us while fitting simultaneously the titration isotherms, and the individual isotherms of cation adsorption measured radiometrically.

The other two Figs. 4 and 5 show an excellent agreement between experimental and theoretical titration isotherms, obtained by using the parameters collected in Tables 2 and 3.

Also a good agreement can be seen in Figs. 7 and 8 between the experimentally measured and theoretically calculated individual isotherms of Cs^+ ion adsorption. The less impressive agreement for sodium ions Na^+, shown in Fig. 6, is due to scattering in the measured experimental data.

Before discussing some intriguing features of ion adsorption, which can be seen in Figs. 7 and 8, we will comment the values of the parameters collected in Tables 2 and 3.

Looking into Table 2, 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.

Table 2. The values of the parameters found by using the interrelations (15), (21) and (23).

a (NaCl)	PZC	pK_{a1}	pK_{a2}	$p^*K_C^{int}$	$p^*K_A^{int}$	c_1^L F/m^2	c_1^R F/m^2	$\frac{pK_{a1}+pK_{a2}}{2}$	$\frac{p^*K_C^{int}+p^*K_A^{int}}{2}$
0.1	6.25	3.80	8.70	7.70	4.80	0.60	0.90	6.25	6.25
0.01	6.25	3.80	8.70	6.70	5.80	0.70	0.80	6.25	6.25
0.001	6.25	3.80	8.70	6.10	6.40	0.70	0.75	6.25	6.25

Table 3. The values of the parameters found by using the interrelations (15), (21) and (23).

a (CsCl)	PZC	pK_{a1}	pK_{a2}	$p^*K_C^{int}$	$p^*K_A^{int}$	c_I^L F/m^2	c_I^R F/m^2	$\frac{pK_{a1}+pK_{a2}}{2}$	$\frac{p^*K_C^{int}+p^*K_A^{int}}{2}$
0.1	5.80	3.80	8.40	6.60	4.60	0.85	0.85	6.10	5.60
0.01	5.99	3.90	9.02	6.00	5.25	0.80	0.65	6.46	5.62
0.001	6.43	3.80	10.91	6.04	5.21	0.80	0.60	7.35	5.62

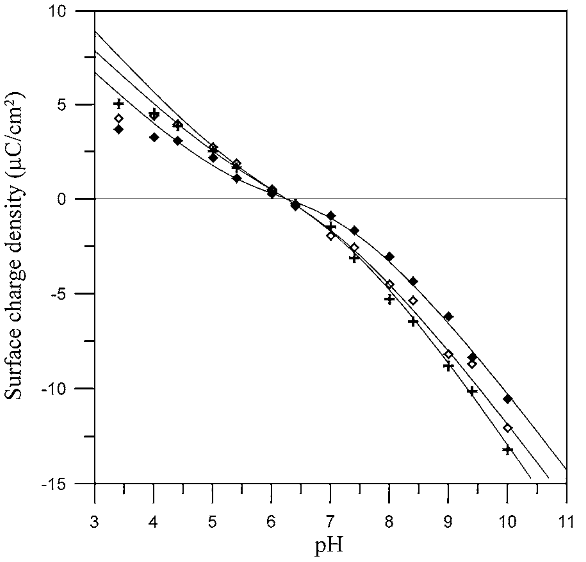

Figure 4. The comparison between the experimental titration isotherms in the system TiO$_2$/NaCl and the theoretical ones (——), calculated by using the parameters collected in Table 2. The experimental points are related to the following electrolyte concentrations: 0.1 mol/dm^3(+++), 0.01 mol/dm^3 (◇◇◇), and 0.001 mol/dm^3 (◆◆◆).

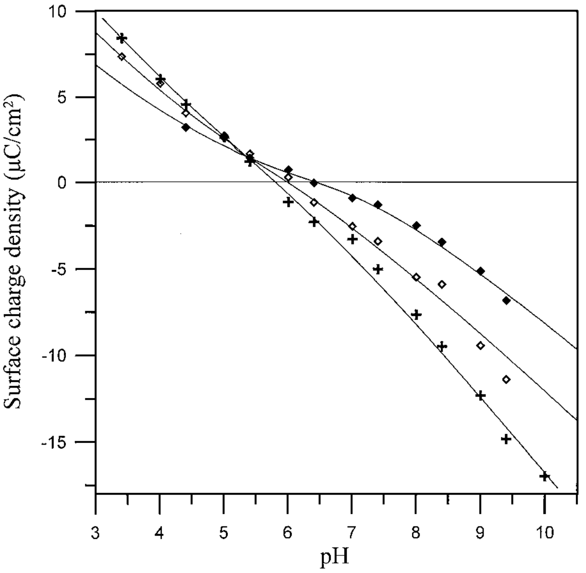

Figure 5. The comparison between the experimental titration isotherms in the system TiO$_2$/CsCl, and the theoretical ones, calculated by using the parameters collected in Table 2. The meaning of the solid lines (——) and the experimental points (+, ◇, ◆) is the same as in Fig. 4.

In the system TiO$_2$/NaCl, in which PZC and CIP coincide, the estimated parameters pK_{a1}^{int}, 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 parameters $p^*K_C^{int}$ and $p^*K_A^{int}$. Of course, these variations must be considered together with the variation in the estimated values of c_I^L and c_I^R parameters. One can launch three hypotheses concerning the origin of these variations.

1. 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
2. These variations reflect real changes in the reaction equilibrium constants, induced by the changing environment caused by the changing electrolyte concentration.
3. Both the above mentioned hypotheses are true.

Saying more in favour of one or another hypothesis would require having much more complete experimental data, and applying more refined theoretical treatments. Meanwhile, we will focus our attention on the differences between the systems where PZC = CIP, and the systems where PZC and CIP do not coincide.

In the latter systems, (see Table 3), pK_{a2}^{int} increases significantly with the decreasing electrolyte concentration, whereas pK_{a1}^{int} remains 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

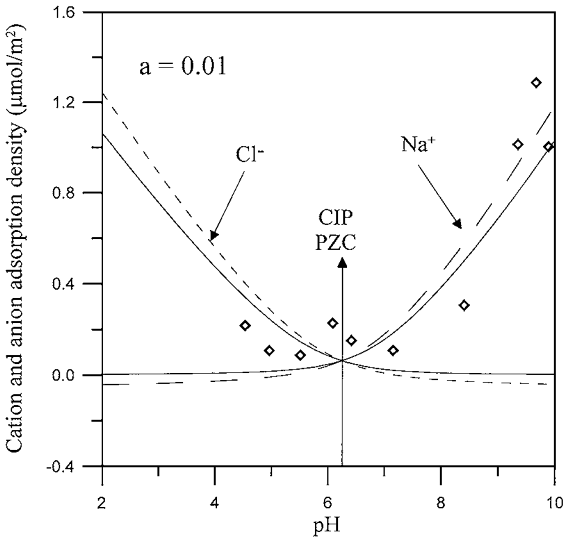

Figure 6. The comparison between the individual isotherms of Na^+ adsorption, measured radiometrically at the concentration 10^{-2} mol/dm^3 (◇◇◇), and the theoretically calculated ones using the parameters collected in Table 2. The solid lines (——) denote the calculated amounts of ions adsorbed in the 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 from Eqs (24).

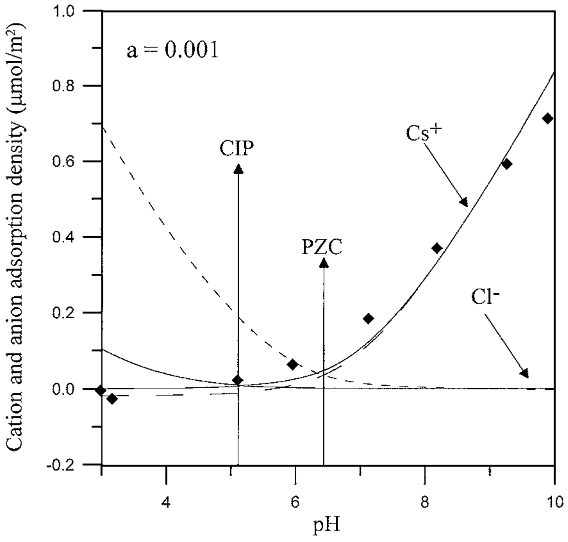

Figure 7. The comparison between the adsorption of Cs^+ ions, measured radiometrically at the concentration 10^{-3} mol/dm^3 (◆◆◆) and the calculated theoretically ones by using the parameters collected in Table 3. The meaning of the solid and broken lines is the same as in Fig. 6.

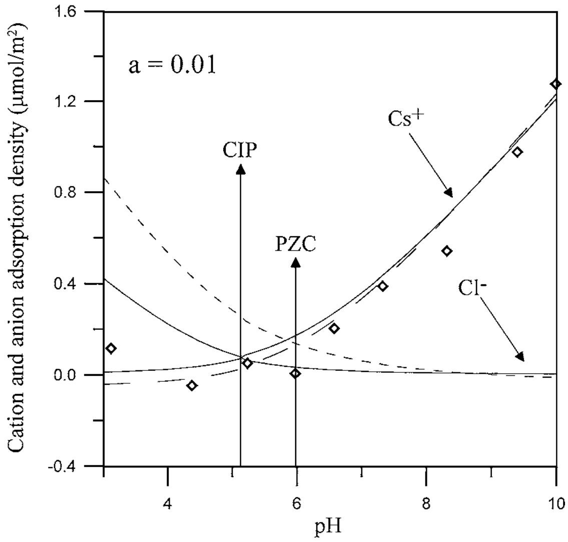

Figure 8. The comparison between the adsorption of Cs^+ ions, measured radiometrically at the concentration 10^{-2} mol/dm^3 (◇◇◇) and the calculated theoretically ones by using the parameters collected in Table 3. The meaning of the solid and broken lines is the same as in Fig. 6.

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 β-layer pretty stable, and then it appears that $p^*K_C^{\mathrm{int}}$ remains constant. This conclusion is not opposed by the observed obvious changes in the value of c_1^R parameter.

The disadvantage of the currently applied TLM model is the discontinuity of the c_1 value. So, the analysis of the TiO_2/CsCl system, where this assumption overshadows the analysis of only a small portion of the experimental data corresponding to small pH values, might imply some important conclusions. From this point of view, the analysis of the data corresponding to the smallest electrolyte concentration $a = 0.001$ mol/dm^3, seems to be extremely interesting.

Looking into Fig. 7, one can see, that at this smallest electrolyte concentration, cation (Cs^+) adsorption in the β-layer so strongly dominates over the anion (Cl^-) adsorption, that the features of the β-layer must be determinated practically only by the presence of one kind of ion (cation) adsorption. This would imply, that the parameters determined for such physical situation are probably closest to the actual ones, because the system is free of the simplifying assumption that anions and cations are located in the same layer, and have identical effect on the capacitance c_1.

So, let us focus our attention on the parameters determined for this smallest electrolyte concentration. Perhaps the most striking feature is the difference between PZC and the average $(pK_{a1}^{int} + pK_{a2}^{int})/2$. At the same time the analysis of the data for the TiO_2/NaCl system (see Table 2) suggests that the equality PZC $= \frac{1}{2}(pK_{a1}^{int} + pK_{a2}^{int})$ exist. So, the natural question arises which of these conclusions is true. Does the equality PZC $= \frac{1}{2}(pK_{a1}^{int} + pK_{a2}^{int})$ exist or not?

Trying to answer that question, let us turn our attention to the values of the parameters determined for the TiO_2/CsCl system, but for the highest studied electrolyte concentration $a = 0.1$ mol/dm^3. The value of $\frac{1}{2}(pK_{a1}^{int} + pK_{a2}^{int})$ found for that high electrolyte concentration differs only slightly from PZC which could easily by ascribed to the experimental errors. Let us, however, remark that this is the physical situation, where adsorption of anions (Cl^-) is not more negligible compared to adsorption of cations. So, also the presence of anions must affect features of the β-layer. And this is the situation, which we face in the case of the TiO_2/NaCl system, at all the electrolyte concentrations.

This is well illustrated in Fig. 9, where the ratio θ_C/θ_A is shown for both TiO_2/NaCl and TiO_2/CsCl, and for various electrolyte concentrations. We can see, that for the system TiO_2/CsCl, and the lowest electrolyte concentration the ratio θ_C/θ_A is the highest over a large region of pH values. So, this is the physical situation which is the closest to the simple model in which the features of the β-layer are determined by practically only one kind of ions. This would imply that the inequality PZC $\neq \frac{1}{2}(pK_{a1}^{int} + pK_{a2}^{int})$ reflects the true physical situation, whereas, the equality PZC $= \frac{1}{2}(pK_{a1}^{int} + pK_{a2}^{int})$ is an apparent one, found due to shortcomings of the applied model of adsorption system. And this would be true for both the systems in which PZC = CIP and for the systems in which PZC ≠ CIP.

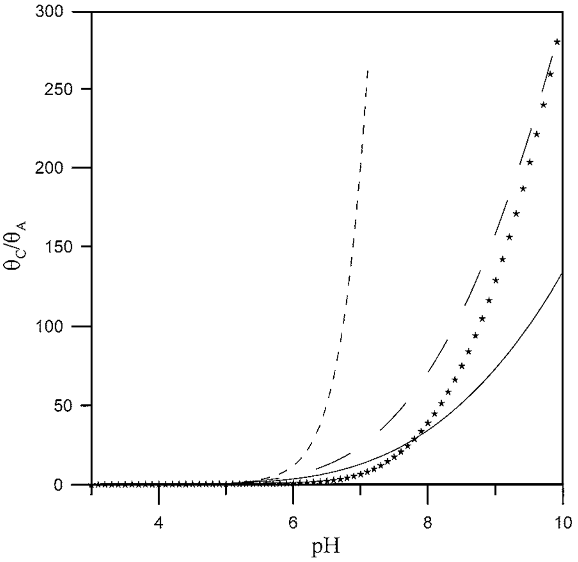

Figure 9. The ratio θ_C/θ_A calculated for the system TiO_2/CsCl, and the three electrolyte concentrations: 0.001 mol/dm^3 (- - - -), 0.01 mol/dm^3 (— — —), and 0.1 mol/dm^3 (———). The stars (⋆⋆⋆) represent the ratio θ_C/θ_A for the system TiO_2/NaCl, and the electrolyte concentration 0.01 mol/dm^3. The calculations have been done using the parameters collected in Tables 2 and 3.

This conclusion opposes the common belief, that the equality PZC $= \frac{1}{2}(pK_{a1}^{int} + pK_{a2}^{int})$ is one of the fundamental features of these adsorption systems. This equality, obtained formally for the system in which PZC = CIP, would be a result of using our adsorption model, and the related theoretical approach. Thus, paradoxically, using an electrolyte for which PZC ≠ CIP may be a way of better determination of the equilibrium constants for the first and the second proton adsorption. Of course, the hypothesis the inequality PZC $\neq \frac{1}{2}(pK_{a1}^{int} + pK_{a2}^{int})$ is a fundamental feature of the oxide/electrolyte adsorption systems requires further extensive study. Such study must involve analyzing more experimental data, and using more refined models, along with their corresponding more sophisticated theoretical approaches.

One interesting feature of the systems in which PZC ≠ CIP is that a large portion of one kind of ions is adsorbed in the diffuse layer. This can be seen in Figs. 7 and 8. This is in contrast to the systems, (see Fig. 6), in which PZC = CIP, and where only a small portion of the ions is located in the diffuse layer. Then CIP is observed at pH where $\theta_C = \theta_A$ (see Figs. 6–8).

Conclusions

Drawing formal (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.

Analyzing the experimental data obtained for different electrolyte concentrations using these numerical methods, and applying the popular TLM model of the adsorbed phase we arrive at somewhat different values of the parameters.

Such numerical studies applied to the adsorption systems in which PZC and CIP do not coincide seem to lead to a very intriguing conclusion that the inequality $\mathrm{PZC} \neq \frac{1}{2}(pK_{a1}^{\mathrm{int}} + pK_{a2}^{\mathrm{int}})$ may be a fundamental feature of these adsorption systems. This conclusion opposing the view generally expressed in literature still needs to be verified by applying more refined adsorption models and related theoretical approaches.

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