

A four layer model for bivalent cations adsorption at electrolyte/oxide interface

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The model is used to describe low concentration of bivalent ions adsorption in the systems of environmental importance. A theory has been developed based on a picture of a heterogeneous solid surface, with different adsorption sites – the outermost surface oxygens. The theoretical study indicates that the binding-to-surface energies of different surface complexes, formed on different surface oxygens, vary in an independent way from one surface oxygen to another. Furthermore, the idea of the Four Layer Model, where a new layer was reserved for the bivalent metal ions, was accepted. Cations and anions of basic electrolyte were placed in the same layer as in the popular Triple Layer Model.

1. INTRODUCTION

The models of surface complexation are the most frequently applied ones to describe ion adsorption within the double electrical layer formed at metal oxide/electrolyte interfaces.

The adsorption of Me^{2+} metal ions at electrolyte/oxide interfaces at low ion concentrations is a subject of rapidly growing interest. These are problems of great practical importance: the adsorption of highly poisoning cations of some heavy elements in soil; the adsorption of radioactive ions in soil in the areas where nuclear plants are located; the adsorption of radioactive ions on corroded parts of nuclear plant installations. In all these systems, concentrations of the ions are low, and their adsorption characteristics are strongly affected by the oxide surface energetic heterogeneity.

Of all the models published so far, the most frequently used was the so called the "Triple Layer Model" (TLM) [1], which according to the up-to-date,

more realistic outlook has been modified by us by assuming that the surfaces of real oxides are geometrically deformed and energetically heterogeneous [2-5].

Our previous paper [5] presented the theoretical studies based on the TLM model in which the bivalent metal ions formed so called 'inner-sphere' complexes in the surface layer, where the potential determining ions H^+ are adsorbed.

Such an assumption was made in the studies by Hayes and Leckie [6-9]. They stated that it is more consistent with reality than assuming formation of so called 'outer-sphere' complexes in which the bivalent metal ions are adsorbed in the same layer as cations and anions of the basic electrolyte. Although the model presented in paper [5] was more realistic, it allocates ions of very different sizes and degrees of hydration in the same plane (especially protons and bivalent ions). However, introducing another plane would involve a large increase in mathematical complexity.

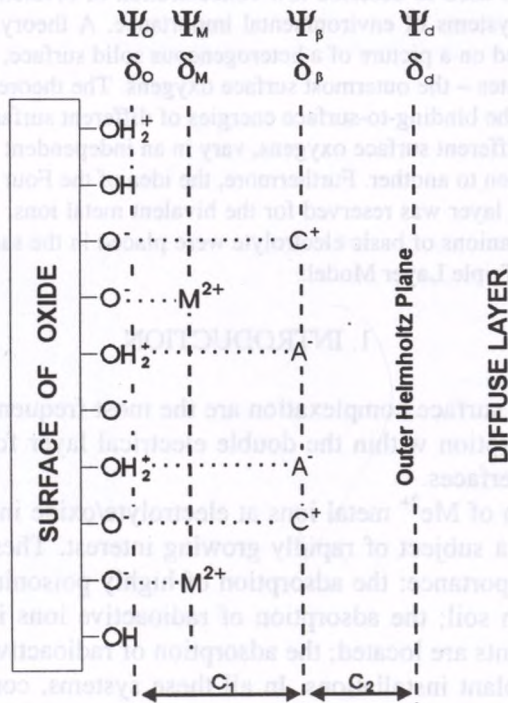


Figure 1. Diagrammatic presentation of the model of the metal oxide/electrolyte interface. ψ_0 , δ_0 - the surface potential and the surface charge density in the 0-plane; ψ_M , δ_M - the potential and the charge coming from the bivalent cations adsorbed; ψ_β , δ_β - the potential and the charge coming from the specifically adsorbed ions (cations C^+ and anions A^-) of the basic electrolyte; ψ_d , δ_d - the diffuse layer potential and its charge; c_1 , c_2 - the electrical capacitances, constant in the regions between planes

So, recently we have accepted the idea of the Four Layer Model (FLM) introduced to literature by Bowden et al. [10,11] as well as in the papers by Barrow [12,13] and Sposito [14]. A new layer, (the fourth one as the name indicates, but situated as the second, next to the surface layer "0" where protons are adsorbed), was reserved first for the bivalent metal ions. Cations and anions of basic electrolyte were placed in the same layer as in the Triple Layer Model. A schematic picture of FLM taking into account the bivalent cation adsorption is shown in Figure 1. That model is used here by us to describe low-concentration of bivalent ions in systems of environmental importance.

2. ADSORPTION MODEL FOR A HOMOGENEOUS SURFACE OF OXIDE

The potential determining ions H^+ , and the cations C^+ and anions A^- of the basic electrolyte form the following surface complexes: SOH^0 , SOH_2^+ , SO^-C^+ and $SOH_2^+A^-$ where S is the surface metal atom. The concentrations of these complexes on the surface are denoted by $[SOH^0]$, $[SOH_2^+]$, $[SO^-C^+]$ and $[SOH_2^+A^-]$, respectively. $[SO^-]$ is the surface concentration of the free sites (unoccupied surface oxygens). Except for protons, which are located in the potential layer ψ_0 , the anions and the cations are situated within the layer of potential ψ_β . Then we consider the coadsorption of another cation (a strongly adsorbed bivalent ion), which is introduced to the system in the form of a MA_2 salt. Its addition causes the formation of complexes $[SO^-M^{2+}]$ in the separate M-plane (Figure 1).

Table 1. Surface reactions and equilibrium equations in the FLM

Surface reaction	Equilibrium equation
$SOH_2^+ \xrightleftharpoons{K_{a1}^{int}} SOH^0 + H^+$	$K_{a1}^{int} = \frac{[SOH^0](a_H)}{[SOH_2^+]} \cdot \exp\left\{-\frac{e\psi_0}{kT}\right\}$
$SOH^0 \xrightleftharpoons{K_{a2}^{int}} SO^- + H^+$	$K_{a2}^{int} = \frac{[SO^-](a_H)}{[SOH^0]} \cdot \exp\left\{-\frac{e\psi_0}{kT}\right\}$
$SOH^0 + C^+ \xrightleftharpoons{K_c^{int}} SO^-C^+ + H^+$	$*K_c^{int} = \frac{[SO^-C^+](a_H)}{[SOH^0](a_C)} \cdot \exp\left\{-\frac{e(\psi_0 - \psi_\beta)}{kT}\right\}$
$SOH_2^+A^- \xrightleftharpoons{K_A^{int}} SOH^0 + H^+ + A^-$	$*K_A^{int} = \frac{[SOH^0](a_H)(a_A)}{[SOH_2^+A^-]} \cdot \exp\left\{-\frac{e(\psi_0 - \psi_\beta)}{kT}\right\}$
$SOH^0 + M^{2+} \xrightleftharpoons{K_M^{int}} SO^-M^{2+} + H^+$	$*K_M^{int} = \frac{[SO^-M^{2+}](a_H)}{[SOH^0](a_M)} \cdot \exp\left\{-\frac{e(\psi_0 - 2\psi_M)}{kT}\right\}$

According to the mass action law, the equations for equilibrium, and the commonly used in literature constants for the reactions occurring at the oxide/electrolyte interface take the form presented in Table 1, where a_c , a_A , a_M and a_H are the activities of cations, anions, bivalent cations and protons respectively.

According to the diagram in Figure 1, the surface charge density, δ_0 , must be proportional to the sum of the concentrations of the following surface complexes:

$$\delta_0 = B([\text{SOH}_2^+] + [\text{SOH}_2^+ \text{A}^-] - [\text{SO}^-] - [\text{SO}^- \text{C}^+] - [\text{SO}^- \text{M}^{2+}]) \quad (1)$$

The charge of the adsorbed bivalent ions in M-plane has the following meaning:

$$\delta_M = 2B[\text{SO}^- \text{M}^{2+}] \quad (2)$$

and the charges of the specifically adsorbed ions of the basic electrolyte in their plane, are given by:

$$\delta_\beta = B([\text{SO}^- \text{C}^+] - [\text{SOH}_2^+ \text{A}^-]) \quad (3)$$

where B is the surface density in the appropriate units of charge.

For the whole compact layer, there must be fulfilled the electroneutrality condition:

$$\delta_0 + \delta_M + \delta_\beta + \delta_d = 0 \quad (4)$$

The value of the diffuse layer charge, δ_d , is given by:

$$\delta_d = B([\text{SO}^-] - [\text{SOH}_2^+] - [\text{SO}^- \text{M}^{2+}]) \quad (5)$$

The total number of the sites capable of forming the surface complexes on the surface, N_s , is equal to:

$$N_s = [\text{SO}^-] + [\text{SOH}^0] + [\text{SOH}_2^+] + [\text{SO}^- \text{C}^+] + [\text{SOH}_2^+ \text{A}^-] + [\text{SO}^- \text{M}^{2+}] \quad (6)$$

The relationships between the potentials and the charges within the individual electric layers are following:

$$\psi_0 - \psi_\beta = \frac{\delta_0}{c_1} \quad \psi_M = \alpha_M \psi_0 \quad \psi_\beta - \psi_d = \frac{-\delta_d}{c_2} \quad (7)$$

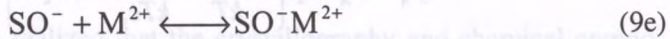
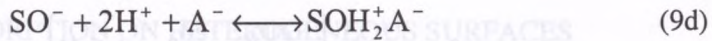
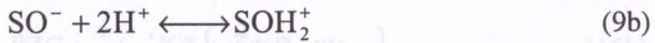
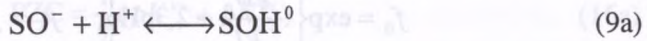
where α_M is the model parameter. We assume that the potential ψ_M changes linearly with the potential ψ_0 .

Next, we introduce the surface coverages θ_i 's by the individual surface complexes ($i=0,+,\text{C},\text{A},\text{M}$) and free sites ($i=-$),

$$\theta_0 = [\text{SOH}^0]/N_s \quad \theta_+ = [\text{SOH}_2^+]/N_s \quad \theta_A = [\text{SOH}_2^+ \text{A}^-]/N_s$$

$$\theta_C = [\text{SO}^- \text{C}^+]/N_s \quad \theta_M = [\text{SO}^- \text{M}^{2+}]/N_s \quad \theta_- = [\text{SO}^-]/N_s = 1 - \sum_i \theta_i, \quad (8)$$

The equivalent description of the reactions leading to the adsorption of ions onto the free sites SO^- is now following:



And now we have the following equilibrium constants:

$$K_0 = \frac{1}{K_{a2}^{\text{int}}} \quad K_+ = \frac{1}{K_{a1}^{\text{int}} K_{a2}^{\text{int}}} \quad K_C = \frac{K_C^{\text{int}}}{K_{a2}^{\text{int}}} \quad K_A = \frac{1}{K_{a2}^{\text{int}} \cdot K_A^{\text{int}}} \quad (10)$$

along with the following equilibrium equations:

$$K_{a2}^{\text{int}} \exp\left\{\frac{e\psi_0}{kT}\right\} = \frac{(a_H)\theta_-}{\theta_0} \quad (11a)$$

$$K_{a1}^{\text{int}} \cdot K_{a2}^{\text{int}} \exp\left\{\frac{2e\psi_0}{kT}\right\} = \frac{(a_H)^2 \theta_-}{\theta_+} \quad (11b)$$

$$K_{a2}^{\text{int}} / K_C^{\text{int}} \exp\left\{\frac{e\psi_\beta}{kT}\right\} = \frac{(a_C)\theta_-}{\theta_C} \quad (11c)$$

$$K_{a2}^{\text{int}} \cdot K_A^{\text{int}} \exp\left\{\frac{e(2\psi_0 - \psi_\beta)}{kT}\right\} = \frac{(a_H)^2 (a_A)\theta_-}{\theta_A} \quad (11d)$$

$$K_{a2}^{\text{int}} / K_M^{\text{int}} \exp\left\{\frac{2e\psi_M}{kT}\right\} = \frac{(a_M)\theta_-}{\theta_M} \quad (11e)$$

The set of the nonlinear eqs 11 can be transformed into another one, having the form of multicomponent Langmuir-like adsorption isotherms of ions θ_i 's ($i=0,+A,C,M$):

$$\theta_i = \frac{K_i f_i}{1 + \sum_i K_i f_i}, \quad i = 0, +, A, C \quad (12)$$

where f_i 's, ($i=0,+ ,A,C,M$), are the following functions of activity of protons, bivalent and salt ions in the equilibrium bulk electrolyte,

$$f_0 = \exp\left\{-\frac{e\psi_0}{kT} - 2.3\text{pH}\right\}, \quad f_+ = f_0^2 \quad (13ab)$$

$$f_C = a_C \exp\left\{-\frac{e\psi_0}{kT} + \frac{e\delta_0}{kTc_1}\right\}, \quad f_M = a_M \exp\left\{-\frac{2e\alpha_M\psi_0}{kT}\right\} \quad (13cd)$$

$$f_A = a_A \exp\left\{-\frac{e\psi_0}{kT} - \frac{e\delta_0}{kTc_1} - 4.6\text{pH}\right\} \quad (13e)$$

The surface potential function ψ_0 (pH) defined in the equations for the equilibrium of the surface complexation reactions can theoretically be calculated from the equation, developed by Bousse and co-workers [15] and used in our papers [2-5]. The simplified linear form of this equation is given by,

$$\psi_0 = \frac{\beta}{\beta+1} \frac{2.3kT}{e} (\text{PZC} - \text{pH}) \quad (14)$$

which readily shows the difference between the ψ_0 (pH) dependence and the Nernstian one.

Only for relatively large values β , $\beta/(\beta+1) \approx 1$, the potential change corresponding to one pH unit in this equation becomes that one predicted by the Nernst equation i.e. $2.3kT/e$ Volts for a pH unit.

The nonlinear equation system 12 can be transformed into a one nonlinear equation by taking into account eq 1,

$$\delta_0 = B_s \frac{K_+ f_+ + K_A f_A - K_C f_C - K_M f_M - 1}{1 + \sum_i K_i f_i} \quad i = 0, +, A, C, M \quad (15)$$

This nonlinear equation for δ_0 can be solved by means the iteration method, to give the value of δ_0 for each pH. Having calculated these values, one can evaluate the individual adsorption isotherms from eqs 12.

The Rudziński-Charmas criterion [3,4] for the common intersection point (CIP) can be applied to study the relations between the intrinsic equilibrium constants of the reactions in Table 1, and the point of zero charge (PZC) for this model.

Introducing the notation: $PZC = pH_{\delta_o=0, \psi_o=0} = -\log H$ where H is the activity of protons in the bulk solution at PZC, $pK_{ai}^{int} = -\log K_{ai}^{int}$ ($i=1,2$), $p^*K_i^{int} = -\log^*K_i^{int}$ ($i=C,A$) and assuming that the concentration of M^{2+} is very small, the relations reducing the number of the independent equilibrium constants take the following form [3,4]:

$$PZC = \frac{1}{2}(pK_{a1}^{int} + pK_{a2}^{int}) \quad (16a)$$

$$PZC = \frac{1}{2}(p^*K_C^{int} + p^*K_A^{int}) \quad (16b)$$

3. ADSORPTION ON HETEROGENEOUS SURFACES

It is now commonly realized that the crystallography and chemical composition of the actual oxide surfaces do not represent an extrapolation of appropriate bulk crystal properties. The actual (really existing) solid surfaces are characterized by a more or less decreased crystallographic order, leading also to variations in the local chemical composition. This, in turn, causes variations in adsorptive properties of adsorption sites, across the surface. That phenomenon known as the "energetic heterogeneity" of the real solid surfaces is believed now to be one of the fundamental, common features of the actual solid surfaces [16,17].

The quantitative measure of the degree of surface heterogeneity in the model of the one-site-occupancy adsorption is the differential distribution of the fraction of surface sites among the corresponding values of adsorption energy ε , $\chi(\varepsilon)$,

$$\int_{\Delta\varepsilon} \chi(\varepsilon) d\varepsilon = 1 \quad (17)$$

where $\Delta\varepsilon$ is the physical domain of ε . Very often $\chi(\varepsilon)$ is approximated by a simple analytical function and $\Delta\varepsilon$ is assumed to be either $(0, +\infty)$ or $(-\infty, +\infty)$ interval for the purpose of mathematical convenience. Such simplifications do not usually introduce a significant error in the latter theoretical calculations, except for some extreme physical regimes [16]. The exact function $\chi(\varepsilon)$ for a real physical surface is expected to have a complicated shape in general. However, to a first crude approximation, it may be approximated by a simple smooth, gaussian-like function. Thus, we will represent $\chi(\varepsilon)$ by the following gaussian-like function [18],

$$\chi(\varepsilon) = \frac{\frac{1}{c} \exp\left\{\frac{\varepsilon - \varepsilon^0}{c}\right\}}{\left[1 + \frac{1}{c} \exp\left\{\frac{\varepsilon - \varepsilon^0}{c}\right\}\right]^2} \quad (18)$$

centered at $\varepsilon = \varepsilon^0$, the spread (variance) of which is described by the heterogeneity parameter c . (The variance σ is equal to $\pi c/\sqrt{3}$).

In the case of monolayer adsorption the use of this function leads to the Langmuir-Freundlich isotherm which is probably the most commonly applied to correlate the experimental data at not very high surface coverages. Using such a simple function $\chi(\varepsilon)$ is a necessity in practical calculations, to avoid introducing many unknown parameters. As it was discussed by Rudziński et al. [2] the intrinsic constants K_i 's can be written as follows:

$$K_i = K'_i \exp\left\{\frac{\varepsilon_i}{kT}\right\}, \quad i = 0, +, A, C, M \quad (19)$$

where ε_i is the adsorption (binding) energy of the i th surface complex, and K'_i is related to its molecular partition function.

The experimentally measured adsorption isotherms have to be related to the following averages, θ_{ii} ,

$$\theta_{ii}(\{a\}, T) = \int \dots \int_{\Delta\varepsilon} \theta_i(\{\varepsilon\}, \{a\}, T) \chi(\{\varepsilon\}) d\varepsilon_0 d\varepsilon_+ d\varepsilon_A d\varepsilon_C d\varepsilon_M \quad (20)$$

where $\{a\}$ is the set of the bulk concentrations $\{a_H, a_C, a_A\}$, $\{\varepsilon\}$ is the set of the adsorption energies $\{\varepsilon_0, \varepsilon_+, \varepsilon_A, \varepsilon_C, \varepsilon_M\}$, $\Delta\varepsilon$ is the physical domain of $\{\varepsilon\}$, and $\chi(\{\varepsilon\})$ is the multidimensional differential distribution, normalized to unity, of the number of adsorption sites among various sets $\{\varepsilon\}$.

In the case of a heterogeneous oxide surface ε_i has different values on different SO sites of the oxide surface. This is accompanied by the changes in K'_i , constant, but it is generally believed, that these changes are of a secondary importance compared to the changes in the chemical bond energy ε_i .

Then, for the reasons explained in the previous paper by Rudziński et al. [4] we accept the random model of surface topography, where centres corresponding to various sets $\{\varepsilon\}$ are randomly scattered on a solid surface. Such random centre distribution causes that the probability of finding any other centre close to an adsorption centre is the same. As a result a microscopic composition of the adsorbed phase close to any centre is the same and it is identical with a mean composition of the adsorbed phase on the whole surface $\{\theta_{ii}\}$. It means that all interaction potentials are a function of the averaged concentrations of the surface complexes $\{\theta_{ii}\}$. In eq 12 the functions θ_i 's have the same form as

for the homogeneous surface model except for the fact that sets $\{\theta_i\}$ should be replaced now by sets $\{\theta_{ii}\}$. The adsorption system constitutes a thermodynamic entity characterized by one electrostatic capacity.

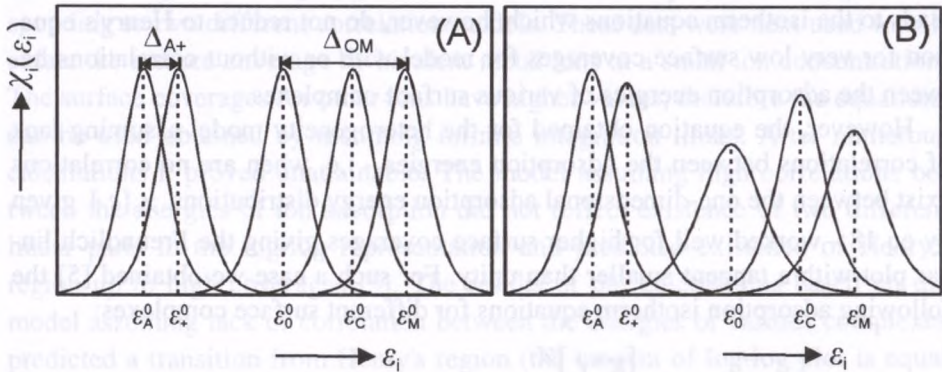


Figure 2. (A) Schematic visualization of the adsorption energy distributions $\chi_i\{\varepsilon_i\}$, ($i=0,+A,C,M$) for the model assuming high correlations to exist between the adsorption energies of various surface complexes. (B) Schematic visualization of the adsorption energy distributions $\chi_i\{\varepsilon_i\}$, ($i=0,+A,C,M$) for the model assuming lack of correlations between the adsorption energies of various surface complexes

Now, we have to consider another factor, discussed in detail in [5], characterizing the properties of a heterogeneous surface. This is the degree of correlation between adsorption energies of various complexes on various centres:

(1) The case of high correlations between adsorption energies (Figure 2A).

Though the energies ε_i and $\varepsilon_{j \neq i}$ change on passing from one centre to another, their difference $\Delta_{ji} = \varepsilon_j - \varepsilon_i$ remains unchanged. Therefore the function $\chi(\{\varepsilon\})$ in eq 20 reduces to one-dimensional differential distribution $\chi\{\varepsilon\}$.

(2) The case of lack of correlations between adsorption energies on various centres (Figure 2B).

Then the function $\chi(\{\varepsilon\})$ in eq 20 becomes a product of one-dimensional distribution functions.

The model of a heterogeneous surface taking into account these two extreme cases of random surface topography was used in the calculations presented in our previous paper [5]. We used it to explain the behavior of adsorption isotherms of bivalent ions. The concentrations of these ions are low, and their adsorption characteristics are strongly affected by surface energetic heterogeneity. The logarithm of the adsorbed amount, plotted vs the logarithm of the ion concentration in solution is always a Freundlich linear plot with a tangent much

smaller than unity. However, at a sufficiently low ion concentration, a transition occurs into a Henry's plot, typical for a homogeneous solid surface, with the tangent equal to unity. Firstly, we simplified the mathematical calculations assuming that $\Delta\varepsilon$ is the interval $(-\infty, +\infty)$. Assuming such integration limits leads to the isotherm equations which, however, do not reduce to Henry's equation for very low surface coverages for model with or without correlations between the adsorption energies of various surface complexes.

However, the equation obtained for the heterogeneity model assuming lack of correlations between the adsorption energies - i.e. when are no correlations exist between the one-dimensional adsorption energy distributions $\chi_i\{\varepsilon_i\}$ given by eq 18 - worked well for higher surface coverages giving the Freundlich linear plot with a tangent smaller than unity. For such a case we obtained [5] the following adsorption isotherm equations for different surface complexes:

$$\theta_{it} = \frac{[K_i^0 f_i]^{1/c_i}}{1 + \sum_i [K_i^0 f_i]^{1/c_i}} \quad i = 0, +, A, C, M \quad (21)$$

where

$$K_i^0 = K_i' \exp\left\{\frac{\varepsilon_i^0 - \varepsilon_i}{kT}\right\} \quad (22)$$

and where c_i 's are the heterogeneity parameters for different surface complexes, $i=0, +, A, C, M$. The way of solving of the equation set 21 was shown in our previous paper [5].

The general form of adsorption isotherm in the FLM described here is identical to eq 21 obtained originally for TLM. The difference appears only in the form of the function f_M .

Now, we are going to establish the correlations between the intrinsic equilibrium constants in a similar way as in the case of the homogeneous surface model, considered in the previous section. The Rudziński-Charmas criterion leads now to the following interrelations [4]:

$$\left(\frac{H^2}{K_{a1}^{\text{int}} \cdot K_{a2}^{\text{int}}}\right)^{1/c_A} + \left(\frac{kT/c_C}{kT/c_A} - 1\right) \cdot \left(\frac{K_C^{\text{int}} a}{K_{a2}^{\text{int}}}\right)^{1/c_C} - 1 = 0 \quad (23a)$$

$$\frac{kT}{c_A} \left(\frac{H^2 a}{K_{a2}^{\text{int}} \cdot K_A^{\text{int}}}\right)^{1/c_A} + \frac{kT}{c_C} \left(\frac{K_C^{\text{int}} a}{K_{a2}^{\text{int}}}\right)^{1/c_C} = 0 \quad (23b)$$

In the studies on monolayer adsorption of gases Rudziński and Everett [16] showed that a correction for the physically reasonable limited domain $\Delta\varepsilon$, i.e.

existence of minimum and maximum values ε_i^l and ε_i^m should be made to arrive at an isotherm equation reducing correctly to Henry's law.

Assuming such finite integration limits for the two different models of random surface we obtained [5] two different sets of equations for θ_{ii} , corresponding to two different correlation models. These sets were next used to calculate the surface coverage by bivalent metal ions at a small ion concentration. The surface coverages for other ions have higher values, therefore the equations can be used obtained by assuming infinite integration limits. After numerous calculations it proved unattainable. The model assuming high correlations between the energies of ion adsorption did not reflect existence of two different linear parts in the log-log representation and predicted existence of Henry's region up to high coverages [5]. The results of our calculations based on the model assuming lack of correlation between the energies of various complexes predicted a transition from Henry's region (the tangent of log-log plot is equal to one) to Freundlich's region (the tangent smaller than one). The problem is that the tangent in this transition region reaches values larger than unity [5]. Such behavior has never been observed in the experiment. However, the different behavior of the log-log plots suggest, that the degree of the correlations between the adsorption energies of ions may affect strongly the behavior of these adsorption systems at low ion concentrations.

Therefore we have decided that the equation describing a real adsorption isotherm θ_{ji} of the heavy metal ions will be represented by an analytical formula corresponding to the assumption that $\chi_j(\varepsilon_j)$ is the following rectangular energy distribution:

$$\chi_j(\varepsilon_j) = \begin{cases} \frac{1}{\varepsilon_j^m - \varepsilon_j^l} & \text{for } \varepsilon_j \in < \varepsilon_j^l, \varepsilon_j^m > \\ 0 & \text{elsewhere} \end{cases} \quad (24)$$

The rectangular distribution is a good approximation in the case of strongly heterogeneous surfaces [16]. And this is just the case of the bivalent metal ion adsorption (Freundlich's plots with $kT/c_j \ll 0.9$). As the transition from Henry's to Freundlich's plot has been observed in adsorption on so different materials, we arrive at the following important conclusion. The model assuming high correlations between the adsorption energies of various surface complexes is to be abandoned in the studies of ion adsorption within the electrical double layer formed at the water/oxide interfaces.

On the contrary, our model calculations corresponding to the assumption that no correlations exist between the adsorption energies of different surface complexes, could reproduce very well the transition from Henry's to Freundlich's plot [5]. The adsorption isotherm equation obtained by using the rectan-

gular distribution function for the random model without correlation takes the form [5],

$$\theta_{ji} = \frac{1 + (K_j^0 f_j)^{1/c_j}}{1 + \sum_j (K_j^0 f_j)^{1/c_j}} \cdot \frac{kT}{\varepsilon_j^m - \varepsilon_j'} \ln \frac{1 + \exp\left\{\frac{\varepsilon_j^m - \varepsilon_{jc}}{kT}\right\}}{1 + \exp\left\{\frac{\varepsilon_j' - \varepsilon_{jc}}{kT}\right\}}, \quad j = M \quad (25)$$

where ε_{jc} has the following form,

$$\varepsilon_{jc} = -kT \ln K_j^0 f_j + \varepsilon_j^0, \quad j = M \quad (26)$$

The form of the eq 25 obtained for the TLM [5] will be identical for FLM as well. The difference is only in the form of the function f_M .

The others θ_{ji} ($j=0,+A,C$) can be calculated from eq 15 as their coverages reach higher values.

4. RESULTS AND DISCUSSION

For the FLM model and the heterogeneous surface model without any correlations between adsorption energies (eq 25), we are going to demonstrate its utility to fit the experimental data. Similarly as in our previous investigations [5], we took the set of parameters obtained by Davis and Leckie [19] analyzing their titrations curves (Table 2).

Table 2. Values of the parameters obtained by Davis and Leckie [19], who analyzed their titration data for the amorphous iron hydroxide in terms of the homogeneous surface model

$pK_{a1}^{\text{int}} = 5.10$	$p^*K_C^{\text{int}} = 9.00$
$pK_{a2}^{\text{int}} = 10.70$	$p^*K_A^{\text{int}} = 6.90$
PZC = 7.90	$N_s = 10$ sites/nm ²
$c_1 = 1.40$ F/m ²	$I = 0.1$ mol/dm ³ (NaNO ₃)
T = 25°C	–

We calculated, however, the corresponding pK_{a2}^{int} and $p^*K_A^{\text{int}}$ values from relations 23ab and then adjusted the other parameters: pK_M^{int} , ε_j' , ε_j^m , and α_M to fit the experimental isotherms of Cd²⁺ ions for the three pH values. The results of these numerical exercises are shown in Figure 3.

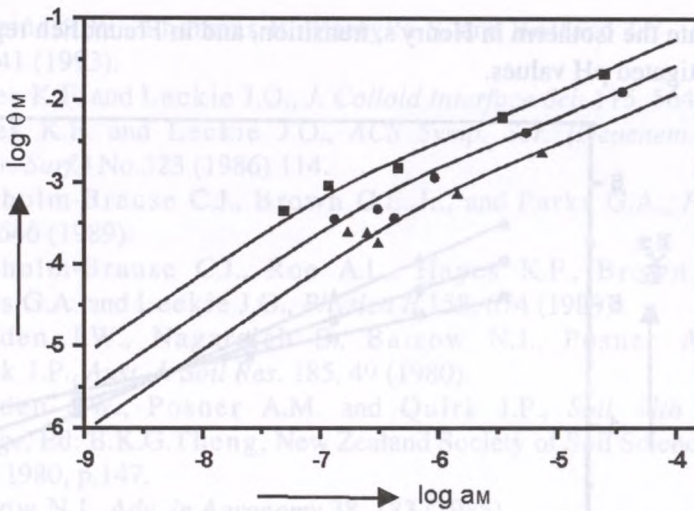


Figure 3. Effects of pH on the isotherms of cadmium ions, adsorbed on the amorphous iron oxyhydroxide investigated by Benjamin and Leckie [20]. Experimental data for three pH values: (\blacktriangle) pH=6.6; (\bullet) pH=6.9; (\blacksquare) pH=7.2. Our theoretical lines (solid) were calculated using eq 25 and the same set of the best fit parameters for each pH

Our theoretical lines were calculated from eq 25 by using for the investigated system the constants: N_s and PZC and the parameters pK_{a1}^{int} , $p^*K_C^{int}$ and c_1 collected in Table 2. As to the values of these three parameters their precise determination is necessary to analyze the experimental data concerning the adsorption of basic electrolyte ions (radiometric curves, potentiometric titration curves for different salt concentrations and electrokinetic curves) [4]. And because we did not have such data for the studied system, the values of Davis and Leckie parameters were used as acceptable approximation because they do not affect significantly the log-log adsorption curve of bivalent metal ion adsorption.

Moreover, the parameters characterizing the heterogeneous surface model without correlations between the energies of adsorption of various surface complexes kT/c_i ($i=0,+A,C$) were assumed to be equal to 0.7, as these values do not affect significantly the adsorption of bivalent ions. The values of the parameters $pK_{a2}^{int}=10.7$ and $p^*K_A^{int}=6.8$ were calculated from relations 23ab.

So, in our numerical exercises we adjusted only the three other parameters: $pK_M^{int}=4.4$, $\varepsilon_M^l = -8$ kJ/mol, $\varepsilon_M^m = 8$ kJ/mol. The strategy of application of eq 25 has been presented in our previous paper [5]. As the slope of the Freundlich part of all these isotherms is equal to 0.66, we took the kT/c_M as equal to this value

to calculate the isotherm in Henry's, transition, and in Freundlich regions for all the investigated pH values.

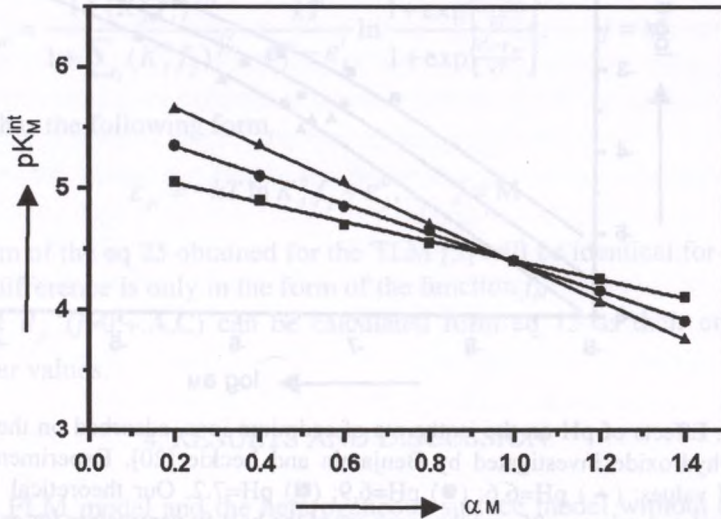


Figure 4. Relations between the correlated parameters pK_M^{int} and α_M in the four layer model studied. Calculations were made for the system presented in Figure 3, separately for the three pH values: (\blacktriangle) pH=6.6; (\bullet) pH=6.9; (\blacksquare) pH=7.2

To sum up the above considerations, it can be stated, that the log-log adsorption curves are sensitive to the last three parameters as well as to the parameter α_M characteristic for the FLM. α_M , which was accepted as equal to one, because our model investigations showed that it is strongly correlated with the adsorption constant pK_M^{int} . The extent of this correlation is given in Figure 4.

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CURRICULA VITAE



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He organised the three international symposia: "*Effects of Surface Heterogeneity in Adsorption and Catalysis on Solids*"-ISSHAC. (Poland, 1992, 1995, 1998).

For his outstanding scientific achievements, he was awarded five times by the Polish Ministry of Education and once by the Rector of Maria Curie-Skłodowska University. He was also awarded by the Polish Chemical Society.

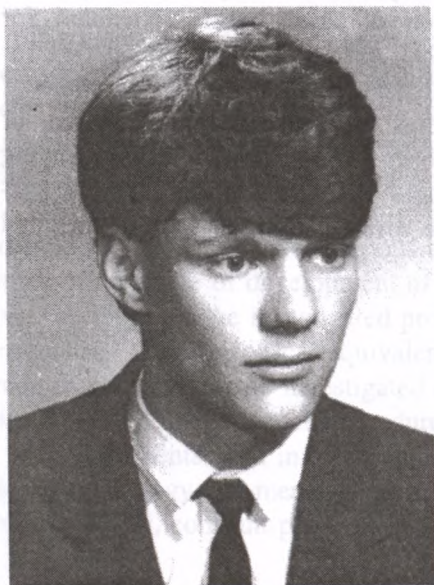
Besides many short visits to many Universities of the world, he also paid long-term visits to Queens University (Canada), University of Vienna (Austria), University of Leipzig (Germany), Tohoku University (Japan), CNRS Laboratory at the University of Montpellier (France), Ruhr University in Bochum

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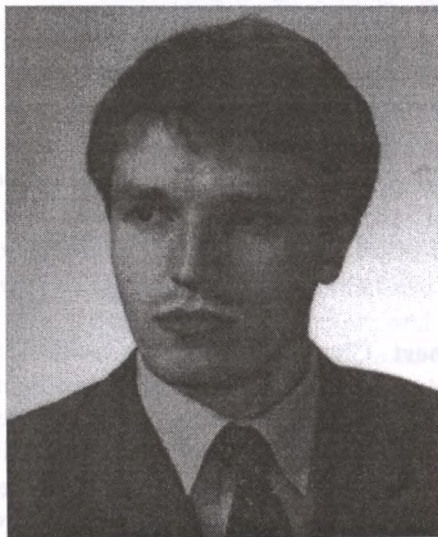
Selected publications:

1. "Adsorption of Aromatics in Zeolites ZSM-5: A Thermodynamic-Calorimetric Study Based on the Model of Adsorption on Heterogeneous Adsorption Sites"
Langmuir, 13, 1095 (1997)
2. "A New Method to Estimating the Solid Surface Energetic heterogeneity from TPD Spectra, Based on the Statistical Rate Theory of Interfacial Transport"
Langmuir, 13, 3445 (1997)
3. "Calorimetric Effects Accompanying Ion Adsorption at the Charged Metal Oxide/Electrolyte Interfaces: Effects of Oxide Surface Heterogeneity"
Langmuir, 14, 5210 (1998)
4. "Adsorption of Cationic Surfactants on Hydrophilic Silica: Effects of Surface Energetic Heterogeneity"
Colloids & Surfaces, A145, 243 (1998)



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oxide/electrolyte interface. The result of the investigations is over 10 original papers.