Effects of Surface Heterogeneity of Oxides in Simple Ion Adsorption at Oxide/Electrolyte Interfaces

W. RUDZIŃSKI AND R. CHARMAS

Department of Theoretical Chemistry, Maria Curie—Sklodowska Univ., M. Curie Sklodowska Sq. 3, 20-031 Lublin, Poland

Abstract. It has been shown that the adsorption of ions at oxide/electrolyte interface should be treated in terms of adsorption on a heterogeneous solid surface. This is because the adsorption runs via formation of complexes with surface oxygen atoms. Because of the small degree of oxide surface organization, different surface oxygens may have different status with respect to electrostatic interactions and the strength of the chemical bonds formed between the surface oxygens and the adsorbed protons or metal ions. We have shown that the equations describing the equilibria of formation of surface complexes can be transformed to Langmuir-like equations for multicomponent adsorption. One can apply, therefore, for these systems theoretical methods used to describe mixed-gas adsorption on heterogeneous solid surfaces.

Keywords: oxide/electrolyte interface, ion adsorption, energetic heterogeneity

Introduction

It is now generally recognized that the surfaces of oxides are geometrically distorted and therefore energetically heterogeneous for adsorption. It has been realized by the scientists investigating adsorption from the gas phase for a long time. A variety of experimental techniques has been used to study the nature of these surface imperfections, and dozens of papers have been published on this subject. The reported results have already been a subject of a number of reviews (Nowotny and Wepper, 1989). Dozens of papers were published showing that successful correlations of the experimental data for gas adsorption onto oxides can be done only by using equations corresponding to a heterogeneous surface model (Rudziński and Everett, 1991; Jaroniec and Madey, 1988). The experimental studies were stimulated strongly by the widely spread view that these are the surface imperfections creating catalytic centres for many important catalytic reactions.

Bakaev's computer simulations (Bakaev, 1987, 1988; Bakaev and Dubinin, 1987; Bakaev and Chelnokova, 1989) of oxide surfaces suggest that even

in the case of oxides having a well defined bulk crystal structure, the degree of the surface disorder may be larger than it is generally believed.

Our attention here will be focused on the extremely important class of adsorption systems, composed of water being in contact with oxide surfaces. The reasons, why the behaviour of water/oxide interfaces is so important for various areas of science, life and industry, are well-known.

The calorimetric studies of the surface heterogeneity of oxides were initiated half a century ago, and experimental findings as well as their theoretical interpretation have been reviewed by Rudziński and Everett (1991). The last two decades have brought a true Renaissance of adsorption calorimetry. A new generation of fully automatized and computerized microcalorimeters has been developed, far more accurate and easy to manipulate. This was stimulated by the still better recognized fact that calorimetric data are much more sensitive to the nature of an adsorption system than adsorption isotherm for instance. It is related to the fact that calorimetric effects are related to temperature derivatives of appropriate thermodynamic

functions, and temperature appears generally in exponential terms.

The adsorption of ions and the formation of the electric double layer at water/oxide interface are the physical phenomena the importance of which in life and technology can hardly be overestimated. So, no surprise that the mechanism of the formation of the electric double layer at water/oxide interfaces has been studied thoroughly in hundreds of papers and it would take far too long to review even the most fundamental of them. Various techniques have been used to measure proton and accompanying ion adsorption on the outermost surface oxygens of oxides. The most popular of these techniques are potentiometric titration and ζ-potential measurements. Then, radiometric methods allow the adsorption of individual ions to be monitored.

The interpretation of electrokinetic data is accompanied by some assumptions which introduce a certain degree of uncertainty. On the contrary, the potentiometric titration and the radiometric methods are directly related to the adsorption isotherms of ions. Thus, the most fundamental conclusions have been drawn from a suitable theoretical analysis of these adsorption isotherms being mainly based on a model of a homogeneous oxide surface.

As the accuracy of the adsorption isotherm measurements increased, the necessity to fit the experimental data quantitatively led to more and more refined theories of the electric double layer. However, these more refined and complicated theories failed to correlate experimental adsorption isotherms in some systems. The general feeling started to grow that the model of a homogeneous surface is too crude to explain well these adsorption phenomena.

Thus, in view of this large body of experimental and theoretical evidence of the surface heterogeneity of the actual oxides, it may only surprise us, that this important physical factor received so little attention from the scientists investigating ion adsorption at electrolyte/oxide interfaces.

At the early stage of the theories of adsorption onto oxide surfaces, the emphasis was given to electrostatic interactions. The fact that adsorption frequently involves chemical bonding as well was not so commonly recognized until recently. This implies a dispersion of chemical bonding energies to be possible, arising form the different local status of the outermost surface oxygens.

At the end of the seventies Garcia-Miragaya and Page (1976, 1977) and Street et al. (1977) reported

a successful correlation by Freundlich equation of the data of trace Cd^{2+} adsorption by both clay minerals and soils. Benjamin and Leckie (1981) found the same for the trace adsorption of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} onto amorphous iron oxyhydride. The use of Freundlich equation was also suggested in the works by Sposito (1979, 1980b). In the theories of gas adsorption the applicability of Freundlich equation was long ago associated with the energetic heterogeneity of the adsorption sites on the actual solid surfaces. It was also known, that Freundlich equation is a simplified form of a more general isotherm equation which is now commonly called Langmuir-Freundlich isotherm. Thus, Sposito (1980b) suggested that it was high time it were used also in the case of ion adsorption at water/oxide interfaces.

Benjamin and Leckie (1981) were among the first who initiated the studies of the surface heterogeneity effects in 1981. They reported that the adsorption of Me^{2+} metal ions onto oxyferrihydride could be described only by assuming a large dispersion of adsorption site affinities. Two years later Kinniburgh et al. (1983) tried to correlate such adsorption isotherms by using other empirical equations employed earlier to correlate experimental adsorption isotherms for single gas adsorption onto heterogeneous solid surfaces.

Theoretical studies of surface heterogeneity effects on ion adsorption within the electrical double layer were much advanced by Koopal and Van Riemsdijk (1989), Van Riemsdijk et al. (1986, 1987a, 1987b), and Gibb and Koopal (1990). Rudziński et al., (1991) have subjected calorimetric effects accompanying ion adsorption to their theoretical analyses. They showed that surface heterogeneity of oxides affected enthalpies of ion adsorption. A similar effect has been known for a long time in gas adsorption onto solid surfaces. In another paper, Rudziński et al. (1992) showed that titration curves were much less sensitive to the surface heterogeneity than individual adsorption isotherms of ions measured by using radiometric methods. Titration curves probably involve a certain mutual cancellation of heterogeneity effects. This deserves some further experimental and theoretical studies. Rudziński et al. (1993) developed the theory reproducing the behaviour of the log-log plots of the experimental adsorption isotherms of bivalent ions on oxides at low surface concentrations. These experimental adsorption isotherms show a transition from a linear log-log (Henry's) plot with a tangent equal to unity to a Freundlich log-log plot with tangent smaller than unity.

The Nature of the Energetic Heterogeneity of the Actual Water/Oxide Interfaces

So far, we have considered idealized surface structures of oxides. It is now commonly realized that the crystallography and chemical composition of the actual solid 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 heterogenity" of the real solid surfaces is believed now to be one of the fundamental, common features of the actual solid surfaces (Rudziński and Everett, 1991; Jaroniec and Madey, 1988).

In our case, the energetic surface heterogeneity means, first of all, the variations in the chemical status and the adsorptive features of the outermost surface oxygen atoms with respect to hydrogen bonding. The existence of the surface energetic heterogenity of oxides, with respect to water adsorption has been known for a long time. The most spectacular evidence came from calorimetric measurements.

Zettlemoyer and his co-workers (1958, 1960) were among the first who demonstrated strong evidence for a great role of the surface energetic heterogeneity of oxides in their immersional experiments. Morimoto and co-workers (1978) wrote that "the differential heat on TiO_2 decreased with increasing amount of chemisorbed water, suggesting an ordinary type of surface heterogeneity". In their studies of water adsorbed onto alumina Della Gatta et al. (1973) concluded that "surface rehydroxylation involves rather high differential heat values (initial heat of about 40 kcal/mole), and the heat evolution is typical for a heterogeneous surface". Wightman et al. (1983) reported that in their studies of water adsorption onto titania dioxide, "the isosteric heat of adsorption decreased with increasing coverage indicating the heterogeneous nature of the titanium dioxide samples". The first quantitative fit of the experimental heats of immersion in pure water (Rudziński and Partyka, 1982) and in solutions of varying pH was done by Rudziński et al. (1991), who assumed that the surfaces of oxides were energetically heterogeneous.

Although, the view about the energetic heterogeneity of oxide surfaces is now commonly accepted, the nature of that phenomenon and its role in adsorption is not well understood yet. The structure of oxide surfaces is still often assumed to be corresponding to their ideal crystallographic structure.

Meanwhile, as long ago as at the beginning of the sixties Peri (1960, 1965a, 1965b) argued that after strong dehydratation the structure of aluminium oxides was very irregular, as shown in Fig. 1(A). Flockhardt et al. (1966a, 1966b) assumed a lesser distorted structure of alumina oxides, as shown in Fig. 1(B). Hiemstra et al. (1989a, 1989b, 1990) assumed that the surface heterogeneity of alumina oxides arose solely from a different status of various surface oxygens, as shown in Fig. 1(C).

Bakaev (1988, 1992a, 1992b), on the contrary, believes that for the majority of the actual, i.e., really existing, oxide surfaces, the picture of an amorphous surface phase should be more realistic than that of a crystalline surface with defects [Fig. 1(D)]. It means, Bakaev's model is similar to that assumed by Peri. Bakaev's computer simulation provides an impressive support for random topography of oxide surfaces. Of course, some degree of surface organization should exist, and it will increase when going more and more deeply into the solid bulk phase. The outermost layers of surface atoms (ions) may be amorphous, but the interior may have a well-defined structure.

The fact that the surfaces of the actual oxides are geometrically distorted and energetically heterogeneous is crucial for almost all catalytic reactions running on oxide surfaces as demonstrated by the numerous works published by Samorjai's school. Still new papers are published showing the importance of the geometric nonuniformity and energetic heterogeneity in various adsorption and catalytic systems. So, various experimental techniques have been used to study that important phenomenon. These findings were reported by Samorjai (1981) and more recently by Hirschwald (1989). This latter review includes the impressive images of the surfaces of the actual oxides obtained by STM (Scanning Tunneling Microscopy) (De Lozanne, 1993).

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 corresponding values of adsorption energy ϵ, $\chi(\epsilon)$, such that

$$\int_{\Delta\epsilon} \chi(\epsilon)\, d\epsilon = 1 \tag{1}$$

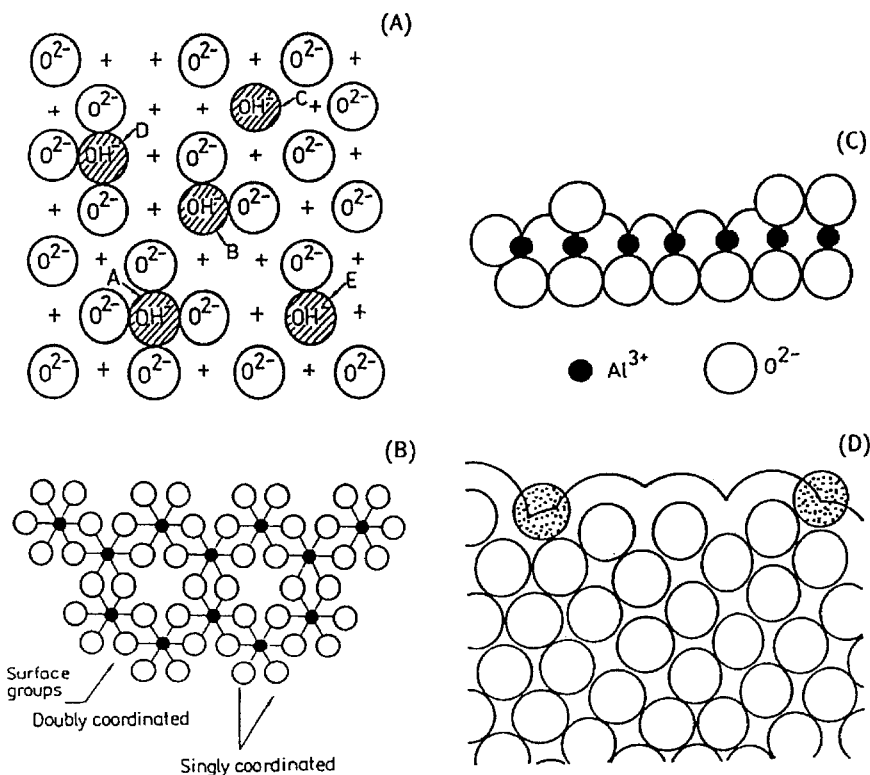where $\Delta\epsilon$ is the physical domain of ϵ.

Figure 1. (A) Peri's model of aluminium oxide surface after strong dehydration. (B) Flochard's model of aluminium oxide surface. (C) Hiemstra's model of aluminium oxide surface. (D) Bakaev's picture of an oxide surface.

Very often $\chi(\epsilon)$ is approximated by a simple analytical function and $\Delta\epsilon$ 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 (Rudziński and Everett, 1991). The exact function $\chi(\epsilon)$ 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 $\chi(\epsilon)$ by the following gaussian-like function (Rudziński et al., 1986, 1987)

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

centered at $\epsilon = \epsilon^0$, the spread (variance) of which is described by the heterogeneity parameter c. (The variance σ is equal to $\pi c/\sqrt{3}$).
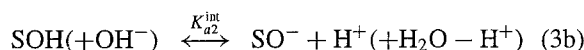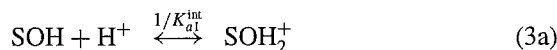
In the case of monolayer adsorption the use of this function leads to the Langmuir-Freundlich isotherm which is probably the most commonly applied to correlate the experimental data at not very high surface coverages when the effects of multilayer adsorption can still be neglected.

Using such a simple function $\chi(\epsilon)$ is necessary in practical calculations, to avoid introducing many unknown parameters. That procedure is common for the majority of theoretical works on adsorption on heterogeneous solid surfaces.

Metal Oxide/Electrolyte Interface

It is generally known that metal oxide surface is covered with hydroxyl groups when oxide is placed in water. The presence of two free electron pairs of oxygen atom and possibility of hydrogen ion dissociation is the evidence of amphoteric character of these groups. On account of this, the most useful parameter in description of the water/metal oxide interface is pH of the solution

being in contact with the surface. Adsorption of H^+ or OH^- ions causes protonization or deprotonization of the surface according to the equations:

$$SOH + H^+ \overset{1/K_{a1}^{int}}{\longleftrightarrow} SOH_2^+ \qquad (3a)$$

$$SOH(+OH^-) \overset{K_{a2}^{int}}{\longleftrightarrow} SO^- + H^+(+H_2O - H^+) \quad (3b)$$

where S is the surface metal atom, and the SO^-, SOH and SOH_2^+ denote the surface structures which are assumed to be negative, neutral and positively charged surface complexes, respectively.

To describe in detail such a specific system as the metal oxide/solution interface, it is necessary to prepare a model describing dependences between potential and surface charge and draw up reactions, the occurrence of which leads to the changes of surface charge δ_0. The reaction equations describing an equilibrium state between the surface and solution as well as values of equilibrium constants of these reactions provide detailed information about stoichiometry of the reaction enabling theoretical calculations of surface charge and individual adsorption isotherms of each surface complex.

The models describing hydrolysis and adsorption on oxide surfaces are called surface complexation models in literature. They differ in the assumptions concerning the structure of the double electrical layer, i.e., in the definition of planes situation, where adsorbed ions are located and equations associating the surface potential with surface charge ($\psi = f(\delta)$). The most important models are presented in the papers by Westall and Hohl (1980). The most commonly used is the triple layer model proposed by Davis et al. (1978) and Davis and Leckie (1978, 1980) from conceptualization of the electrical double layer discussed by Yates et al. (1974) and by Chan et al. (1975). Reviews and representative applications of this model have been given by Davis and Leckie (1979) and by Morel et al. (1981). We will base our consideration on this model. The schematic picture of the triple layer model is shown in Fig. 2.

While changing pH of the solution being in contact with oxide surface by bringing in acid or base, acid radical ions (most frequently oxygen-free or monovalent) or alkaline metal ions are being introduced. As a result, besides potential determining ions H^+ responsible for pH of the solution, there are cations C^+ and anions A^- (e.g., K^+, Na^+, Cl^-, Br^-, NO_3^-, etc.) which according to this theory are found not only in the counterion (diffuse) layer but also in the compact one. To avoid complications caused by the increase of the concentration
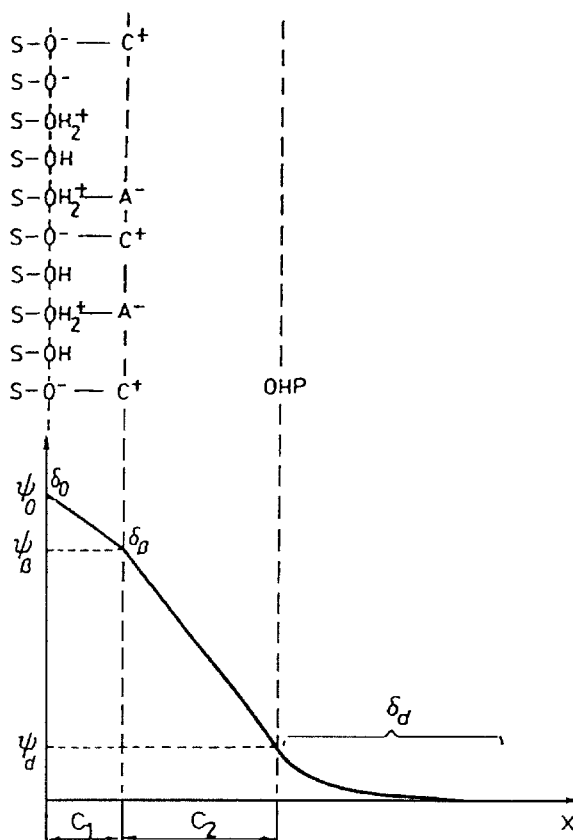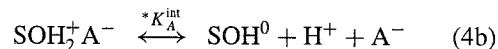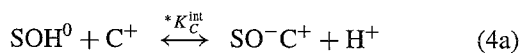

Figure 2. Scheme of the triple layer of ions formed at metal oxide/electrolyte interface. ψ_0, δ_0—The surface potential and the surface charge density in the 0-plane; ψ_β, δ_β—The potential and the charge coming from the specifically adsorbed ions of the basic electrolyte in the β-plane; ψ_d, δ_d—The diffuse layer potential and its charge; c_1, c_2—The electrical capacitances, constant in the regions between planes.

of anions A^- or cations C^+ while adding acid or base (when pH is changed), the electrolyte solution being in contact with the oxide surface already at the beginning of the experiment contains added salt CA as a basic electrolyte.

So, besides the surface reactions (3a) and (3b) there are also reactions leading to formation of the surface complexes SO^-C^+ and $SOH_2^+A^-$, which have the character of ion pairing.

$$SOH^0 + C^+ \overset{*K_C^{int}}{\longleftrightarrow} SO^-C^+ + H^+ \qquad (4a)$$

$$SOH_2^+A^- \overset{*K_A^{int}}{\longleftrightarrow} SOH^0 + H^+ + A^- \qquad (4b)$$

As a result (Rudziński, 1992) we obtain the following set of the multicomponent Langmuir-like equations for

the surface coverages θ_i's ($i = 0, +, A, C$) by the individual surface complexes SOH, SOH_2^+, $SOH_2^+A^-$ and SO^-C^+ respectively:

$$\theta_i = \frac{K_i f_i}{1 + \sum_i K_i f_i}, i = 0, +, A, C \qquad (5)$$

where K_i's ($i = 0, +, A, C$) are the functions of intrinsic equilibrium constants of the reactions (3), (4):

$$K_0 = \frac{1}{K_{a2}^{int}} \qquad K_+ = \frac{1}{K_{a1}^{int} \cdot K_{a2}^{int}}$$

$$K_C = \frac{{}^*K_C^{int}}{K_{a2}^{int}} \qquad K_A = \frac{1}{K_{a2}^{int} \cdot {}^*K_A^{int}} \qquad (6)$$

and f_i's ($i = 0, +, A, C$) are the following functions of proton activity (as a pH) and salt ions, a_i ($i = A, C$):

$$f_0 = \exp\left\{-\frac{e\psi_0}{kT} - 2.3\,\text{pH}\right\}, \qquad (7a)$$

$$f_+ = f_0^2 \qquad (7b)$$

$$f_C = a_C \exp\left\{-\frac{e\psi_0}{kT} + \frac{e\delta_0}{kTc_1}\right\}, \qquad (7c)$$

$$f_A = a_A \exp\left\{-\frac{e\psi_0}{kT} - \frac{e\delta_0}{kTc_1} - 4.6\,\text{pH}\right\} \qquad (7d)$$

where δ_0 is the surface charge density, ψ_0 is the surface potential, c_1 is the electrical capacitance constant in the region between "0" and "β" planes (see Fig. 2), T is the temperature, e is the elementary charge and k is the Boltzman constant.

The knowledge of PZC (Point of Zero Charge) experimental value and the knowledge that in most systems the PZC value does not practically depend on salt concentration in the bulk solution, (i.e., a common intersection point (CIP) occurs at pH = PZC) (Davis and Leckie, 1978; Kallay et al., 1990; Sprycha, 1984) make it possible to obtain the following relations (Rudziński et al., 1992):

$$^*K_A^{int} = \frac{H^2}{{}^*K_C^{int}} \quad \text{and} \quad K_{a1}^{int} = \frac{H^2}{K_{a2}^{int}} \qquad (8)$$

where $H = 10^{-PZC}$. Equation (8) relating the parameters K_{a1}^{int} and K_{a2}^{int}, and $^*K_C^{int}$ and $^*K_A^{int}$ reduce the number of the unknown equilibrium constants determined from fitting suitable experimental data from four to two.

Except of the two intrinsic equilibrium constants and the density of the surface sites N_s as the parameters (Rudziński et al., 1992), the triple layer model assumes two values of the parameter c_1 to exist, depending on the sign of the charge of the surface (Blesa and Kallay, 1988):

$$c_1 = c_{1(1)} \text{ for pH} < \text{PZC}$$

$$c_1 = c_{1(2)} \text{ for pH} > \text{PZC} \qquad (9)$$

The parameter c_1 is connected with the distance between the surface layer "0" and the layer "β" where cations and anions of basic electrolyte are located. For pH < PZC, i.e., in the acidic medium, there is much more of $SOH_2^+A^-$ complexes formed by anion adsorption, but when pH > PZC, SO^-C^+ complex is strongly predominant. Two different values of parameter c_1 suggest that the adsorbed anion and adsorbed cation are situated at different distances from the surface.

Adsorption of Simple Ions and the Heterogeneous Surface Model

As it was discussed by Rudziński et al. (1991) the intrinsic constants K_i's can be written as follows:

$$K_i = K_i' \exp\left\{\frac{\epsilon_i}{kT}\right\}, \qquad i = 0, +, A, C \qquad (10)$$

where ϵ_i is the adsorption (binding) energy of the ith 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_{it},

$$\theta_{it}(\{a\}, T) = \int_{\Delta\epsilon} \cdots \int \theta_i(\{\epsilon\}\{a\}, T)\chi(\{\epsilon\})$$
$$\times d\epsilon_0\, d\epsilon_+\, d\epsilon_A\, d\epsilon_C \qquad (11)$$

where $\{a\}$ is the set of the bulk concentrations $\{a_H, a_C, a_A\}$, $\{\epsilon\}$ is the set of the adsorption energies $\{\epsilon_0, \epsilon_+, \epsilon_A, \epsilon_C\}$, $\Delta\epsilon$ is the physical domain of $\{\epsilon\}$, and $\chi(\{\epsilon\})$ is the multidimentional differential distribution of the number of adsorption sites among various sets $\{\epsilon\}$, normalized to unity.

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

Then, for the reasons explained in the paper by Rudziński et al. (1992), we accept the random model of surface topography. Random type surfaces where centres corresponding to various sets $\{\epsilon\}$ 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 phase on the whole surface $\{\theta_{it}\}$. It means that all interaction potentials are a function of the averaged concentration of surface complexes $\{\theta_{it}\}$. In Eq. (11) functions θ_i's have the same form as for homogeneous surface model except for the fact that sets $\{\theta_i\}$ should be replaced by sets $\{\theta_{it}\}$. The adsorption system constitutes a thermodynamic entity characterized by one electrostatic capacity.

Now we have to consider another factor characterizing the properties of a heterogeneous surface is the degree of correlation between adsorption energies of various complexes on various centres.

(1) The case of high correlations between adsorption energies; though energies ϵ_i and $\epsilon_{j \neq i}$ change on passing from one to another centre, their difference $\Delta_{ji} = \epsilon_j - \epsilon_i$ remains unchanged. Therefore the function $\chi(\{\epsilon\})$ in Eq. (11) reduces to one-dimensional differential distribution $\chi_i(\epsilon_i)$.

(2) The case of lack of correlations between adsorption energies on various centres. Then the function $\chi(\{\epsilon\})$ in Eq. (11) becomes a product of one-dimensional distribution functions.

So far, mainly extreme physical situations have been taken into account. The reason for that was of a mathematical nature. Only for such extreme situations it was possible to reduce the integral equation set 11 to the set of integral equations with single integrals.

The physical situation of very high correlations between the adsorption energies of various surface complexes was considered by Van Riemsdijk and co-workers (1986, 1987). They assumed that no matter which is the adsorption site, the difference between the adsorption energies ϵ_i and ϵ_j is still the same and equal to Δ_{ij}. So, the one-dimensional distributions of the number of adsorption sites among ϵ_i, $\chi_i(\epsilon_i)$ are the same. Of course, the sequence of the most probable adsorption energies ϵ_i^0 can change from one to another oxide. Assuming also that $\chi_i(\epsilon_i)$ is the gaussian-like

function 2, one obtains the adsorption isotherm equations for different surface complexes (Rudziński et al., 1992):

$$\theta_{jt} = \frac{K_j^0 f_j}{\sum_j K_j^0 f_j} \frac{\left[\sum_j K_j^0 f_j\right]^{kT/c}}{1 + \left[\sum_j K_j^0 f_j\right]^{kT/c}},$$
$$j = 0, +, A, C \quad (12)$$

where

$$K_j^0 = K_j \exp\left\{\frac{\epsilon_i^0 - \epsilon_i}{kT}\right\} \quad (13)$$

and where c is the heterogeneity parameter.

Now we are going to establish the correlations between the intrinsic equilibrium constants in a similar way as in the case of the triple layer model (homogeneous surface model), considered in the previous section. The condition for CIP to exist leads now to the following interrelations (Rudziński et al., 1992):

$$K_{a2}^{int} = \frac{H^2}{K_{a1}^{int}} \cdot \left(\frac{H}{K_{a2}^{int}} + \frac{H^2}{K_{a1}^{int} \cdot K_{a2}^{int}}\right)^{kT/c-1}$$

and

$${}_*K_A^{int} = \frac{H^2}{{}_*K_C^{int}} \quad (14)$$

The another extreme model of surface heterogeneity, when Δ_{ij}'s are not correlated at all, has already been elaborated by Rudziński and co-workers (Rudziński et al., 1985; Rudziński, 1988), for the case of adsorption of liquid mixtures of non-electrolytes on heterogeneous solid surfaces. There are no relations between the one-dimensional adsorption energy distributions $\chi_i(\epsilon_i)$ given by Eq. (2). Appropriate considerations (Rudziński et al., 1992) lead now to the following adsorption isotherm equations for different surface complexes:

$$\theta_{it} = \frac{\left[K_i^0 f_i\right]^{kT/c_i}}{1 + \sum_i \left[K_i^0 f_i\right]^{kT/c_i}}, \quad i = 0, +, A, C \quad (15)$$

where

$$K_i^0 = K_i \exp\left\{\frac{\epsilon_i^0 - \epsilon_i}{kT}\right\} \quad (16)$$

and where c_i's are the heterogeneity parameters for different surface complexes, $i = 0, +, A, C$.

Condition for CIP to exist, leads now to the following interrelations (Rudziński et al., 1992):

$$\left(\frac{H^2}{K_{a1}^{int}K_{a2}^{int}}\right)^{kT/c_+} + \left(\frac{\frac{kT}{c_C}}{\frac{kT}{c_A}} - 1\right)\left(\frac{{}^*K_C^{int}a}{K_{a2}^{int}}\right)^{kT/c_C} - 1 = 0 \tag{17a}$$

$$\frac{kT}{c_A}\left(\frac{H^2 a}{K_{a2}^{int*}K_A^{int}}\right)^{kT/c_A} - \frac{kT}{c_C}\left(\frac{{}^*K_C^{int}a}{K_{a2}^{int}}\right)^{kT/c_C} = 0 \tag{17b}$$

For the purpose of a theoretical analysis we took the experimental data from the Ph.D. Thesis by Thomas (1987), which were also published in part (Thomas et al., 1989). A successful theory should, for a certain set of parameters, fit simultaneously experimental titration curves, electrokinetic curves, and the individual adsorption isotherms of cation and anion measured radiometrically.

Titration curves are practically insensitive to the heterogeneity effects (Rudziński et al., 1992). Some authors argue that they are practically insensitive to the accepted physical models (Johnson, 1984; Sposito, 1980, 1983). Titration curves probably involve a certain mutual cancellation of heterogeneity effects.

On the contrary, the ζ-potential curve and the radiometrically measured individual adsorption isotherms of cation and anion appear to be sensitive to the surface energetic heterogeneity of oxides. The model of surface heterogeneity assuming lack of correlations between different surface complexes leads to good fit of the experimental data. Neglecting the surface heterogeneity leads to a serious underestimation of the concentration of SO^-C^+ complexes at low pH values and of $SOH_2^+A^-$ complexes at high pH values.

While taking into account effects of surface heterogeneity, Van Riemsdijk et al. (1986) applied a somewhat simplified model, in which the surface charge, δ_0 is predominantly affected by the following surface reaction:

$$SOH^{1/2-} + H^+ \longleftrightarrow SOH_2^{1/2+} \tag{18}$$
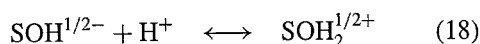
Three isotherm equations were considered to represent the formation of the complex $SOH_2^{1/2+}$: (1) Langmuir-Freundlich isotherm, (2) Sips isotherm and (3) Toth isotherm. The authors demonstrated next that the agreement between the theory and experiment obtained with this simplified model is similar to that obtained with triple layer model. However, the above conclusion was reached by considering titration

isotherms which are known for that they are not much sensitive to the model of adsorption.

For the situation when adsorbent is a mixture of oxides, Gibb and Koopal (1990) proposed a patchwise model wich discrete adsorption energy distribution.

Adsorption of Bivalent Cations at Low Concentrations

The adsorption of M^{2+} metal ions at water/oxide interfaces at low ion concentration is a subject of a continuously growing interest. There are three problems of a great practical importance which stimulate that growing interest: (1) the adsorption in soil of highly poisoning cations of some heavy elements like Cd^{2+} or Pb^{2+}; (2) the adsorption in soil of radioactive ions in the areas where nuclear plants are located; (3) 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 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 (Kurdi and Doner, 1982).

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 (Benjamin and Leckie, 1981; Elarshidi and O'Connor, 1982).

If a strongly adsorbing bivalent metal ion M^{2+} is added to the system described by Eqs. 3 and 4, in which competitive adsorption of protons and ions of basic electrolyte occurs, then according to the triple layer model (Davis et al., 1978; Davis and Leckie, 1978, 1980) its addition can cause the formation of two kinds of surface complexes: inner-sphere complexes SOM^+ formed at the 0-plain of the triple layer and outer-sphere complexes SO^-M^{2+} formed at the β-plain. Some recent studies by Hayes and Leckie (1986, 1987), Chisholm-Brause (1989a, 1989b) suggest that the formation of the inner-sphere complexes is more probable for divalent cations like Cu^{+2}, Pb^{+2}, Cd^{+2}, etc., than the formation of outer-sphere surface complexes. So, in general (Hayes and Leckie, 1986, 1987):

$$SOH + M^{2+} \xleftrightarrow{K_M^{int}} SOM^+ + H^+ \tag{19}$$
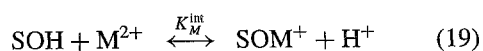
Individual adsorption isotherms of ions θ_i are defined through a set of Eqs. (5)-like but it is now a set of five equations ($i = 0, +, A, C, M$), where besides the constants K_i's and functions f_i's given by Eqs. (6) and (7), there is a new constant K_M and a function f_M defined as follows:

$$K_M = \frac{K_M^{int}}{K_{a2}^{int}} \quad \text{and} \quad f_M = a_M \exp\left\{-\frac{2e\psi_0}{kT}\right\} \quad (20)$$

The above consideration can be extended for the model of heterogeneous surface by taking into account two extreme cases of random surface topography: one with high correlations between adsorption energies and another one assuming lack of correlations between adsorption energies of different surface complexes formed on different adsorption sites. To simplify mathematical calculations it will be assumed that $\Delta\epsilon$ is the interval $(-\infty, +\infty)$. Assuming such integration limits leads to an isotherm equation which does not reduce to Henry's equation for very low coverages. However, this equation works well for higher surface coverages.

In the studies on monolayer adsorption of gases Rudziński and Everett (1991) showed that a correction for physically reasonable limited domain $\Delta\epsilon$, 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 region.

Assuming the finite integration limits for the two different models of random surface we obtained (Rudziński et al., 1993) two different sets of equations for θ_{it}, corresponding to two different correlation models. These sets were used to calculate the surface coverage by bivalent metal ions which are found at a small ion concentration. The surface coverages for other ions have higher values, therefore Eqs. (12) and (15) obtained assuming infinite integration limits can be used.

After numerous calculations it proved unattainable. The model assuming high correlations between energies of ion adsorption did not reflect existence of two different linear areas in the coordinate system log-log and predicts existence of Henry's region up to high coverages (Rudziński et al., 1993). The results of calculations based on the model assuming lack of correlation between energies of various complexes predict 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

(Rudziński et al., 1993). Such behaviour has never been observed in the experiment. However, the different behaviour of the log-log plots suggest, that the degree of the correlations between the adsorption energies of ions may affect strongly the behaviour of these adsorption systems at low ion concentrations. This seems to create hope that the studies of the adsorption at low ion concentrations may provide the answer to the fundamental question, which correlation model is to be accepted.

Therefore we have decided that the equation describing a real adsorption isotherm θ_{jt} of the heavy metal ions will be represented by an analytical formula. Such possibility is offered by the assumption that $\chi_j(\epsilon_j)$ is the rectangular energy distribution

$$\chi_j(\epsilon_j) = \begin{cases} \frac{1}{\epsilon_j^m - \epsilon_j^l} & \text{dla } \epsilon_j \in \langle \epsilon_j^l, \epsilon_j^m \rangle \\ 0 & \text{elsewhere} \end{cases} \quad (21)$$

The rectangular distribution is a good approximation in the case of strongly heterogeneous surfaces (Rudziński and Everett, 1991). And this is just the case of the bivalent metal ion adsorption (Freundlich's plots with $\frac{kT}{c_j} \ll 0.9$).

Taking such distribution into account, the assumption of the high correlations between the adsorption energies of different surface complexes is responsible for this non-physical behaviour. 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 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 (Rudziński et al., 1993). The adsorption isotherm equation obtained using the rectangular distribution function for the random model without correlation takes the form (Rudziński et al., 1993).

$$\theta_{jt} = \frac{1 + \left(K_j^0 f_j\right)^{kT/c_j}}{1 + \sum_j \left(K_j^0 f_j\right)^{kT/c_j}}$$

$$\times \frac{kT}{\epsilon_j^m - \epsilon_j^l} \ln \frac{1 + \exp\left\{\frac{\epsilon_j^m - \epsilon_{jc}}{kT}\right\}}{1 + \exp\left\{\frac{\epsilon_j^l - \epsilon_{jc}}{kT}\right\}}, \quad j = M \quad (22)$$

The others θ_{jt}, $(j = 0, +, A, C)$ are calculated from Eq. (15) as their coverages reach higher values.

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