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Feature Article

Theoretical Description of Calorimetric Effects of Proton Adsorption on Metal Oxides from Electrolyte Solutions Based on 1-pK and 2-pK Surface Protonation Models

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A rigorous thermodynamic description of ion adsorption on metal (hydr)oxide/electrolyte solution interface, including calorimetric effects, is given. Temperature dependence of potentiometric titration curves for suspensions, the heat (enthalpy) of proton adsorption, and the influence of surface potential on calculated quantities are analyzed. The calculations were based on the 1-pK Basic Stern Model (BSM) and the 2-pK Triple Layer Model (TLM) of the oxide/electrolyte interface. Comparison of the results obtained by means of these two models with experimental data is presented.

INTRODUCTION

Good understanding of processes occurring at the metal (hydr)oxide/electrolyte interface is of great importance for explanation of phenomena such as mineral dissolution, migration of contaminants in soils, stability of colloid suspensions, *etc*. A complete physicochemical description of the interface requires the analysis of calorimetric effects accompanying the process of the electric charge formation on mineral surfaces and ion adsorption. Analysis of calorimetric data provides much more information about the course of these phenomena than the values of free energy alone.

The most commonly used experimental technique in investigations of oxide/electrolyte interface is potentiometric titration, which makes it possible to determine the surface charge as a function of pH. The heat of ion adsorption can be measured in appropriate calorimetric experiments, or deduced from the temperature dependence of adsorption data.

Berube and de Bruyn[1] were the first to start research on the heats accompanying proton adsorption, which was based on recording PZC changes (Point of Zero Charge) with temperature. Such investigations were conducted later by other researchers.[2–11] The influence of temperature on the surface charge isotherm was also studied.[12–17] For example, in their pioneering papers, Machesky, Wesolowski, and Palmer[16,17] presented the results obtained for rutile and magnetite under hydrothermal conditions up to 300 °C.

The first direct calorimetric experiments were reported by Griffiths and Fuerstenau[18] and by Foissy,[19] who measured the heat of immersion of a degassed solid oxide sample into solutions of changing pH.

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The last experimental technique, titration calorimetry, was developed by De Kaizer *et al.*,[20] Machesky *et al.*,[21–23] Mehr *et al.*,[24] and by Casey.[25] Here, the measurement procedure is as follows: after introducing the solid sample into a solution, the pH of the solution is measured. Next, the titration step is carried out, and the evolved heat as well as the equilibrium pH are recorded. Kallay *et al.*[26–28] have recently designed an experiment of this kind, aimed at determining the conditions under which the obtained experimental data could be free of the electrostatic contribution to the measured heat of ion adsorption. According to Kallay,[26] the electrostatic contributions to the enthalpy will cancel if the difference between the initial pH of the suspension and the point of zero charge equals the difference between final pH and pH_{pzc}.

Valuable information about calorimetric measurements for the (hydr)oxide/electrolyte system has been collected in the short review by Machesky.[29]

At the beginning, however, development of this experimental technique was not accompanied by a suitable progress in the theoretical interpretation of the experimental results. This was caused by the fact that the measured heats of adsorption are due to a number of simultaneously occurring surface reactions. It was only in the 1990s that Rudziński and co-workers proposed a rigorous thermodynamic description of enthalpic effects accompanying ion adsorption at the metal oxide/electrolyte interface.[30–41]

Charge formation on oxide surfaces is commonly described in terms of the site-dissociation model. There are many versions of this model; all of them are a combination of a double-layer model and a model describing the adsorption of protons by means of one or several surface reactions.[42,43] The most popular double-layer models are the Triple Layer Model (TLM)[44] and the Basic Stern Model (BSM).[45] The charging mechanism of the metal (hydr)oxide surface is described by the 2-pK,[44,46] 1-pK[47] or MUSIC approach.[48,49]

In this paper, we present the results of theoretical calculations based on the 1-pK BSM and 2-pK TLM, which include analyses of potentiometric titration curves, the heat of proton adsorption, and the influence of temperature on the surface charge isotherm. The 1-pK BSM is the simplest model, which can describe correctly different experimental data and the 2-pK TLM is the most popular model. The presented results are based on our earlier papers.[50–53] Since the models are similar, we only give a short theoretical description of 1-pK BSM.

THEORY

Essentials of the 1-pK Basic Stern Model

According to the 1-pK Basic Stern Model,[43,47] protons, along with the anions and cations of the basic electrolyte, form the following surface complexes: $SOH_2^{\frac{1}{2}+}$, $SOH_2^{\frac{1}{2}+}A^-$ and $SOH^{\frac{1}{2}-}C^+$ (Figure 1):

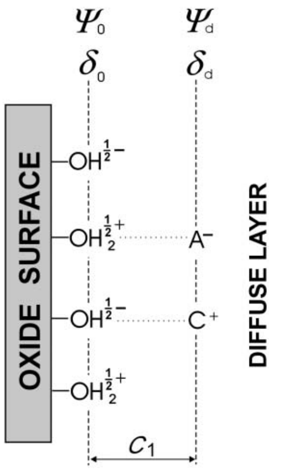

Figure 1. Diagrammatic presentation of the 1-pK model with two charged planes (Basic Stern Model). ψ_0, δ_0 – surface potential and surface charge density in the 0-plane; ψ_d, δ_d – diffuse layer potential and charge; c_1 – electric capacitance of the rigid layer.

$$SOH^{\frac{1}{2}-} + H^+ \xleftrightarrow{1/{}^1K_H^{int}} SOH_2^{\frac{1}{2}+},$$

$$\text{where} \quad {}^1K_H^{int} = \frac{[SOH^{\frac{1}{2}-}](a_H)}{[SOH_2^{\frac{1}{2}+}]} \cdot \exp\left\{-\frac{e\psi_0}{kT}\right\} \tag{1a}$$

$$SOH^{\frac{1}{2}-} + C^+ \xleftrightarrow{{}^1K_C^{int}} SOH^{\frac{1}{2}-}C^+,$$

$$\text{where} \quad {}^1K_C^{int} = \frac{[SOH^{\frac{1}{2}-}C^+]}{[SOH^{\frac{1}{2}-}](a_C)} \cdot \exp\left\{\frac{e\psi_d}{kT}\right\} \tag{1b}$$

$$SOH_2^{\frac{1}{2}+} + A^- \xleftrightarrow{{}^1K_A^{int}} SOH_2^{\frac{1}{2}+}A^-,$$

$$\text{where} \quad {}^1K_A^{int} = \frac{[SOH_2^{\frac{1}{2}+}A^-]}{[SOH_2^{\frac{1}{2}+}](a_A)} \cdot \exp\left\{-\frac{e\psi_d}{kT}\right\}. \tag{1c}$$

The above reactions, leading to the formation of these surface complexes onto the free surface sites $SOH^{\frac{1}{2}-}$, have the following equilibrium constants: $K_+^1 = 1 / {}^1K_H^{int}$, $K_C^1 = {}^1K_C^{int}$ and $K_A^1 = {}^1K_A^{int} / {}^1K_H^{int}$ for the adsorption of protons, cations and anions, respectively. The last equilibrium constant corresponds to the combination of reactions, (1a) and (1c), leading to the following reaction:

$$SOH^{\frac{1}{2}-} + H^+ + A^- \xleftrightarrow{K_A^1} SOH_2^{\frac{1}{2}+}A^-,$$

$$K_A^1 = \frac{[SOH_2^{\frac{1}{2}+}A^-]}{[SOH^{\frac{1}{2}-}](a_H)(a_A)} \cdot \exp\left\{\frac{e(\psi_0 - \psi_d)}{kT}\right\}. \tag{1d}$$

In Eqs. (1a–1d), ψ_0 is the surface potential and ψ_d is the mean potential at the onset of the diffuse layer. Further, a_H, a_C and a_A are the bulk activities of protons, anions and cations, respectively.

As can be deduced from Figure 1, the following relations between the charges and the potentials within the compact and the diffuse layer hold:

$$\psi_0 - \psi_\mathrm{d} = \frac{\delta_0}{c_1} \tag{2a}$$

$$\psi_\mathrm{d} = \frac{2kT}{|z|e} \ln\left[\frac{-\delta_\mathrm{d}}{\sqrt{8\varepsilon_0\varepsilon_\mathrm{r}kTI}} + \sqrt{\frac{\delta_\mathrm{d}^2}{\sqrt{8\varepsilon_0\varepsilon_\mathrm{r}kTI}} + 1}\right] \tag{2b}$$

where ε_r, is the relative permittivity of the solvent, ε_0 is the permittivity of the free space, and I is the ionic strength of the solution (ions m^{-3}). Eq (2b) follows the Gouy-Chapman theory of the diffuse layer.

The above relations can be combined to yield the following equation:

$$\psi_0 = \frac{\delta_0}{c_1} + \frac{2kT}{|z|e} \ln\left[\frac{-\delta_\mathrm{d}}{\sqrt{8\varepsilon_0\varepsilon_\mathrm{r}kTI}} + \sqrt{\frac{\delta_\mathrm{d}^2}{\sqrt{8\varepsilon_0\varepsilon_\mathrm{r}kTI}} + 1}\right]. \tag{3}$$

We may rewrite the equation system (1a–1d) into the following Langmuir-like form:

$$\theta_i = \frac{K_i^1 f_i}{1 + \sum_i K_i^1 f_i}, \quad i = +,\ \mathrm{A},\ \mathrm{C} \tag{4}$$

where θ_i is the surface coverage (i = +, A, C) and f_i refers to the following functions,

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

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

$$f_\mathrm{A} = a_\mathrm{A} \exp\left\{-\frac{e\delta_0}{kTc_1} - 2.3\mathrm{pH}\right\}. \tag{5c}$$

We can express the surface charge δ_0 as follows,

$$\delta_0 = \frac{1}{2}B(\theta_+ + \theta_\mathrm{A} - \theta_- - \theta_\mathrm{C}) \quad \text{where} \quad B = e \cdot N_s \tag{6}$$

where N_s is the total number of surface sites.

As it has been shown in recently published papers,[43,53] the surface potential ψ_0 in the 1-pK model can be expressed as a function of δ_0 (we assume that $H = a_\mathrm{H}$ and $a = a_\mathrm{C} = a_\mathrm{A}$):

$$\psi_0 = -\frac{kT}{e} \ln\left(\frac{\frac{1}{2}B(aHK_A^1X - 1) - \delta_0(1 + aHK_A^1X)}{HK_+^1\left[\delta_0\left(1 + \frac{aK_\mathrm{C}^1}{HK_+^1X}\right) - \frac{1}{2}B\left(1 - \frac{aK_\mathrm{C}^1}{HK_+^1X}\right)\right]}\right)$$

where $$X = \exp\left(-\frac{e\delta_0}{kTc_1}\right). \tag{7}$$

Theoretical Description of the Temperature Dependence of Surface Charge Curves and Titration Calorimetry Data

In the 1-pK charging model, the heats accompanying reaction (1a, 1b, 1d) are given by the following expressions:[50]

$$Q_+^1 = Q_\mathrm{aH}^1 - e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},\mathrm{pH}} \tag{8a}$$

$$Q_\mathrm{C}^1 = Q_\mathrm{aC}^1 - e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},\mathrm{pH}} + $$
$$e\frac{\delta_0}{c_1} + \frac{e\delta_0T}{(c_1)^2}\left(\frac{\partial c_1}{\partial T}\right)_{\{\theta_i\},\mathrm{pH}} + k\left(\frac{\partial \ln a_\mathrm{C}}{\partial(1/T)}\right)_\mathrm{pH} \tag{8b}$$

$$Q_\mathrm{A}^1 = Q_\mathrm{aA}^1 - e\frac{\delta_0}{c_1} - \frac{e\delta_0T}{(c_1)^2}\left(\frac{\partial c_1}{\partial T}\right)_{\{\theta_i\},\mathrm{pH}} + $$
$$k\left(\frac{\partial \ln a_\mathrm{A}}{\partial(1/T)}\right)_\mathrm{pH} \tag{8c}$$

where Q_aH^1, Q_aC^1, and Q_aA^1 denote the non-configurational heats of reactions (1a, 1b, 1d):

$$Q_\mathrm{aH}^1 = -k\frac{\mathrm{d}\ln({}^1K_\mathrm{H}^\mathrm{int})}{\mathrm{d}(1/T)} = 2.3\,k\frac{\mathrm{dpH_{pzc}}}{\mathrm{d}(1/T)} \tag{9a}$$

$$Q_\mathrm{aC}^1 = -k\frac{\mathrm{d}\ln(1/{}^1K_\mathrm{C}^\mathrm{int})}{\mathrm{d}(1/T)} \tag{9b}$$

$$Q_\mathrm{aA}^1 = -k\frac{\mathrm{d}\ln({}^1K_\mathrm{H}^\mathrm{int}/{}^1K_\mathrm{A}^\mathrm{int})}{\mathrm{d}(1/T)}. \tag{9c}$$

As we can see, configurational heats Q_+^1, Q_C^1 and Q_A^1 depend on the surface potential and its derivative over temperature. This temperature derivative of the potential may be calculated[50] from relation (7).

Frequent asymmetry of the surface charge curves relative to pH$_\mathrm{pzc}$ forced us to assume that the innermost capacitance c_1 can have different values on both sides of

$\mathrm{pH_{pzc}}$. Thus, while calculating the derivative $\left(\frac{\partial c_1}{\partial T}\right)_{\{\theta_i\},\mathrm{pH}}$, it was assumed that there were two different values of the c_1 parameter: one for the acid region ($\mathrm{pH} < \mathrm{pH_{pzc}}$) and the other for the basic region ($\mathrm{pH} > \mathrm{pH_{pzc}}$). The simplest way to take account of the temperature dependence of c_1 is treating it as the linear function of temperature:

$$c_1 = c_1^{\mathrm{L}} = c_1^{\mathrm{L},0} + \alpha_1^{\mathrm{L}} \cdot \Delta T \quad \mathrm{pH} < \mathrm{pH_{pzc}} \tag{10a}$$

$$c_1 = c_1^{\mathrm{R}} = c_1^{\mathrm{R},0} + \alpha_1^{\mathrm{R}} \cdot \Delta T \quad \mathrm{pH} > \mathrm{pH_{pzc}}\,. \tag{10b}$$

The above equations may be considered as the formal Taylor expansion for c_1 around $T = T_0$, so that $c_1^{\mathrm{L}}(T_0) = c_1^{\mathrm{L},0}$ and $c_1^{\mathrm{R}}(T_0) = c_1^{\mathrm{R},0}$. The coefficients α_1^{L} and α_1^{R} play an important role in fitting the experimental values of ion adsorption heats.

In order to calculate the surface charge at different temperatures, we have to know the values of $\mathrm{pH_{pzc}}$ and the equilibrium constants of reactions (1a, 1b, 1d) at these temperatures. When these values are given at one temperature, the following equations can be used to calculate $\mathrm{pH_{pzc}}$ and equilibrium constants at another temperature:

$$\mathrm{pH_{pzc}}\,(T_2) = \mathrm{pH_{pzc}}\,(T_1) + \frac{Q_{\mathrm{aH}}^{1}}{2.3kT}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{11a}$$

$$\mathrm{p}^1K_{\mathrm{H}}^{\mathrm{int}}\,(T_2) = \mathrm{p}^1K_{\mathrm{H}}^{\mathrm{int}}\,(T_1) + \frac{Q_{\mathrm{aH}}^{1}}{2.3kT}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{11b}$$

$$\mathrm{p}^1K_{\mathrm{C}}^{\mathrm{int}}\,(T_2) = \mathrm{p}^1K_{\mathrm{C}}^{\mathrm{int}}\,(T_1) + \frac{Q_{\mathrm{aC}}^{1}}{2.3kT}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{11c}$$

$$\mathrm{p}^1K_{\mathrm{A}}^{\mathrm{int}}\,(T_2) = \mathrm{p}^1K_{\mathrm{A}}^{\mathrm{int}}\,(T_1) + \frac{Q_{\mathrm{aA}}^{1} - Q_{\mathrm{aH}}^{1}}{2.3kT}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]. \tag{11d}$$

The other way of determining the temperature dependence of the surface charge is:[52]

$$\delta_0\,(T_2, \mathrm{pH}) = \delta_0\,(T_1, \mathrm{pH}) + \int_{T_1}^{T_2}\left(\frac{\partial \delta_0}{\partial T}\right)_{\mathrm{pH}} \mathrm{d}T\,. \tag{12}$$

The derivative $\left(\frac{\partial \delta_0}{\partial T}\right)_{\mathrm{pH}}$ can be calculated by applying the following equation:[52]

$$\left(\frac{\partial \delta_0}{\partial T}\right)_{\mathrm{pH}} = -\frac{1}{T^2}\left(\frac{\partial \delta_0}{\partial (1/T)}\right)_{\mathrm{pH}} = \frac{1}{T^2}\,\frac{\left(\frac{\partial G}{\partial (1/T)}\right)_{\delta_0,\mathrm{pH}}}{\left(\frac{\partial G}{\partial \delta_0}\right)_{T,\mathrm{pH}}} \tag{13}$$

where

$$G = \psi_0 - \frac{\delta_0}{c_1} + \frac{2kT}{|z|e}\ln\left[\frac{-\delta_{\mathrm{d}}}{\sqrt{8\varepsilon_0\varepsilon_{\mathrm{r}}kTI}} + \sqrt{\frac{\delta_{\mathrm{d}}^2}{8\varepsilon_0\varepsilon_{\mathrm{r}}kTI} + 1}\,\right] = 0\,. \tag{14}$$

As explained in the Introduction, the experimental calorimetric data most suitable for the theoretical analysis are those obtained from titration calorimetry. In this experiment, the heat of the proton adsorption was measured. As follows from Eqs. (1a, 1b, 1d) the molar heat of proton adsorption is a composite quantity that can be expressed by the following equation:

$$Q_{\mathrm{pr}} = \frac{\displaystyle\int_{\mathrm{pH}}^{\mathrm{pH}+\Delta\mathrm{pH}} \sum_i Q_i^1 \left(\frac{\partial \theta_i}{\partial \mathrm{pH}}\right)_T \mathrm{dpH}}{\displaystyle\int_{\mathrm{pH}}^{\mathrm{pH}+\Delta\mathrm{pH}} \left[\left(\frac{\partial \theta_+}{\partial \mathrm{pH}}\right)_T + \left(\frac{\partial \theta_{\mathrm{A}}}{\partial \mathrm{pH}}\right)_T\right] \mathrm{dpH}}$$

$$i = +,\ \mathrm{C},\ \mathrm{A} \tag{15}$$

where heats Q_i's are given by Eqs. (8a–8c), and the derivatives $\left(\frac{\partial \theta_i}{\partial \mathrm{pH}}\right)_T$ can be calculated numerically applying Eq. (4).

How Can the Number of Parameters Be Reduced?

In the most investigated systems, charge curves intersect in one point, called CIP (Common Intersection Point), which corresponds to PZC. This makes it possible to establish the relations between the intrinsic equilibrium constants ${}^1K_{\mathrm{H}}^{\mathrm{int}}$, ${}^1K_{\mathrm{C}}^{\mathrm{int}}$ and ${}^1K_{\mathrm{A}}^{\mathrm{int}}$ under the condition that the experimentally observed $\mathrm{pH_{pzc}}$ is practically independent of the salt concentration. From the system of equations:

$$\delta_0(\mathrm{pH_{pzc}}) = 0 \quad \text{and} \quad \frac{\partial \delta_0\,(\mathrm{pH_{pzc}})}{\partial a} = 0 \tag{16}$$

the following relations are obtained:

$$H = {}^1K_{\mathrm{H}}^{\mathrm{int}} \quad \text{and} \quad \frac{{}^1K_{\mathrm{C}}^{\mathrm{int}}}{{}^1K_{\mathrm{A}}^{\mathrm{int}}} = 1\,. \tag{17}$$

Thus, for the 1-pK model, Eqs. (17) reduce the number of unknown equilibrium constants determined from fitting suitable experimental data, from three to one.

It follows from Eqs. (17) and (9) that

$$Q_{\mathrm{aA}}^1 = Q_{\mathrm{aH}}^1 + Q_{\mathrm{aC}}^1 \tag{18}$$

This means that the heat of binding indifferent electrolyte ions according to reactions (1b, 1d) is the same for cations and anions of different electrolytes if only CIP occurs. The simplest explanation of this fact is to assume that the enthalpies of binding C^+ to $SOH^{\frac{1}{2}-}$ group and A^- to $SOH_2^{\frac{1}{2}+}$ equal zero because the inert electrolyte ions interact with the oxide surface in the electrostatic way. Moreover, the last relation makes it possible to eliminate one of the three parameters Q^1_{aH} ,Q^1_{aC} ,Q^1_{aA} from further calculations.

RESULTS AND DISCUSSION

We would like to present some results on the enthalpic effects of ion adsorption obtained by means of the 1-pK Basic Stern Model and 2-pK Triple Layer Model. Theoretical analysis will concern experimental data obtained from potentiometric titrations at different temperatures and ionic strengths,[12] and from titration calorimetry.[22–25]

First, we analyze the influence of temperature on surface charge curves δ_0(pH). The data reported by Blesa *et al.*[12] were used to test and compare the 1-pK BSM and 2-pK TLM. These data are the potentiometric titration curves for magnetite at three concentrations of the inert electrolyte (KNO_3), 0.001, 0.01 and 0.1 mol dm^{-3}, and at three temperatures, 30, 50 and 80 °C. It was found that the 1-pK BSM produces results of the same quality as the more complicated 2-pK TLM (*i.e.*, demanding more parameters) in describing the experimental values reported by Blesa *et al.*

Calculations were started from the lowest temperature (30 °C) in order to fit three charging curves at three concentrations. Applying Eqs. (11) or Eq. (12), we could fit the curves measured at two higher temperatures (50 °C and 80 °C). Figure 2 depicts the potentiometric titration data and theoretical curves for the 0.01 mol dm^{-3} electrolyte concentration.

Although it was assumed that the equilibrium constants ${}^1K^{\mathrm{int}}_{\mathrm{C}}$ and ${}^1K^{\mathrm{int}}_{\mathrm{A}}$ did not depend on temperature, an increase of cation and a decrease of anion adsorption with temperature was observed. It was attributed to the temperature dependence of the double layer capacitance, because the parameters c_1 and ${}^1K^{\mathrm{int}}_{\mathrm{C(A)}}$ were highly correlated. We found that not all double layer parameters could be treated independently if some simplifying assumptions had not been made (*e.g.*, the heat of adsorption of inert electrolyte ions was equal to zero).

Having at our disposal the equilibrium constants of reactions and their enthalpies, we can calculate entropy changes applying the basic thermodynamic formula,

$$T\Delta S^1_{\mathrm{aH}} = \Delta H^1_{\mathrm{aH}} - \Delta G^1_{\mathrm{aH}} = \Delta H^1_{\mathrm{aH}} - 2.303RT\cdot \mathrm{p}^1K^{\mathrm{int}}_{\mathrm{aH}} \quad (19)$$

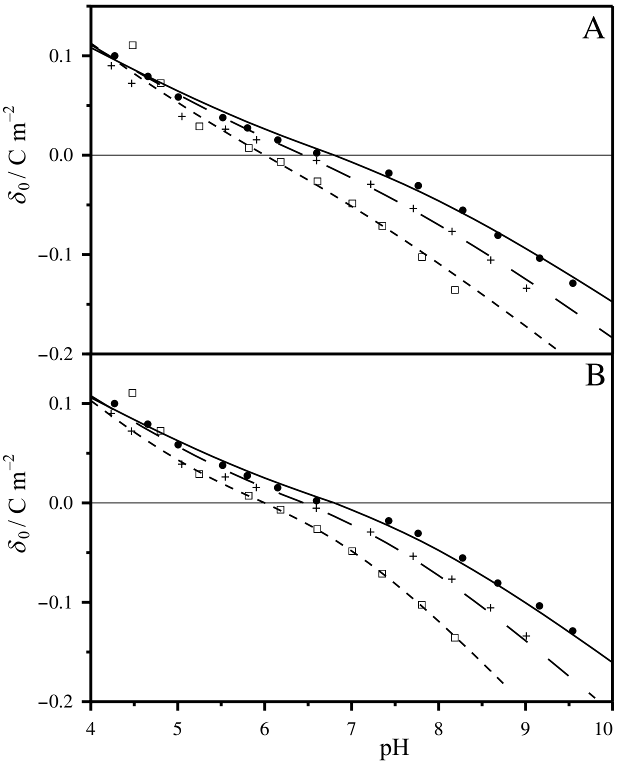

Figure 2. Comparison[52] of the theoretical potentiometric titration curves (lines) calculated using 2-pK TLM [A] and 1-pK BSM [B] with the experimental data (points) obtained by Blesa *et al.*[12] for the system magnetite/KNO_3 solution at a concentration of 0.01 mol dm^{-3} and at three temperatures: 30 °C (———, ●), 50 °C (— — —, +), and 80 °C (- - - - -, □).

In this equation $\Delta H^1_{\mathrm{aH}} = -Q^1_{\mathrm{aH}}$ and $\mathrm{p}^1K^{\mathrm{int}}_{\mathrm{aH}} = \mathrm{pH_{pzc}}$.

It was found that the heat of proton Q^1_{aH} adsorption equaled 32.8 kJ mol^{-1}, the entropy change during the process (at a temperature of 25 °C) $T\Delta S^1_{\mathrm{aH}}$= 6.5 kJ mol^{-1}, and the entropy change corresponding to the electrolyte ions adsorption amounted to 2.3 kJ mol^{-1} (enthalpy equaled zero). Thus, enthalpy is the driving force for proton adsorption and the small entropic effect for electrolyte adsorption.

Now we consider the heat of proton adsorption Q_{pr}(pH) measured by means of titration calorimetry and surface charge isotherms δ_0(pH). Experimental results for three oxides (Al_2O_3, TiO_2, SiO_2) in NaCl solution were analyzed[50] by means of 1-pK BSM and 2-pK TLM. We applied the following procedure: in the first step, the surface charge isotherm was calculated roughly. During calculations, the surface reaction equilibrium constants and electric capacitance of the double layer c_1 were found. In the next step, the calorimetric data were fitted. The parameter values obtained in the first step were precisely adjusted and the values of additional parameters, such as heats of the surface reaction (Q^1_{aH}, Q^1_{aC}, Q^1_{aA}) and temperature coefficients of electric capacitance (α^{L}_1, α^{R}_1), were found at this stage.

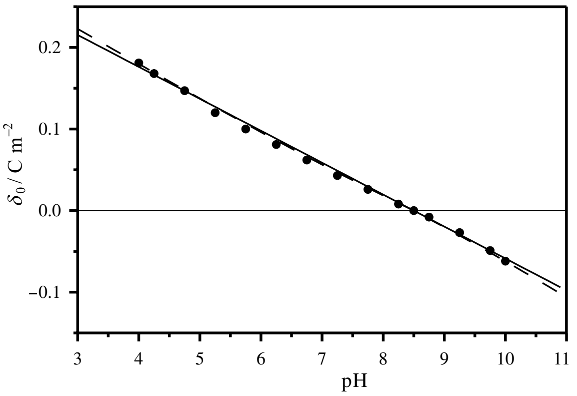

Figure 3. Comparison[50] of the experimental potentiometric titration data (●) for the Al_2O_3/NaCl solution system measured by Machesky and Jacobs,[22] with the theoretical δ_0(pH) curves calculated by means of 1-pK BSM (———) and 2-pK TLM (— — —).

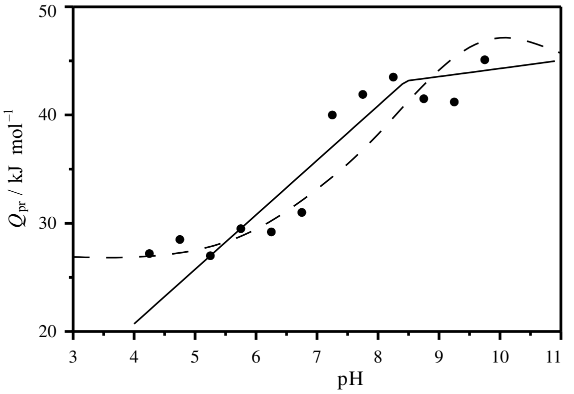

Figure 4. Comparison[50] of the experimental Q_{pr} data (●) for the Al_2O_3/NaCl solution system,[22] with the theoretical Q_{pr}(pH) functions calculated by means of 1-pK BSM (———) and 2-pK TLM.

Figures 3 and 4 display how the 1-pK and 2-pK models fit the potentiometric titration and titration calorimetry data for the Al_2O_3 / NaCl solution system. These two models provide different theoretical Q_{pr}(pH) curves. The 2-pK approach is more flexible than the 1-pK one. It is easy to model the shape of the Q_{pr}(pH) curve in the former model and it is difficult to obtain the desired shape in the latter.

Table I presents the values of free energy, enthalpy, and entropy of proton adsorption determined by applying 1-pK BSM. Since pH_{pzc} is the measure of surface acidity, the higher the pH_{pzc}, the more negative are the protonation enthalpies. The enthalpy is connected with the chemical bond formation energy while net solvation changes are responsible for entropy in aqueous solutions.[30] The small and almost constant value of entropy suggests that the processes occurring in the solution have a second order significance for proton adsorption onto the investigated metal (hydr)oxides and silica. These results clearly suggest that enthalpy is the driving force of proton adsorption.

TABLE I. Values of the free energy ΔG^1_{aH}, enthalpy ΔH^1_{aH} and entropy $T\Delta S^1_{aH}$ of proton adsorption determined by applying[50] 1-pK BSM

System	ΔG^1_{aH} / kJ mol^{-1}	ΔH^1_{aH} / kJ mol^{-1}	$T\Delta S^1_{aH}$ / kJ mol^{-1}
Al_2O_3 / NaCl	–48.5	–46.0	2.5
TiO_2 / NaCl	–36.5	–33.0	3.5
SiO_2 / NaCl	–20.0	–17.0	3.0

Sverjensky and Sahai have recently proposed a new method of theoretical prediction of single-site enthalpies of surface protonation for oxides and silicates in water, based on the combination of the crystal chemical and Born solvation theories.[54] For the same system, the values of heats obtained by us and those obtained by Sverjesnky and Sahai are generally in good agreement.[50]

As can be seen, the 2-pK model is more flexible than the 1-pK one, but both approaches give comparable results. In the 1-pK model, two main parameters can be found directly from experiment. The proton dissociation constant $p^1K^{int}_{aH}$ equals pH_{pzc} and heat Q^1_{aH} can be determined from the temperature dependence of pH_{pzc}, as it follows from Eq. (9a). The 2-pK model has two parameters more than 1-pK (two protonation constants and two proton adsorption heats), so its parameters cannot be unambiguously found.

As it follows from Eqs. (8), the heats of ion adsorption depend on the surface potential ψ_0 and its temperature derivative. There are several procedures[53] of calculating ψ_0. Hence, the question arises how the surface potential and its temperature derivative can influence the calculated ion adsorption enthalpies.

Different procedures of surface potential calculation give very similar values of ψ_0. Greater discrepancies are observed in the case of the temperature derivative of ψ_0. The molar heats of proton adsorption Q_{pr} are calculated by means of the same set of parameters, but various surface potentials have different values (especially when the Nernst equation is used).[53]

Figure 5 presents the Q_{pr} values calculated by means of 1-pK BSM applying Eq. (15). Despite the use of the

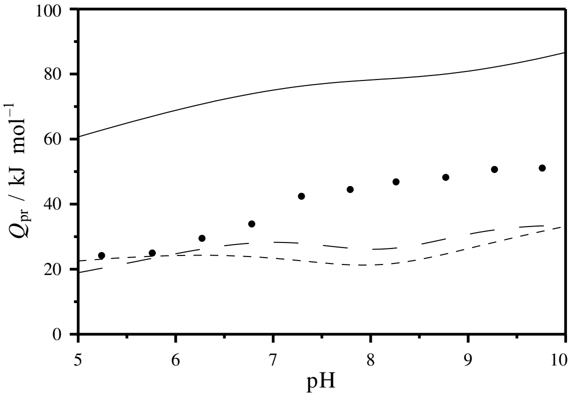

Figure 5. The molar heat of proton adsorption Q_{pr}(pH) calculated[53] by means of 1-pK BSM and assuming exact potential given by Eq. (7) (– – – –), simplified potential neglecting electrolyte ions adsorption (— — —), and the Nernst potential (———). Experimental points for the Al_2O_3/NaCl solution system.[22]

same set of parameters, the differences between the heats calculated by applying various surface potential equations are very clear. Especially the Nernst equation gives too high values of Q_{pr}. Use of the Nernst equation in 1-pK BSM causes the configurational heat Q_{+}^{1} (see Eq (8a)) to be constant and equal to zero in the whole pH range.[53] This means that the heat of proton attachment to the surface, Q_{aH}^{1}, is compensated by electrostatic work connected with this process.

The results presented in our recent article[53] suggest a significant influence of the assumed surface potential upon the other calculated quantities (especially the electrokinetic potential ζ). The best results are obtained when ψ_0 and its temperature derivative are calculated applying the exact equation (7), which is an integral part of the 1-pK approach.

It follows from the above considerations that surface complexation models can successfully describe calorimetric effects accompanying ion adsorption on metal oxides. However, the results obtained strongly depend on simplifications applied during calculations, *e.g.*, proton adsorption enthalpy is very sensitive to small changes in the surface potential.

REFERENCES

1. Y. G. Berube and P. L. De Bruyn, *J. Colloid Interface Sci.* **27** (1968) 305–318.
2. P. H. Tewari and A. W. McLean, *J. Colloid Interface Sci.* **40** (1972) 267–272.
3. P. H. Tewari and A. B. Campbell, *J. Colloid Interface Sci.* **55** (1976) 531–539.
4. L. G. J. Fokkink, A. de Keizer, and J. Lyklema, *J. Colloid Interface Sci.* **127** (1989) 116–131.
5. L. G. J. Fokkink, *Ph. D. Thesis,* Agricultural University, Wageningen, 1987.
6. S. Subramanian, J. A. Schwarz, and Z. Hejase, *J. Catal.* **117** (1989) 512–518.
7. J. F. Kuo and T. F. Yen, *J. Colloid Interface Sci.* **121** (1989) 220–225.
8. K. Ch. Akratopulu, L. Vordonis, and A. Lycourghiotis, *J. Chem. Soc., Faraday Trans. 1* **82** (1986) 3697–3708.
9. K. Ch. Akratopulu, C. Kordulis, and A. Lycourghiotis, *J. Chem. Soc., Faraday Trans.* **86** (1990) 3437–3440.
10. M. A. Blesa, A. J. G. Maroto, and A. E. Regazzoni, *J. Colloid Interface Sci.* **140** (1990) 287–290.
11. M. Kosmulski, J. Matysiak, and J. Szczypa, *J. Colloid Interface Sci.* **164** (1994) 280–284.
12. M. A. Blesa, N. M. Figliolia, A. J. G. Maroto, and A. E. Regazzoni, *J. Colloid Interface Sci.* **101** (1984) 410–418.
13. A. E. Regazzoni, *Ph. D. Thesis,* Universidad National de Tucuman, Argentina, 1984.
14. P. V. Brady, *Geochim. Cosmochim. Acta* **56** (1992) 2941–2946.
15. M. Kosmulski, *Colloids Surf. A* **83** (1994) 237–243.
16. M. L. Machesky, D. J. Wesolowski, D. A. Palmer, and K. Ichiro-Hayashi, *J. Colloid Interface Sci.* **200** (1998) 298–309.
17. D. J. Wesolowski, M. L. Machesky, D. A. Palmer, and L. M. Anovitz, *Chem. Geol.* **167** (2000) 193–229.
18. D. A. Griffiths and D. W. Fuerstenau, *J. Colloid Interface Sci.* **80** (1981) 271–283.
19. A. Foissy, *Ph. D. Thesis,* Universite de Franche-Comte, Bescancon, 1985.
20. A. de Keizer, L. G. J. Fokkink, and J. Lyklema. *Colloids Surf.* **49** (1990) 149–163.
21. M. L. Machesky and M. A. Anderson, *Langmuir* **2** (1986) 582–587.
22. M. L. Machesky and P. F. Jacobs, *Colloids Surf.* **53** (1991) 297–314.
23. M. L. Machesky and P. F. Jacobs, *Colloids Surf.* **53** (1991) 315–328.
24. S. R. Mehr, D. J. Eatough, L. D. Hansen, E. A. Lewis, and J. A. Davis, *Thermochim. Acta* **154** (1989) 129–143.
25. W. H. Casey, *J. Colloid Interface Sci.* **163** (1994) 407–419.
26. N. Kallay, S. Žalac, and G. Štefanić, *Langmuir* **9** (1993) 3457–3460.
27. N. Kallay and S. Žalac, *Croat. Chem. Acta* **67** (1994) 467–479.
28. S. Žalac and N. Kallay, *Croat. Chem. Acta* **69** (1996) 119–124.
29. M. L. Machesky, *Chemical Modelling in Aqueous Systems II*; D. C. Melchior, R. L. Bassett (Eds.), Amer. Chem. Soc. Sym. Ser. Vol 416, Washington D. C., 1990.
30. W. Rudzinski, R. Charmas, and S. Partyka, *Langmuir* **7** (1991) 354–362.
31. W. Rudzinski, R. Charmas, S. Partyka, and A. Foissy, *New J. Chem.* **15** (1991) 327–335.
32. W. Rudzinski, R. Charmas, S. Partyka, F. Thomas, and J. Y. Bottero, *Langmuir* **8** (1992) 1154–1164.
33. W. Rudzinski, R. Charmas, J. M. Cases, M. Francois, F. Villieras, and L. J. Michot, *Langmuir* **13** (1997) 483–495.
34. W. Rudzinski, R. Charmas, W. Piasecki, J. M. Cases, M. Francois, F. Villieras, and L. Michot, *Colloids and Surf. A* **137** (1998) 57–68.
35. W. Rudzinski, R. Charmas, W. Piasecki, N. Kallay, J. M. Cases, M. Francois, F. Villieras, and L. Michot, *Adsorption* **4** (1998) 287–297.
36. R. Charmas, *Langmuir* **14** (1998) 6179–6191.
37. W. Rudzinski, R. Charmas, W. Piasecki, F. Thomas, F. Villieras, B. Prelot, and J. M. Cases, *Langmuir* **14** (1998) 5210–5225.
38. W. Rudzinski, R. Charmas, W. Piasecki, B. Prelot, F. Thomas, F. Villieras, and J. M. Cases, *Langmuir* **15** (1999) 5977–5983.
39. W. Rudzinski, G. Panas, R. Charmas, W. Piasecki, N. Kallay, and T. Preočanin, *J. Phys. Chem. B* **104** (2000) 11912–11922.
40. W. Rudzinski, G. Panas, R. Charmas, W. Piasecki, N. Kallay, and T. Preočanin, *J. Phys. Chem. B* **104** (2000) 11923–11935.
41. W. Rudzinski, W. Piasecki, R. Charmas, and G. Panas, *Adv. Colloid Interface Sci.* **95** (2002) 95–143.
42. J. Westall and H. Hohl, *Adv. Colloid Interface Sci.* **12** (1980) 265–294.
43. W. Piasecki, W. Rudzinski, and R. Charmas, *J. Phys. Chem. B* **105** (2001) 9755–9771.
44. J. A. Davis, R. O. James, and J. O. Leckie, *J. Colloid Interface Sci.* **63** (1978) 480–499.
45. P. Venama, T. Hiemstra, and W. H. van Riemsdijk, *J. Colloid Interface Sci.* **181** (1996) 45–59.
46. D. E. Yates, S. Levine, and T. W. Healy, *J. Chem. Soc., Faraday Trans. 1* **70** (1974) 1807–1818.

47. G. H. Bolt and W. H. van Riemsdijk, *Physico-chemical Models,* in: G. H. Bolt, (Ed.), *Soil Chemistry B*, 2nd ed., Elsevier, Amsterdam, 1982.
48. T. Hiemstra, W. H. van Riemsdijk, and G. H. Bolt, *J. Colloids Interface Sci.* **133** (1989) 91–104.
49. T. Hiemstra, J. C. M. de Wit, and W. H. van Riemsdijk, *J. Colloids Interface Sci.* **133** (1989) 105–117.
50. W. Piasecki, *Langmuir* **18** (2002) 4808–4818.
51. W. Piasecki, *Langmuir* **18** (2002) 8079–8084.
52. W. Piasecki, *J. Colloids Interface Sci.* **254** (2002) 56–63.
53. W. Piasecki, *Phys. Chem. Chem. Phys.* **5** (2003) 713–719.
54. D. A. Sverjensky and N. Sahai, *Geochim. Cosmochim. Acta* **62** (1998) 3703–3716.

SAŽETAK

Adsorpcija protona iz elektrolitnih otopina na kovinske okside. Teorijska interpretacija kalorimetrijskih efekata temeljena na 1-pK i 2-pK modelu protoniranja površine

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Dana je stroga termodinamička interpretacija adsorpcije iona na međupovršinu kovinski (hidro)oksid/elektrolitna otopina, koja uključuje i kalorimetrijske efekte. Analizirana je temperaturna ovisnost potenciometrijskih titracijskih krivulja suspenzija, topline (entalpije) adsorpcije protona i utjecaj površinskoga potencijala na računane vrijednosti. U računima za međupovršinu oksid/elektrolit primijenjeni su 1-pK temeljni Sternov model (Basic Stern Model) i 2-pK model trosloja (Triple Layer Model). Rezultati dobiveni pomoću ova dva modela uspoređeni su s eksperimentalnim podacima.