Determination of Electrostatic Contribution to the Enthalpy of Charging at a Metal Oxide/Electrolyte Interface

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Interpretation of calorimetric measurements concerning the charging of metal oxide/aquous electrolyte interface was developed. The interpretation is based on the surface complexation model and involves both the 1-pK and 2-pK concepts. The resulting relationships enable determination of standard reaction enthalpies of each assumed surface reaction, and also evaluation of the dependency of surface potential on pH.

INTRODUCTION

The basic process at the metal oxide aqueous interface is charging due to the interaction of the surface with H^+ and OH^- ions. According to the surface complexation model, the charging can be interpreted mainly by two approaches, *i.e.* by the 1-pK and 2-pK concepts.[1,2] Present experimental data do not allow us to distinguish between these two different models; the experimental results agree with both theoretical concepts. In addition to the adsorption results, there are several reports on the enthalpy of surface charging. As to the enthalpy, two experimental approaches are in use: calorimetric measurements[3–5] and measurement of the temperature dependency of the point of zero charge (pH$_{pzc}$).[6–8]
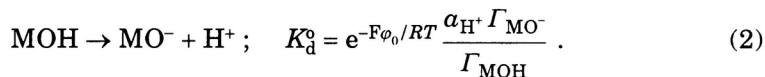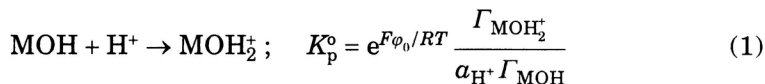
The values obtained from calorimetric measurements were usually interpreted as enthalpies with respect to the surface charge.[3,4] The problems related to the calorimetric determination of enthalpy are twofold. First, the measured heat is a sum of contributions of several reactions taking place in the calorimeter; *e.g.* in the case of the 2-pK mechanism: protonation and

deprotonation, association of counterions with charged surface groups. Another problem is related to the electrostatic contribution to the enthalpy. It was previously shown[9-11] that calorimetric experiments performed so that pH_{pzc} is the mean value of the initial and final pH (»symmetric« experiment) yield standard values of reaction enthalpies. In this cases, the electrostatic contribution is canceled. If the 2-pK model is applied, extents of protonation and deprotonation reactions are equal in magnitude but opposite in sign, so that one obtains the difference in standard enthalpies of the deprotonation and protonation reactions ($\Delta_d H^\circ - \Delta_p H^\circ = \Delta_{ch} H^\circ$). By this method it was not possible to deduce separate values for protonation and deprotonation reactions. The same shortcoming applies to the temperature dependency of p.z.c. However, interpretation on the basis of the 1-pK model is simpler and results in standard enthalpy of the corresponding reaction.

This report deals with the interpretation of calorimetric experiments outside the pH_{pzc} region, where electrostatic contribution dominates and evaluation of the extents of surface reactions is more complicated. The electrostatic contribution was related to the surface potential and the results were compared with the Nernst equation. The proposed method of interpretation enables, in the case of the 2-pK model, evaluation of separate values for $\Delta_d H^\circ$ and $\Delta_p H^\circ$.

2-pK model

One approach to the surface reactions at aqueous metal oxide interface is to consider hydrated surface sites (MOH) as amphoteric groups involved in protonation (p) and deprotonation (d) reactions.[1] This model is sometimes called »2-pK model«. The following equilibria were assumed:

$$MOH + H^+ \rightarrow MOH_2^+ ; \quad K_p^o = e^{F\varphi_0/RT} \frac{\Gamma_{MOH_2^+}}{a_{H^+}\Gamma_{MOH}} \qquad (1)$$

$$MOH \rightarrow MO^- + H^+ ; \quad K_d^o = e^{-F\varphi_0/RT} \frac{a_{H^+}\Gamma_{MO^-}}{\Gamma_{MOH}} . \qquad (2)$$
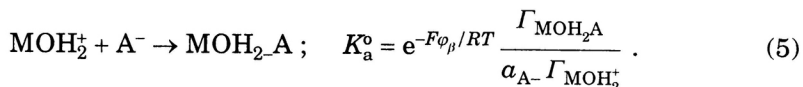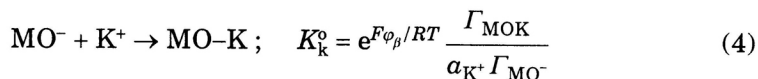
Symbol M denotes the metal atom at the solid surface and Γ_i is the surface concentration of component i (amount of surface groups divided by the surface area).

Calorimetric determination of the enthalpies of deprotonation and protonation reactions involves addition of an acid or a base to the metal oxide suspension at a certain pH. In such a case, neutralization (n) also takes place

$$OH^- + H^+ \rightarrow H_2O ; \quad K_n^o = 1/K_w^o = (a_{H^+} \, a_{OH^-})^{-1} \tag{3}$$
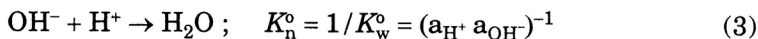
with the equilibrium constant, K_n^o, related to the »ionic product« of water, K_w^o.

Surface charge is simultaneously reduced by association of counterions (cations K^+ and anions A^-) from the solution (reactions k and a)

$$MO^- + K^+ \rightarrow MO{-}K ; \quad K_k^o = e^{F\varphi_\beta/RT} \frac{\Gamma_{MOK}}{a_{K^+} \Gamma_{MO^-}} \tag{4}$$

$$MOH_2^+ + A^- \rightarrow MOH_2{-}A ; \quad K_a^o = e^{-F\varphi_\beta/RT} \frac{\Gamma_{MOH_2A}}{a_{A^-} \Gamma_{MOH_2^+}} . \tag{5}$$

The meassured heat Q is a sum of all reactions taking place in the reaction system, *i.e.* of the products of the particular reaction enthalpies, $\Delta_r H$, and the corresponding changes in extents of reactions, $\Delta \xi_r$. The contribution of the counterion association may be neglected if the experiment is performed at a low ionic strength and/or in the vicinity of pH_{pzc} so that

$$Q = \Delta \xi_p \Delta_p H + \Delta \xi_d \Delta_d H + \Delta \xi_n \Delta_n H . \tag{6}$$

The enthalpy of a particular surface reaction, $\Delta_r H$, can be separated into »chemical« (standard), $\Delta_r H^\circ$, and »electrostatic« terms

$$\Delta_r H = \Delta_r H^\circ + z_r F \varphi_0 \tag{7}$$

where z_r is the change in the charge number of the surface group due to reaction. The surface potential, φ_0, may be approximated by the Nernstian equation[12]

$$\varphi_0 = \frac{RT \ln 10}{F} (pH_{pzc} - pH) \, \alpha \tag{8}$$

where α represents the deviation from ideal slope ($\alpha \leq 1$). The electrostatic contributions to the enthalpies of protonation and deprotonation reactions are equal in magnitude but opposite in sign ($\Delta_p H_{el} = -\Delta_d H_{el}$) since the initial and final electrostatic surface potential are the same for all surface species, but the change in the charge number is opposite in sign and the same in magnitude ($z_p = -z_d$). Since $\Delta_{ch} H^\circ$ is defined as[9]

$$\Delta_{ch} H^\circ = \Delta_d H^\circ - \Delta_p H^\circ \tag{9}$$

$$Q = \Delta\xi_p(\Delta_pH^\circ + \Delta_pH_{el}) + \Delta\xi_d(\Delta_{ch}H^\circ + \Delta_pH^\circ - \Delta_pH_{el}) + \Delta\xi_n\Delta_nH \ . \qquad (10)$$

Equation (10) could be used for interpretation of calorimetric experiments outside the p.z.c. region. The $\Delta_{ch}H^\circ$ value could be determined separately by a »symmetric« experiment[9] or by measuring the temperature dependency of pH_{pzc}.[6-9] The next problem is related to the calculation of the extent of a particular surface reaction. According to Eqs. (1) and (2), the ratio of the extents of surface reactions p and d is given by

$$\frac{\Delta\xi_p}{\Delta\xi_d} = -\frac{K_p^\circ}{K_d^\circ}\frac{a_1(H^+)\,a_2(H^+)}{e^{F(\varphi_{0.1} + \varphi_{0.2})/RT}} \qquad (11)$$

where subscripts 1 and 2 denote the initial and final states of the calorimetry experiment, respectively. At pH_{pzc}, one can take $\Gamma_{MOH_2^+} = \Gamma_{MO^-}$ and $\varphi_0 = 0$, so that

$$pH_{pzc} = 0.5 \log \frac{K_p^\circ}{K_d^\circ} \ . \qquad (12)$$

Combination of the above equation with eqs. (11) and (8) yields

$$D = \frac{\Delta\xi_p}{\Delta\xi_d} = -10^{(1-\alpha)(2pH_{pzc} - pH_2 - pH_1)} = -10^{2(1-\alpha)(pH_{pzc} - pH)} \qquad (13)$$

where pH is the mean value between the initial and final pH; $pH = (pH_1 + pH_2)/2$.

In the case when acid is added to an acidic, or base to a basic suspension, the extent of neutralization can be neglected and the measured heat is given by

$$Q = (\Delta_pH^\circ + \Delta_pH_{el})\Delta\xi_p + (\Delta_{ch}H^\circ + \Delta_pH^\circ - \Delta_pH_{el})\frac{\Delta\xi_p}{D} \ . \qquad (14)$$

The following equation is obtained by rearranging the above expression

$$Q = \left\{\frac{\Delta_{ch}H^\circ}{D} + \left(1 + \frac{1}{D}\right)\Delta_pH^\circ + \left(1 + \frac{1}{D}\right)(pH_{pzc} - pH)\alpha RT\ln 10\right\}\Delta\xi_p \ . \qquad (15)$$

The analysis presented enables reaching two interesting targets. The first one is evaluation of the singular value of standard reaction enthalpies of protonation and deprotonation reactions (Eqs. (1) and (2)) and the other is determination of coefficient α.
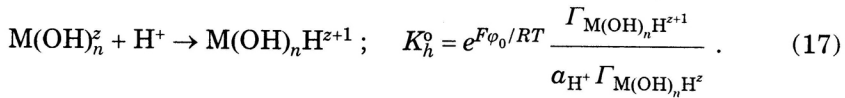
Total changes in the amounts of the H^+ and OH^- ions ($\Delta n(H^+)$, $\Delta n(OH^-)$) are due to the addition of acid or base; they depend on the extents of all reactions in the calorimeter. In the case when acid is added to an acidic suspension, the extent of protonation reaction, $\Delta\xi_p$, can be calculated as

$$\Delta\xi_p = \frac{\Delta n(HNO_3) - \Delta n(H^+)}{1 - \dfrac{1}{D}} = \frac{\Delta n(HNO_3) - c^o\left(\dfrac{V_2\,10^{-pH_2}}{y_2} - \dfrac{V_1\,10^{-pH_1}}{y_1}\right)}{1 - \dfrac{1}{D}} \quad (16)$$

where $\Delta n(HNO_3)$ is the amount of added acid, $\Delta n(H^+)$ is the difference in the equilibrium amount of H^+ ions, V is the volume of liquid medium and y the activity coefficient given by the Debye-Huckel equation.

1-pK model

Another approach is based on the »1-pK« concept.[2,11] The stoichiometry of reaction corresponding to the »1-pK« concept depends on the type of oxide but, in all cases, it is the binding of one H^+ ion to the active surface site (reaction h)

$$M(OH)_n^z + H^+ \to M(OH)_n H^{z+1} ; \quad K_h^0 = e^{F\varphi_0/RT}\,\frac{\Gamma_{M(OH)_n H^{z+1}}}{a_{H^+}\,\Gamma_{M(OH)_n H^z}} . \quad (17)$$

From equations (7) and (8), and introducing $z = 1$, the following relationship for the enthalpy of reaction h was obtained

$$\Delta_h H = \Delta_h H^\circ + \alpha RT(pH_{pzc} - pH)\ln 10 . \quad (18)$$

Consequently,

$$\frac{d\varphi}{d(pH)} = \frac{d(\Delta_h H)}{d(pH)}\,\frac{1}{F} . \quad (19)$$

The extent of reaction (18) can be calculated as

$$\Delta\xi_h = \Delta n(HNO_3) - \Delta n(H^+) = \Delta n(HNO_3) - c^o\left(\frac{v_2\,10^{-pH_2}}{y_2} - \frac{v_1\,10^{-pH_1}}{y_1}\right) . \quad (20)$$

When 1-pK concept is used, one could determine the value of α from the slope in the presentation $\Delta_h H$ vs. pH (see Eqs. (18) and (19)).

The above analysis enables interpretation of calorimetric data on the charging of the metal oxide aqueous interface. The experiment should be performed so that a small subsequent portion of strong acid is added to a slightly acidic solution. In order to deal with a stable dispersed system, the initial pH should be about 2 pH units below p.z.c. The basic region above p.z.c. should be examined in an analogous way by adding base to a basic suspension. Interpretation may be performed by both the 1-pK and 2-pK concepts.

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SAŽETAK

Određivanje elektrostatskog doprinosa entalpiji nabijanja međupovršine kovinski oksid/elektrolit

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Razvijena je metoda za interpretaciju kalorimetrijskih mjerenja povezanih s električnim nabijanjem međupovršine kovinski oksid/vodena otopina elektrolita. Interpretacija se temelji na modelu površinskog kompleksiranja i uzima u obzir koncepcije »1-pK« i »2-pK«. Dobiveni izrazi omogućuju određivanje standardne reakcijske entalpije za svaku pretpostavljenu površinsku reakciju, a moguće je odrediti i ovisnost površinskog potencijala o pH.