

Interfacial Acid–Base Reactions of Aluminum Oxide Dispersed in Aqueous Electrolyte Solutions. 2. Calorimetric Study on Ionization of Surface Sites

Etelka Tombácz,^{*,†} Márta Szekeres,[†] and Erwin Klumpp[‡]

Department of Colloid Chemistry, University of Szeged, Aradi Vt. 1, H-6720 Szeged, Hungary, and Department of Applied Physical Chemistry, Research Center Jülich, D-52425 Jülich, Germany

Received September 15, 2000. In Final Form: December 18, 2000

Calorimetric acid–base titration of purified aluminum oxide C (Degussa) was performed under delicate experimental conditions. The initial state of titration was fixed at the reference state of aqueous suspensions of the oxide (25 °C, pH of suspension at point of zero charge, indifferent electrolyte). Suspensions containing 0.01, 0.1, or 1 M KNO₃ were titrated with HNO₃ and KOH solutions, within the dissolution free pH range. The measured data were corrected by the heats of mixing and neutralization. The amount of charged surface species formed in the H⁺ and OH⁻ association reactions (S–OH + H⁺ ⇌ S–OH₂⁺, log *K*₁^{int} = 6.8; S–OH + OH⁻ ⇌ S–O⁻ + H₂O, log *K*₂^{int} = 9.2) was calculated assuming constant capacitance model, and the corrected heats were related to their amounts. The surface protonation (S–OH + H⁺ ⇌ S–OH₂⁺) reaction is exothermic, while the deprotonation (S–OH ⇌ S–O⁻ + H⁺) is endothermic. With increasing ionic strength, the partial molar enthalpy of surface protonation process (ΔH_{pr}) decreases in absolute value from -34 to -28 kJ/mol, and that of deprotonation (ΔH_{depr}) increases from 34 to 41 kJ/mol. Their difference ($\Delta H_{\text{depr}} - \Delta H_{\text{pr}}$) is a constant value (69.2 ± 1.2 kJ/2 mol of H⁺) and independent of the ionic strength. Thus, the standard enthalpy for a single surface protolysis reaction (SOH₂^{1/2+} ⇌ SOH^{1/2-} + H⁺) on alumina is $\Delta H_{\text{ch}}^{\circ} = 34.6 \pm 0.6$ kJ/mol. A thermodynamic treatment of Hall¹² for electrostatic enthalpy contribution resulted in a square root ionic strength dependence of enthalpy changes. This theoretically expected linear relationship proved to be valid for our data. The linear extrapolation of partial molar enthalpy (ΔH_{pr} and ΔH_{depr}) vs (*c*_{el})^{1/2} functions to zero ionic strength gives the electrostatic free, standard reaction enthalpy of surface ionization processes, $\Delta H_{\text{pr}}^{\circ} = -34.0$ kJ/mol for protonation and $\Delta H_{\text{depr}}^{\circ} = 34.6$ kJ/mol for deprotonation reactions, in a very good agreement with the calculated standard enthalpy $\Delta H_{\text{ch}}^{\circ}$ of the protolysis reaction.

Introduction

Titration calorimetry is a useful technique for characterization of processes taking place both in homogeneous systems and at interfaces. Heat changes accompanying chemical reactions and interfacial processes, i.e., reaction heats and adsorption or displacement enthalpies can be measured. Interfacial reactions in aqueous oxide suspensions, charge formation due to protonation and deprotonation of the amphoteric surface sites, and also the association of charged surface groups with counterions can be characterized by direct calorimetric measurements. Calorimetric techniques monitor the overall heat flow of simultaneous reactions taking place in the calorimeter cell. In addition to the relatively low accuracy of the suspension measurements, computing the enthalpy of separate reactions from the overall heat flow is not unambiguous. Thus, in the interpretation of measured data one meets the problem of distinguishing between the different contributions.¹ In simple cases, like surface charging due to the adsorption of potential determining ions, calorimetric experiments may be designed in an appropriate way and the measured data may be interpreted.¹ An additional problem is how to account for the incorporated electrostatic effect. The enthalpy of surface charging reaction (ΔH_{r}) can be separated into a “chemical”

(i.e., the standard $\Delta H_{\text{r}}^{\circ}$) and an electrostatic (ΔH_{elec}) contribution²

$$\Delta H_{\text{r}} = \Delta H_{\text{r}}^{\circ} + \Delta H_{\text{elec}} \quad (1)$$

The electrostatic contribution is given by a Gibbs–Helmholtz relationship³

$$\Delta H_{\text{elec}} = F\Delta zT(\partial\psi_0/\partial T)_p + F\Delta z\psi_0 \quad (2)$$

where *F* is the Faraday constant, Δz is the change in charge of the surface due to the adsorption reaction, *T* is the temperature, $(\partial\psi_0/\partial T)_p$ is the temperature coefficient of the surface potential (ψ_0) at constant pressure, and $F\Delta z\psi_0$ is the electrostatic contribution to the Gibbs energy (ΔG_{elec}). The electrostatic enthalpy contribution can be larger or smaller than the electrostatic free energy, depending on the sign of the coefficient $(\partial\psi_0/\partial T)_p$.

The surface protolysis enthalpy,³ i.e., the difference between the standard enthalpies of protonation (SOH + H⁺ ⇌ SOH₂⁺; $\Delta H_{\text{pr}}^{\circ}$) and deprotonation (SOH ⇌ SO⁻ + H⁺; $\Delta H_{\text{depr}}^{\circ}$) of surface groups,² can be determined from the temperature dependence of the point of zero charge (pzc) of amphoteric oxides. The plot pH_{pzc} vs 1/*T* is a linear function, and the standard enthalpy of surface protolysis process (SOH₂⁺ ⇌ SO⁻ + 2H⁺; $\Delta H^{\circ} = \Delta H_{\text{depr}}^{\circ} - \Delta H_{\text{pr}}^{\circ}$) calculated from the slope is 14.6 kJ/mol for TiO₂.¹

It has been proved^{1,2} that the electrostatic contribution to the enthalpy can be neglected in a smartly designed, so-called “symmetric” experiment, where the difference

[†] University of Szeged.

[‡] Research Center Jülich.

(1) Kallay, N.; Zalac, S.; Kobal I. In *Adsorption on New and Modified Inorganic Sorbents Studies in Surface Science and Catalysis*; Dabrowski, A., Tertykh, V. A., Eds.; Elsevier: Amsterdam, 1996; p 857.

(2) Kallay, N.; Zalac, S.; Stefanic, G. *Langmuir* **1993**, *9*, 3457.

(3) Machesky, M. L.; Anderson, M. A. *Langmuir* **1986**, *2*, 582.

in standard enthalpies ($\Delta H^{\circ} = \Delta H_{\text{depr}}^{\circ} - \Delta H_{\text{pr}}^{\circ}$) can be obtained from direct calorimetric measurements. The value, 14.7 kJ/mol, published for TiO_2 agrees well with that from temperature dependence of pH_{pzc} .

There are confusing experimental data and theoretical considerations in the literature. Some metal oxide–aqueous solution systems have been investigated^{3–7} by titration calorimetry; however, the different enthalpy values for interfacial processes scatter widely. Although it is unquestionable that the proton adsorption is an exothermic process and the proton desorption is endothermic, data are given⁶ for surface deprotonation due to the adsorption of hydroxyl ions with an exothermic heat effect. The situation is even worse in a series of papers presenting theoretical analysis of ion adsorption at oxide–electrolyte interfaces based on data from a variety of calorimetric techniques (immersion,⁸ temperature dependence,⁹ flow-adsorption,¹⁰ titration¹¹), since it is not determined whether the sign of the reaction heats is negative or positive, i.e., exothermic or endothermic processes are involved. An essential feature is that the enthalpies of surface charging processes should exhibit an ionic strength dependence; however, there are published results^{3,5,6} showing that the electrolyte concentration practically has no influence on the observed enthalpies. The theoretical analysis^{8–10} resulted in an unexpected asymmetry of reaction heats belonging to the bindings of counterions (e.g., $Q_{\text{ac}} = 0.0$ kJ/mol and $Q_{\text{aA}} = 70.0$ kJ/mol¹⁰ binding of cations on negatively and anions on positively charged surface sites, respectively).

A thermodynamic analysis for the ionization process on the surface of insoluble solids with fixed dissociable groups has been recently published.¹² This paper analyses the difficulties in the interpretation of data obtained from experiments of different kinds and gives derivation of rigorous expressions that link the temperature dependence of potentiometric titration curves to well-defined enthalpies of protonation, which are measurable calorimetrically. It is stated that the partial molar enthalpy of surface group protonation, ΔH_{p} , is physically well defined and accessible via calorimetry. The value of ΔH_{p} does not depend on the surface excess concentration of potential determining ions (Γ_{p}) at constant temperature (T), pressure (p), and bulk concentration of supporting electrolyte ions (m)

$$\left(\frac{\partial \Delta H_{\text{p}}}{\partial \Gamma_{\text{p}}}\right)_{T,p,m} = 0 \quad (3)$$

which is the consequence of temperature congruence. The temperature congruence is unlikely to occur when there is significant specific adsorption of supporting electrolyte ions, or if there are several types of dissociable groups, or when the interactions between neighboring groups are affected by protonation. Hence, the occurrence of temperature congruence implies that all of these effects are insignificant or cancel each other. Hall¹² deduced the following theoretical equation for the total enthalpy changes ($H - H_0$) accompanying the process of charging the surface at constant temperature (T)

$$H - H_0 = -T^2 \sum_i \int_{\Gamma_i=0}^{\Gamma_i} \left(\frac{\partial \left(\frac{\mu_i^{\sigma} - \mu_i^{\theta}}{T} \right)}{\partial T} \right)_{p,\Gamma_i} \times \\ d\Gamma_i - T^2 \int_0^q \left(\frac{\partial (\psi_{\text{d}}/T)}{\partial T} \right)_{p,n_i,q} dq \quad (4)$$

where H_0 is the enthalpy of the system when all Γ_i are zero (state of pzc), Γ_i is the surface excess concentration of i , μ_i^{θ} is the standard chemical potential of i , μ_i^{σ} is the chemical potential of i in adsorbed state, ψ_{d} is the electric potential relative to the bulk solution at the boundary between inner and diffuse regions of the double layer, q is the surface charge density ($q = \sum \nu_i F \Gamma_i$), ν_i is the valence of i , and F is the Faraday constant. The first term on the right-hand side is the contribution from the inner region of the double layer and the second term is that from the diffuse region. We note that eq 4 is the explicit form of eq 1 for ionization of surfaces with fixed dissociable groups. Applying the Poisson–Boltzmann equation for univalent ions, an equation for the enthalpy contribution from the diffuse region denoted by H_{diff} (second term on the right-hand side of eq 4), was deduced

$$\frac{H_{\text{diff}}}{T^2} = -\frac{R(2Rn)^{1/2}}{F(\pi\epsilon T)} \left[1 - \left(1 + \frac{\pi q^2}{2\epsilon nRT} \right)^{1/2} \right] \left(\frac{\partial \epsilon}{\partial T} \right)_{p,N_i} \quad (5)$$

where n is the total electrolyte concentration in moles per unit volume, R is the gas constant, and ϵ denotes the permittivity of water. Hall¹² stated that the heat changes derived from direct calorimetry can be attributed almost entirely to the inner region of the double layer where the chemical reactions actually occur. Any contribution to the total enthalpy change of surface charging ($H - H_0$) from the diffuse layer is insignificant.

The purpose of this study is to characterize calorimetrically the surface charging of alumina, with special attention to the effect of the concentration of indifferent electrolyte. The calorimetric measurements were planned and performed under delicate experimental conditions based on the model description of the preceding potentiometric experiments (part 1) and on the experience of sample pretreatment and dissolution. We show the results of calorimetric acid–base titration and interpret the probable reactions of surface charging. We attempt to characterize the dissociable surface groups of alumina in aqueous medium and to describe the influence of an electric double layer on the partial molar enthalpy of surface group protonation.

Experimental Section

Materials. The same aluminum oxide C (commercial products of Degussa AG) sample was investigated as in part 1 of this work. Only the alumina powder freshly purified by heat treatment at 1000 °C for 6 h was measured. Millipore water was used, and all chemicals were an analytical reagent grade product of Merck.

Procedures. *Titration Calorimetry.* An isothermal microcalorimeter (TAM 2277, thermal activity monitor, Thermometric) was used at 25 °C. One gram of alumina powder was dispersed in 10 mL of electrolyte solution and purged with argon to eliminate dissolved CO_2 impurity. The suspensions were titrated separately with 50- μL portions of either 0.05 M HNO_3 or 0.05 M KOH solution under a CO_2 -free argon atmosphere, i.e., 2.5 μmol of H^+ or OH^- was added in each titration step. The portions of titrants were added hourly; 10 portions of KOH (25 μmol OH^-) or 16 portions of HNO_3 (40 μmol H^+) were added altogether in each series to the suspensions containing 0.01, 0.1, or 1 M KNO_3 . In parallel, blank titrations were performed in the absence of the alumina at the same concentrations of indifferent electrolyte KNO_3 . The heat flow across the titration cell of TAM was continuously

(4) Machesky, M. L.; Jacobs, P. F. *Colloid Surf.* **1991**, *53*, 297.

(5) Machesky, M. L.; Jacobs, P. F. *Colloid Surf.* **1991**, *53*, 315.

(6) De Keizer, A.; Fokkink, L. G. J. *Colloid Surf.* **1990**, *49*, 149.

(7) Casey, W. H. *J. Colloid Interface Sci.* **1994**, *163*, 407.

(8) Rudzinski, W.; Charmas, R.; Partyka, S. *Langmuir* **1991**, *7*, 354.

(9) Rudzinski, W.; Charmas, R.; Cases, J. M.; Francois, M.; Villieras, Michot, L. *J. Langmuir* **1997**, *13*, 483.

(10) Rudzinski, W.; Charmas, R.; Piasecki, W.; Groszek, A. *J. Langmuir* **1999**, *15*, 5921.

(11) Rudzinski, W.; Charmas, R.; Piasecki, W.; Thomas, F.; Villieras, F.; Cases, J. M. *Langmuir* **1998**, *14*, 5210.

(12) Hall, D. G. *Langmuir* **1997**, *13*, 91.

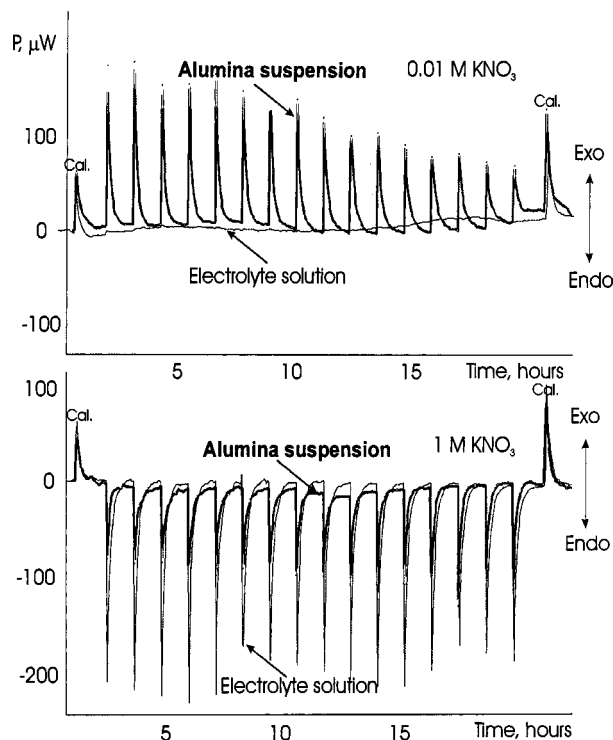


Figure 1. Calorimeter signals recorded during titrations of 10 mL suspensions containing 1 g of aluminum oxide and of blank electrolyte solutions with 50 μ L portions of 0.05 M HNO₃ at low (0.01 M, top) and high (1 M, bottom) ionic strengths.

recorded during 20–22 h as shown in Figure 1. The pH values of suspensions before and after the titration were measured. The initial pH values were between 8.05 and 8.1 and the final pH values were 3.88, 4.13, and 4.36 after addition of the 40 μ mol of HNO₃ and 10.85, 10.66, and 10.55 after addition of 25 μ mol of KOH in 0.01, 0.1, and 1 M electrolyte solutions, respectively. The heat of reactions was calculated from the area of the calorimetric peak using calibration peaks determined before and after the titrations. The accuracy of the measured reaction heats was tested by measuring the standard heat of reaction between THAM ((HO-CH₂)₃-C-NH₂) and HCl ($\Delta H = -55 \pm 1$ kJ/mol).

The measured heat (Q_{meas}) is the overall heat flow of simultaneous chemical reactions and mixing processes in the calorimeter cell

$$Q_{\text{meas}} = Q_{\text{ri}} + Q_{\text{mix}} = \sum_i \Delta H_{r,i} \Delta \xi_i + Q_{\text{mix}} \quad (6)$$

where $\Delta H_{r,i}$ is the enthalpy change of reaction i , $\Delta \xi_i$ is the change of the extent of reaction i , and Q_{mix} is the mixing heat of titrant portion. In the case of acid–base titration the following reactions can be distinguished: reactions with added acid (ΔH_a), reactions with added base (ΔH_b), and water formation (neutralization) reaction (ΔH_n). We separated the reactions with acid and base experimentally by separately performed titrations. Mixing heat was determined in blank experiments. Uncontrolled acid–base reactions with significant heat effects are expected, however, in the presence of any acid- or base-consuming impurities. Therefore special attention had been paid to the cleaning of the alumina sample. In addition, it is of crucial importance to establish a correct initial state in calorimetric titration of aqueous oxide suspensions, to exclude any undefined acid/base reactions on the surface or in the bulk solution. We chose the initial state of suspensions at the point of zero charge (pzc) which has been introduced as a reference state of aqueous metal oxide suspensions long ago. This state can be easily achieved experimentally in the suspensions of carefully purified oxide in the presence of indifferent electrolyte.

Results and Discussion

The heat flow was measured during the titrations of alumina suspensions and of blank electrolyte solutions

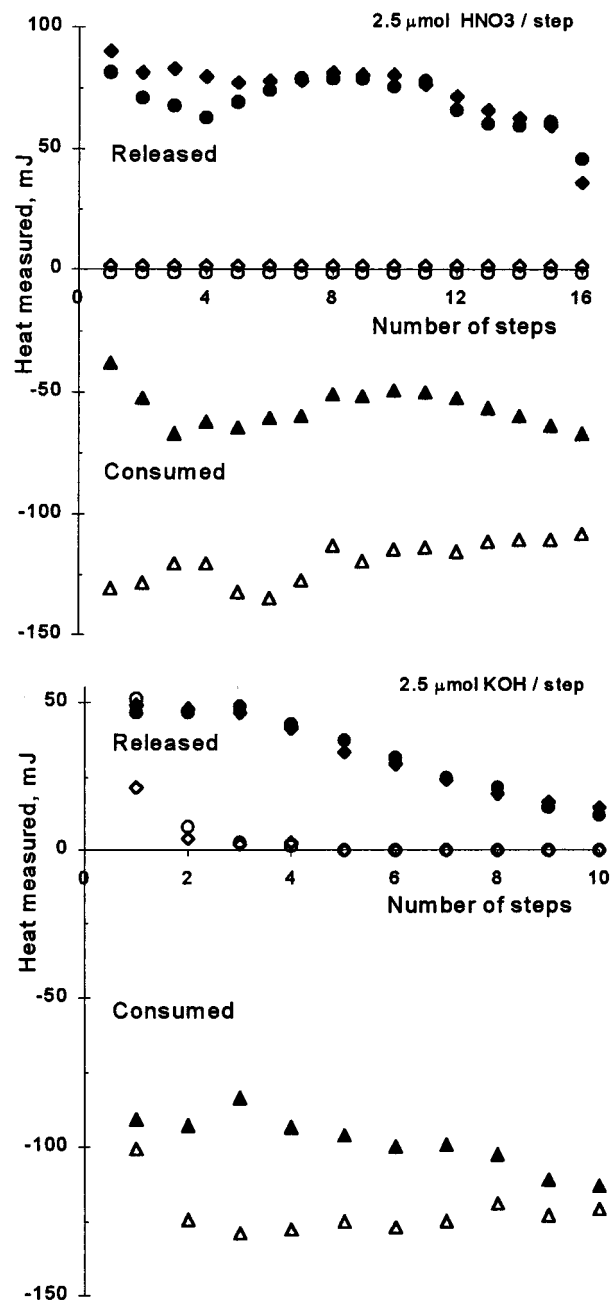


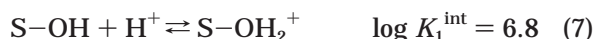
Figure 2. The measured heats of calorimetric titration at 25 °C for the acidic (top) and the alkaline series (bottom) of 1 g/10 mL of aluminum oxide suspensions (close symbols) and blank electrolyte solutions (open symbols) at different concentrations 0.01 (\blacklozenge , \blacklozenge), 0.1 (\bullet , \circ), and 1 (\blacktriangle , \triangle) M of KNO₃.

with standard acid and base titrants in the titration cell of the TAM calorimeter. Representative calorimeter signal records of titrations of alumina suspension and electrolyte solution with HNO₃ are shown in Figure 1. The top of the figure shows exothermic signals of suspension titration and practically zero heat flow for titration of electrolyte solution at low (0.01 M) ionic strength, while the bottom of the figure displays definite endothermic peaks recorded for both suspension and electrolyte solution at high (1 M) ionic strength. The gross amounts of released or consumed heats were calculated in each step and plotted as a function of the number of steps for both the acidic and alkaline series at each ionic strength as shown in Figure 2. Since the heat of mixing measured in the blank experiments proved to be significant, especially at the highest elec-

trolyte concentration, the measured heats for suspension titrations were corrected by them in each step.

The cumulative heat release ($\sum Q_{\text{meas.}}$) vs the amount of added acid ($\sum \mu\text{mol of H}^+$) proved to be linear functions with a regression coefficient larger than 0.99. The corresponding functions for heat release in the alkaline region, however, were not linear for the whole titration, they curved to a smaller slope from the fifth step. The linearity of these functions may suggest that the reactant added in each step is consumed quantitatively in identical reactions during the whole titration. This assumption is appropriate, if a well-defined reaction (e.g., between THAM and HCl) is measured. The surface protolysis of alumina, however, is different in this aspect. To calculate the extent of surface reaction due to the added amount of reactant, we have to apply a reliable model. In part 1 of this work we have arrived at an appropriate model for this system, which we apply also in calculation of the amount of charged surface species forming in the course of the calorimetric experiment. Enthalpy changes belonging to the surface protonation and deprotonation reactions in the separate titration steps were calculated in the following way.

The starting point was fixed at the reference state of aqueous alumina suspension (25 °C, pH of suspension at pzc and presence of indifferent 1:1 electrolyte) and the titration with acid and base solutions was simulated. The material balance for the conditions in the calorimetric titration was calculated by MINTEQA2.¹³ The amounts of charged surface species formed in the H^+ and OH^- association reactions



in each step of titration with 2.5 $\mu\text{mol H}^+/\text{OH}^-$ addition was calculated at different concentrations of 1:1 electrolyte by using the constant capacitance model (CCM). The equilibrium pH values were also calculated. The pH at the 16th step of acid and 10th step of base additions can be compared with the final pH values measured at the end of calorimetric titrations (Table 1).

The relatively good agreement between the measured and calculated values of pH, especially in the alkaline region, means that the simulation describes the experiment properly. So, we use the equilibrium speciation of surface species calculated for the subsequent steps of titration in the evaluation of calorimetric data.

The reaction in eq 7 is the surface protonation process indeed. The OH^- association reaction in eq 8, however, differs from the surface deprotonation reaction



since eq 8 involves water formation



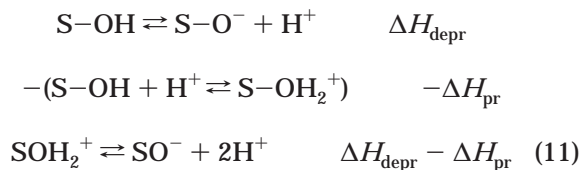
Therefore, if we wish to identify the reaction heat of the negative charge formation on oxide surface, i.e., of surface deprotonation reaction (eq 9), the reaction heat of the formation of a given amount of water in each step must be subtracted from the measured heat effects of titration with base solution (the OH^- association reaction (eq 8)).

Table 1. Comparison of Measured and Calculated pH Values in Aluminum Oxide Suspensions Containing a Given Amount of Added Acid or Base Solutions, Respectively, at Different Electrolyte Concentrations

c_{KNO_3} , M	pH of 10 mL suspensions containing 1 g of alumina after addition			
	40 $\mu\text{mol of H}^+$		25 $\mu\text{mol of OH}^-$	
	measured	calculated	measured	calculated
0.01	3.88	3.91	10.85	10.92
0.1	4.13	4.20	10.66	10.68
1	4.36	4.57	10.55	10.50

The cumulative heats of surface protonation and deprotonation reactions during titration, measured directly or calculated with correction for water formation, are plotted against the calculated amount of surface charges formed in the reactions 7 and 9 (Figure 3). This presentation of experimental data shows a satisfactorily linear relationship for both the protonation (top of Figure 3) and the deprotonation (bottom of Figure 3) reactions on surface sites of alumina. This linearity means that the molar enthalpy changes of surface charging processes (ΔH_{depr} and ΔH_{pr}) are independent of surface charge density within experimental accuracy, i.e., the temperature congruence given in eq 3 proved to be valid under the present experimental conditions. According to the theoretical analysis of Hall,¹² the occurrence of temperature congruence implies that there is no significant specific adsorption of supporting electrolyte ions, there is most of all only one type of surface group (or the contribution of different types is always equal irrespective of pH), and the interaction between neighboring surface groups is not influenced by protonation or deprotonation of either. Therefore, the slope of the cumulative heat of surface charge formation vs charged site amount functions in Figure 3 can be identified with the partial molar enthalpies of surface protonation and deprotonation reactions (ΔH_{pr} and ΔH_{depr}). The calculated values are summarized in Table 2.

While the partial molar enthalpy data for surface protonation and deprotonation reactions (second and third columns of Table 2) show a systematic change with increasing concentration of indifferent electrolyte, the difference between them results in a molar enthalpy which is practically independent of ionic strength. Applying the basic thermochemistry rule, subtracting one reaction (eq 7) from another (eq 9), we get



or written for one proton



and the enthalpy change of the resulting reaction can be calculated.

This combination of stoichiometric equations actually involves two kinds of surface charging models of oxides. One is the amphoteric site concept (2-pK concept) which involves protonation/deprotonation reactions of surface hydroxide groups written in the first two equations. The other is the coordination concept (1-pK concept) which assumes protonation of only one kind of surface sites given in the resulting equation. Kallay et al.¹ analyze the

(13) Allison, J. D.; Brown, D. S.; Novo-Gradac, K. J. *MINTEQA2/PRODEFAZ*, 3.0.; Environmental Research Laboratory: Athens, GA, 1991.

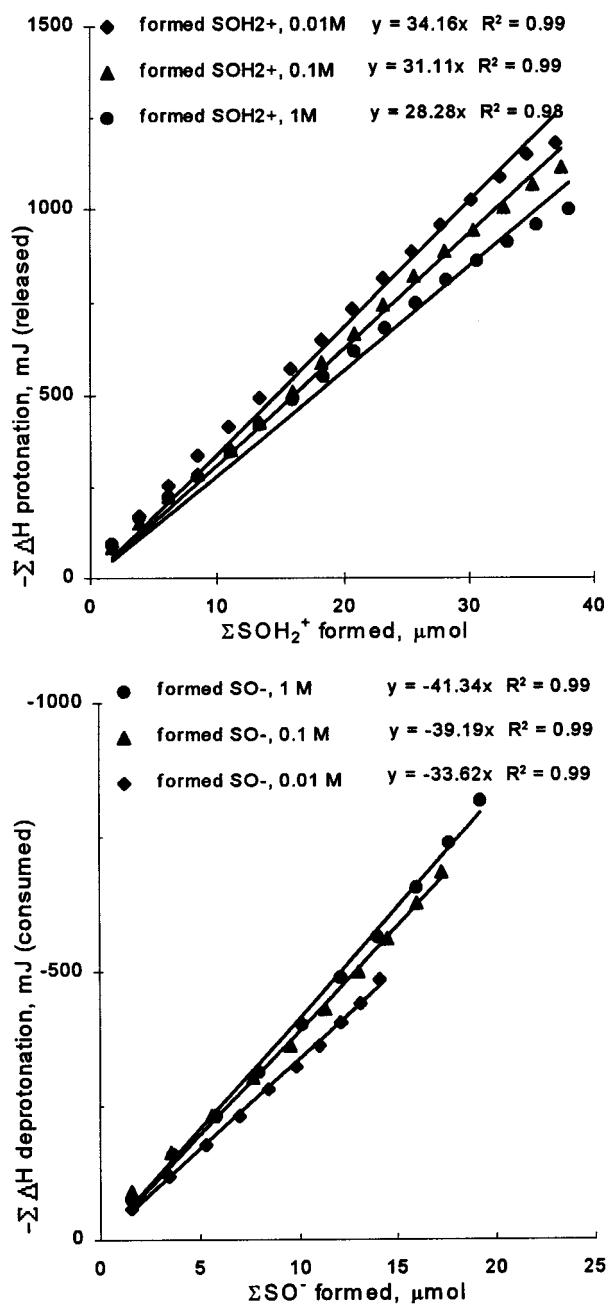


Figure 3. Cumulative heat of surface charge formation as a function of the amount of charged sites formed in protonation (top) and deprotonation (bottom) reactions on surface sites of alumina at different concentrations of KNO_3 .

different concepts, the involved stoichiometric equations and thermodynamic quantities, and give the relationship between them. Our approach entirely harmonizes with the interpretation of Kallay et al.¹ It can be stated that the calculated, ionic strength independent enthalpy value 34.6 ± 0.6 kJ/mol is the same standard reaction enthalpy for surface charging of alumina ($\text{SOH}_2^{1/2+} \rightleftharpoons \text{SOH}^{1/2-} + \text{H}^+$) in thermodynamic sense as that given for titania from temperature dependence of pzc (14.6 kJ/mol) and from calorimetric measurements performed under a “symmetric” condition (14.7 kJ/mol)².

Evaluation of titration calorimetric measurements results in valuable thermodynamic quantities, only if the experiments are performed very carefully, with well-defined and controlled systems without any side reactions from impurity and dissolution, since only these can give us a chance to assign the measured heats to the corre-

sponding reactions. In aqueous medium any acid–base reaction and most of the dilution processes too are accompanied by significant heat release or consumption. In addition, the standard state for electrolyte–oxide interfaces has not been clearly defined yet. The point of zero charge (pzc) has been introduced as a reference state of aqueous metal oxide suspensions long ago. On the basis of our experimental results and theoretical evaluation we can conclude that the state of pzc is a correct initial state in calorimetric titration too, because the electrostatic contribution can be neglected at pzc in the absence of resulting surface charge. The pH of a purified oxide sample spontaneously reaches the characteristic pH of pzc in the presence of indifferent electrolytes at sufficiently high concentration of suspension; the resulting pH, however, is very sensitive to even a small amount of acid or base contaminants. These kinds of impurities make the reference state undefined on the one hand, and its presence involves additional acid–base reactions with significant heat effect, on the other hand. If the pH of the well-defined initial state at pzc is alkaline such as in the case of alumina suspensions, the possible atmospheric CO_2 contamination demands careful experimental work. According to our experience each titration needs freshly prepared suspensions of freshly purified oxide. If the aim of calorimetric experiments is to characterize the surface charging of oxides, the amount of added acid or base solutions must not reach and precede the dissolution limit of the given oxide. Dissolution of solid aluminum oxides cannot be taken into account in a simple way^{4,5,14} by correction of measured calorimetric data.

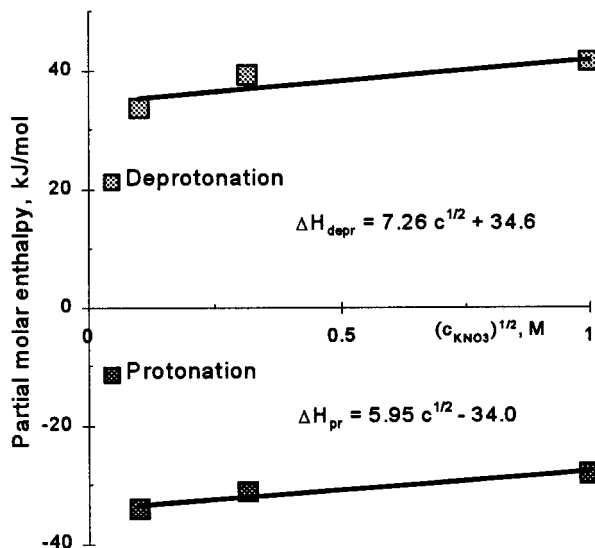
We can conclude that the temperature dependence of pzc and the smartly designed “symmetric” calorimetric experiment can provide not only acceptable thermodynamic quantities, standard reaction enthalpies ($\Delta H_{\text{depr}} - \Delta H_{\text{pr}}$) for acid–base surface reactions of oxides, but also the correct evaluation of calorimetric data from carefully performed titration calorimetry. These results can be hardly compared with the uncertain data published for alumina in the literature.^{4,5} However, the sign of proton adsorption and desorption enthalpies^{4,5} over the pH range (4–10) corresponds with our results and the magnitude is also comparable with our data. The proton adsorption enthalpy value⁴ -42 kJ/mol is comparable with our data between -34 and -28 kJ/mol given in the second column of Table 2, which in general are between -20 and -50 kJ/mol for metal oxides.⁵ Since the obtained difference of partial molar enthalpies ($\Delta H_{\text{depr}} - \Delta H_{\text{pr}}$)_{Cel} in our experiments is independent of ionic strength, calorimetric titration at any single concentration of indifferent electrolyte is sufficient to determine standard reaction enthalpy for surface charging ($\Delta H_{\text{ch}}^\circ$).

Another problem with the calorimetric data for charge formation on oxide surfaces published in the literature^{4,5,6} is that definite ionic strength dependence has not been published yet. Our data in the second and third columns of Table 2 show a small but noticeable, systematic endothermic effect of increasing salt concentration. This is in good harmony with the theoretical prediction of Hall¹² in a certain sense, who expected a systematic but negligible effect from the charge screening of electrolytes. Considering eq 5 for the enthalpy contribution from the diffuse part of electric double layer reported in Hall’s paper,¹² one can expect a linear relationship between the enthalpy change of surface charging process and the square root of electrolyte concentration at constant temperature, as a

(14) Hemingway, B. S.; Sposito, G. In *The Environmental Chemistry of Aluminum*; Sposito, G., Ed.; CRC Press: Boca Raton, FL, 1989; p 55.

Table 2. Partial Molar Enthalpy Values of the Surface Charging Process (kJ/mol) in Indifferent Electrolyte Solutions for Aluminum Oxide at 25 °C

surface reaction c_{KNO_3} , M	$\text{SOH} + \text{H}^+ \rightleftharpoons \text{SOH}_2^+$ exothermic ΔH_{pr}	$\text{SOH} \rightleftharpoons \text{SO}^- + \text{H}^+$ endothermic ΔH_{depr}	$\text{SOH}_2^{1/2+} \rightleftharpoons \text{SOH}^{1/2-} + \text{H}^+$ endothermic $(\Delta H_{\text{depr}} - \Delta H_{\text{pr}})/2$
0.01	-34.16	33.61	33.88
0.1	-31.11	39.19	35.15
1	-28.28	41.34	34.81
average			34.6 ± 0.6

**Figure 4.** Partial molar enthalpies of protonation and deprotonation reactions on aluminum oxide surface as a function of square root of electrolyte concentration.

consequence of a rigorous thermodynamic treatment for ionization surface with fixed dissociable groups. The plot of our partial molar enthalpy data according to the above representation (Figure 4) results in a linear relationship. Extrapolation of the straight lines to zero electrolyte concentration (infinite dilution), where the electrostatic effect is canceled, shows a particularly interesting result. The values are -34.0 kJ/mol for protonation ($\text{S-OH} + \text{H}^+ \rightleftharpoons \text{S-OH}_2^+$) and 34.6 kJ/mol for the deprotonation ($\text{S-OH} \rightleftharpoons \text{S-O}^- + \text{H}^+$) process, opposite in sign, but equal in absolute value within the experimental accuracy of calorimetric data. These values agree well with the standard enthalpy value 34.6 ± 0.6 kJ/mol of reaction $\text{SOH}_2^{1/2+} \rightleftharpoons \text{SOH}^{1/2-} + \text{H}^+$. We may conclude that the linear extrapolation of ΔH_{pr} and ΔH_{depr} vs $(c_{\text{el}})^{1/2}$ functions to infinite dilution results in the standard reaction enthalpy of surface ionization processes.

Conclusions

For pH and ionic strength dependent surface charging of aluminum oxide, the reaction of dissociable surface groups with acid or base in the presence of electrolytes can be characterized by titration calorimetry. To assign the measured heats to the corresponding reactions is possible only if experiments are performed carefully with well-defined and controlled systems without any side reactions from impurity and dissolution. Each titration needs freshly prepared suspensions of freshly purified oxide. Any acidic or alkaline contaminants must be removed. The reference state of aqueous metal oxide suspensions, i.e., the point of zero charge (pzc), proved to be a correct initial state in calorimetric titration, because the electrostatic contribution can be neglected at pzc in the absence of resulting surface charge.

Correct evaluation of reliable experimental data from titration calorimetry for systems with well-defined initial state (aqueous oxide suspensions at pzc) and with controlled addition of acid and base titrants results in thermodynamic data, partial molar enthalpies of surface ionization processes ($\text{S-OH} + \text{H}^+ \rightleftharpoons \text{S-OH}_2^+$, ΔH_{pr} , and $\text{S-OH} \rightleftharpoons \text{S-O}^- + \text{H}^+$, ΔH_{depr}), and standard reaction enthalpy for surface charging ($\text{SOH}_2^{1/2+} \rightleftharpoons \text{SOH}^{1/2-} + \text{H}^+$, $\Delta H_{\text{ch}}^\circ$) which is theoretically comparable with the standard reaction enthalpies from temperature dependence of pzc and from calorimetric measurements performed under a “symmetric” condition.^{1,2} Since the difference of partial molar enthalpies $(\Delta H_{\text{depr}} - \Delta H_{\text{pr}})_{\text{cel}}$ is independent of ionic strength, calorimetric titration at any single concentration of indifferent electrolyte is sufficient to determine standard reaction enthalpy for surface charging ($\Delta H_{\text{ch}}^\circ$).

Our results provide experimental proof supporting the expressions from rigorous thermodynamic treatment of Hall¹² for ionization thermodynamics of surfaces with fixed dissociable groups. The partial molar enthalpy changes of surface charging processes (ΔH_{depr} and ΔH_{pr}) at each constant ionic strength are independent of surface charge density within experimental accuracy; therefore temperature congruence proved to be valid under dissolution free experimental conditions. The occurrence of temperature congruence implies that there is no significant specific adsorption of supporting electrolyte ions. There is most of all only one type of surface group, i.e., hydrated alumina surface seems to be homogeneous with respect to the charged sites, and the interaction between neighboring surface groups is not influenced by the surface ionization state.

In the relevant literature a definite ionic strength dependence from calorimetric measurements of aqueous oxide suspensions has not been published yet. One of our noteworthy results is that the partial molar enthalpy changes of surface charging processes (ΔH_{depr} and ΔH_{pr}) determined at different concentrations of indifferent electrolyte show a small, as expected theoretically,¹² and uniform endothermic effect of increasing salt concentration for both sides of surface charging. The plot of our partial molar enthalpy data according to a theoretically expected¹² linear representation allowed us a linear extrapolation of ΔH_{depr} and ΔH_{pr} vs $(c_{\text{el}})^{1/2}$ functions to zero ionic strength, where the electrostatic effect is canceled; therefore the standard enthalpy of both surface ionization processes can be separately determined. The standard reaction enthalpy for the protonation reaction ($\text{S-OH} + \text{H}^+ \rightleftharpoons \text{S-OH}_2^+$) is $\Delta H_{\text{pr}}^\circ = -34.0$ kJ/mol and that for the deprotonation reaction ($\text{S-OH} \rightleftharpoons \text{S-O}^- + \text{H}^+$) is $\Delta H_{\text{depr}}^\circ = 34.6$ kJ/mol. These values agree well with the standard enthalpy $\Delta H_{\text{ch}}^\circ = 34.6 \pm 0.6$ kJ/mol of the surface protolysis reaction ($\text{SOH}_2^{1/2+} \rightleftharpoons \text{SOH}^{1/2-} + \text{H}^+$).

Acknowledgment. This work was supported by Grants OTKA T022426 and FKFP 0587/1999.

LA001323B