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Calorimetric Effects of Simple Ion Adsorption at the Oxide-Electrolyte Interfaces: Seeking for a Simple Interpretation of the Data Obtained by Titration Calorimetry

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Abstract. The theoretical description of the enthalpic effects accompanying ion adsorption at the oxide-electrolyte interface, developed recently by Rudzinski and co-workers, is used here to analyze the Kallay's experimental procedure of determining nonconfigurational heats of proton adsorption in a simple experiment involving use of titration calorimetry. That theoretical analysis, based on considering a certain real adsorption system, leads to important recommendation at which conditions the Kallay's titration experiment yields the most reliable figures describing the heats of proton adsorption.

Keywords: calorimetry, electrolyte-oxide interface, ion adsorption

Introduction

The oxide-electrolyte interface is the largest interface existing on our planet. Its importance for life on the earth and for technology can hardly be overestimated. No surprise, that studies of the oxide-electrolyte interface are carried out extensively in many laboratories around the world, and hundreds of papers have already been published on that subject.

So far, these studies have been oriented almost exclusively toward adsorption isotherms of ions, (titration isotherms or individual isotherms). The determined equilibrium constants provided, thus, researches with appropriate values of the free energies of ion adsorption. Simultaneously, it has been realized for a long time, that the knowledge of the enthalpic effects accompanying the adsorption of ions may bring more light onto fundamental features of these adsorption systems.

The first attempts to estimate these enthalpic effects started 25 years ago. The enthalpic effects were elucidated first from the temperature dependence of ion adsorption, but now they are more and more frequently measured directly in appropriate calorimetric sets. The measured calorimetric effects carry, however, very complicated information about the enthalpic effects of a number of surface complexation reactions occurring simultaneously.

Attempts to analyze quantitatively that information have been the matter of a series of papers published by Rudziński et al. (1991a, 1991b, 1992, 1997). There, they have launched a theoretical description of the temperature dependence and of the calorimetric effects of ion adsorption at the oxide-electrolyte interfaces.

That theoretical description results into a set of equations which can be solved by computers to decode the complicated combined information inherred in the measured calorimetric data. However, the history of science shows, that simple equations and simple experimental procedures are always the most attractive way of gathering the required information.

Thus, Kallay and coworkers have proposed recently an experimental procedure to elucidate certain important figures describing heats of proton adsorption at the oxide-electrolyte interface (Kallay et al., 1993; Kallay and Žalac, 1994; Žalac and Kallay, 1996). This procedure is a special way of carrying out potentiometric titration, which should eliminate the less interesting configurational coulombic contribution to the heats of proton adsorption.

While proposing that procedure Kallay and coworkers launched certain semiempirical arguments. The purpose of the present publication is to analyze in a fully rigorous way the range of the validity of Kallay's argumentation, and to draw certain recommendations concerning the use of Kallay's experimental procedure. For that purpose, the theoretical description of the enthalpic effects of ion adsorption, developed by Rudziński and coworkers is used to analyze the data obtained by applying the Kallay's procedure.

Theory

The equations which will be used here to analyze the experimental data have been developed in our previous publications (Rudziński et al., 1991a, 1991b, 1992, 1997). Here, for the reader's convenience, we will repeat only some principles and the final form of the developed expressions.

We begin our study with considering the most popular triple layer model proposed by Davies et al. (Davis et al., 1978; Davis and Leckie, 1978, 1980) from the conceptualizations of the electrical double layer discussed by Yates et al. (1974) and Chan et al. (1975). General reviews and representative applications of this model have been given by Davis and Leckie (1979) and by Morel et al. (1981).

Thus, we consider the following surface reactions,

$$\mathrm{SOH_2^+} \longleftrightarrow \mathrm{SOH^0} + \mathrm{H^+} \tag{1a}$$

$$\mathrm{SOH^0} \longleftrightarrow \mathrm{SO^-} + \mathrm{H^+} \tag{1b}$$

$$\mathrm{SOH_2^+A^-} \longleftrightarrow \mathrm{SOH^0} + \mathrm{H^+} + \mathrm{A^-} \tag{1c}$$

$$\mathrm{SOH^0} + \mathrm{C^+} \longleftrightarrow \mathrm{SO^-C^+} + \mathrm{H^+} \tag{1d}$$

where SO^- is the outermost surface oxygen, H^+ is the proton and A^- and C^+ denote the accompanying anion and cation, respectively. The equilibrium constants K_{a1}^{int}, K_{a2}^{int}, $^*K_A^{int}$ and $^*K_C^{int}$ of these reactions were defined in literature (Davis et al., 1978; Davis and Leckie 1978, 1980).

Using the notation,

$$\begin{gathered}\Sigma = [\mathrm{SOH^0}] + [\mathrm{SOH_2^+}] + [\mathrm{SOH_2^+A^-}] \\ + [\mathrm{SO^-C^+}] + [\mathrm{SO^-}] \\ [\mathrm{SOH_2^+}]/\Sigma = \theta_+, \quad [\mathrm{SOH^0}]/\Sigma = \theta_0, \\ [\mathrm{SO^-C^+}]/\Sigma = \theta_\mathrm{C}, \quad [\mathrm{SOH_2^+A^-}]/\Sigma = \theta_\mathrm{A}, \\ [\mathrm{SO^-}]/\Sigma = 1 - \theta_0 - \theta_+ - \theta_\mathrm{C} - \theta_\mathrm{A} = \theta_-\end{gathered} \tag{2}$$

we arrive at the following isotherm equations describing the formation of these surface complexes,

$$\theta_i = \frac{K_i f_i}{1 + \sum_i K_i f_i}, \quad i = 0, +, \mathrm{A}, \mathrm{C} \tag{3}$$

where

$$\begin{gathered}K_0 = \frac{1}{K_{a2}^{int}} \quad K_+ = \frac{1}{K_{a1}^{int} \cdot K_{a2}^{int}} \quad K_\mathrm{C} = \frac{^*K_\mathrm{C}^{int}}{K_{a2}^{int}} \\ K_\mathrm{A} = \frac{1}{K_{a2}^{int} \cdot {}^*K_\mathrm{A}^{int}}\end{gathered} \tag{4}$$

and where f_i, ($i = 0, +, \mathrm{A}, \mathrm{C}$) are the following functions of proton and salt concentrations:

$$\begin{gathered}f_0 = \exp\left\{-\frac{e\psi_0}{kT} - 2.3\,\mathrm{pH}\right\} \quad \text{and} \quad f_+ = f_0^2 \\ f_\mathrm{C} = a_\mathrm{C}\exp\left\{-\frac{e\psi_0}{kT} + \frac{e\delta_0}{kTc_1}\right\} \\ f_\mathrm{A} = a_\mathrm{A}\exp\left\{-\frac{e\psi_0}{kT} - \frac{e\delta_0}{kTc_1} - 4.6\,\mathrm{pH}\right\}\end{gathered} \tag{5}$$

here a_H is the proton activity in the equilibrium bulk phase, and a_A, a_C are the bulk activities of anion and cation, respectively. Further, ψ_0 is the surface potential and ψ_β is the mean potential at the plane of specifically adsorbed counterions, which is given by the equation,

$$\psi_\beta = \psi_0 - \frac{\delta_0}{c_1} \tag{6}$$

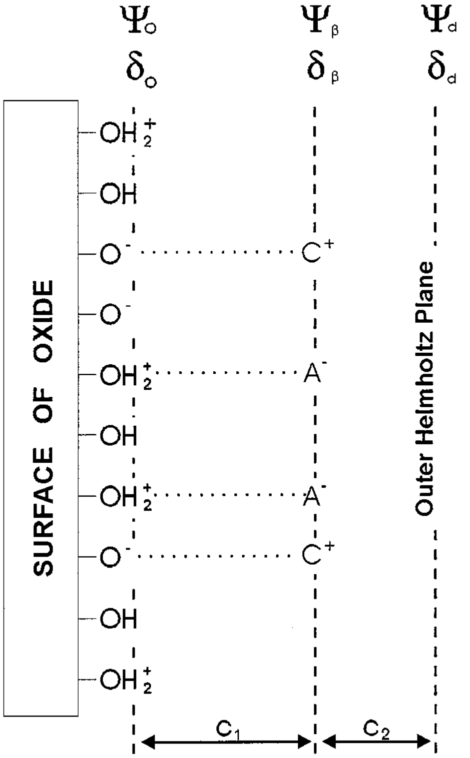

Figure 1. Diagrammatic presentation of the 2-pK model with three charged planes (TLM). ψ_0, δ_0—the surface potential and the surface charge density in the 0-plane; ψ_β and δ_β—the potential and the charge of the β-plane formed by the specifically adsorbed ions (cations C^+ and anions A^-) of the basic electrolyte; ψ_d, δ_d—the potential and charge diffuse layer; c_1, c_2—the electrical capacitances, constant in the regions between the planes.

in which the surface charge δ_0 is defined as follows,

$$\delta_0 = B(\theta_+ + \theta_A - \theta_C - \theta_-), \quad \text{where } B = N_s \cdot e \tag{7}$$

c_1 in Eqs. (5) and (6) is the first integral capacitance and N_s in Eq. (7) is the surface density (sites/m^2).

Figure 1 shows the schematic picture of the triple-layer model accepted to describe ion adsorption at the oxide-electrolyte interfaces.

To express the $\psi_0 - \text{pH}$ dependence, which occurs in Eqs. (3)–(7) for individual adsorption isotherms θ_i and for the surface charge δ_0, we accept the relation used by Yates et al. (1974) and by Bousse et al. (Bousse et al., 1983; van der Vlekkert et al., 1988).

$$2.303(\text{PZC} - \text{pH}) = \frac{e\psi_0}{kT} + \sinh^{-1}\left(\frac{e\psi_0}{\beta kT}\right) \tag{8}$$

where β is given by

$$\beta = \frac{2e^2 N_s}{c_{\text{DL}} kT}\left(\frac{K_{\text{a2}}^{\text{int}}}{K_{\text{a1}}^{\text{int}}}\right)^{1/2} \tag{9}$$

In Eq. (9) c_{DL} is the linearized double-layer capacitance. The value of c_{DL} can be theoretically calculated (depending on the salt concentration in the solution), in the way described in Bousse's work (Bousse et al., 1983):

$$\frac{1}{c_{\text{DL}}} = \frac{2kT/e}{(8\varepsilon_r \varepsilon_0 kTc)^{1/2}} + \frac{1}{c_{\text{Stern}}} \tag{10}$$

where ε_r is the relative permittivity of solvent, ε_0 is the permittivity of free space and c is the concentration of the electrolyte (ions/m^3). The value of the c_{Stern} is assumed to be 0.2 F/m^2.

To evaluate the bulk activity of ions a_i, ($i = \text{A, C}$), we assume that the activity coefficients γ_i's are given by the equation proposed by Davies (1962):

$$\log \gamma_i = -Az^2\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3 \cdot I\right], \quad i = \text{A, C} \tag{11}$$

where z is the valency of ion 'i', I (mol/dm^3) is the ionic strength of the suspension and A is given by

$$A = \frac{1.825 \cdot 10^6}{(\epsilon_r T)^{3/2}} \tag{12}$$

In Eq. (12) ϵ_r is the relative permittivity of the solvent.

Taking into account Eq. (7), the nonlinear equation system (3) can be transformed into a one nonlinear equation, with respect to δ_0,

$$\delta_0 = B\,\frac{K_+ f_+ + K_A f_A - K_C f_C - 1}{1 + \sum_i K_i f_i}, \qquad i = 0, +, \text{A, C} \tag{13}$$

This nonlinear equation for δ_0 can next be easily solved by means of an iteration method, to give the value of δ_0 for each pH value. Having calculated these values, one can easily evaluate the individual adsorption isotherms θ_i's from Eq. (3).

The point of zero charge (PZC) is defined by the condition,

$$\delta_0(\text{pH} = \text{PZC}) = 0 \tag{14}$$

For pH = PZC, $\delta_0 = 0$ and $\psi_0 = 0$, and Eq. (13) can be transformed to the following form:

$$U = \frac{H^2}{K_{\mathrm{a1}}^{\mathrm{int}} K_{\mathrm{a2}}^{\mathrm{int}}} + \frac{H^2 a_{\mathrm{A}}}{K_{\mathrm{a2}}^{\mathrm{int}}\, {}^{*}K_{\mathrm{A}}^{\mathrm{int}}} - \frac{{}^{*}K_{\mathrm{C}}^{\mathrm{int}} a_{\mathrm{C}}}{K_{\mathrm{a2}}^{\mathrm{int}}} - 1 = 0 \tag{15}$$

where

$$H = 10^{-\mathrm{PZC}} \tag{16}$$

The experimental studies show that in the majority of the investigated systems the value of the point of zero charge does not depend practically upon the salt concentration in the bulk solution (Davis et al., 1978; Davis and Leckie, 1978; Sprycha, 1984; Foissy et al., 1982). It seems that this very interesting feature of these systems has not received enough attention so far. We have shown it in our previous publications (Rudziński et al., 1991a, 1992) that, while drawing mathematically rigorous formal consequences of the existence of CIP, one can arrive at interesting physical conclusions.

Namely, except for very low and very high PZC values and very low salt concentrations, one can assume that $a_{\mathrm{C}} = a_{\mathrm{A}} = a$. Thus, the independence of PZC of the salt concentration can be expressed as follows:

$$\frac{\partial U}{\partial a} = \frac{H^2}{K_{\mathrm{a2}}^{\mathrm{int}*} K_{\mathrm{A}}^{\mathrm{int}}} - \frac{{}^{*}K_{\mathrm{C}}^{\mathrm{int}}}{K_{\mathrm{a2}}^{\mathrm{int}}} = 0 \tag{17}$$

Solving the set of Eqs. (15) and (17) we obtain

$${}^{*}K_{\mathrm{A}}^{\mathrm{int}} = \frac{H^2}{{}^{*}K_{\mathrm{C}}^{\mathrm{int}}} \quad \text{and} \quad K_{\mathrm{a2}}^{\mathrm{int}} = \frac{H^2}{K_{\mathrm{a1}}^{\mathrm{int}}} \tag{18}$$

Correlations (18) between the parameters $K_{\mathrm{a1}}^{\mathrm{int}}$, $K_{\mathrm{a2}}^{\mathrm{int}}$ and ${}^{*}K_{\mathrm{C}}^{\mathrm{int}}$, ${}^{*}K_{\mathrm{A}}^{\mathrm{int}}$ reduce the number of the true free parameters—intrinsic equilibrium constants to be found by fitting the experimental data from 4 to 2. This fact has not been realized until we published our three papers (Rudziński et al., 1991a, 1991b, 1992), in which the consequences of the existence of CIP were subjected to a rigorous mathematical analysis.

While accepting relations (18) we obtain the following expressions for the value of the point of zero charge, PZC,

$$\mathrm{PZC} = \frac{1}{2}\left(\mathrm{p}K_{\mathrm{a1}}^{\mathrm{int}} + \mathrm{p}K_{\mathrm{a2}}^{\mathrm{int}}\right) \tag{19}$$

$$\mathrm{PZC} = \frac{1}{2}\left(\mathrm{p}^{*}K_{\mathrm{C}}^{\mathrm{int}} + \mathrm{p}^{*}K_{\mathrm{A}}^{\mathrm{int}}\right) \tag{20}$$

Now, let us consider the calorimetric effects accompanying the formation of the surface complexes SOH^0, SOH_2^+, $\mathrm{SOH}_2^+\mathrm{A}^-$, $\mathrm{SO}^-\mathrm{C}^+$. In the calorimetric experiments reported by Griffiths and Fuerstenau (1981) and by Foissy (1985), they measured the heat of immersion of an outgassed solid sample into a solution of certain pH, $Q_{\mathrm{im}}(\mathrm{pH})$. As we discussed it in our previous publication the theoretical interpretation of this “batch adsorption calorimetry” is rather difficult. Similar conclusions have been drawn by other authors. Much easier to interpret are the heat effects measured in the experiment called “titration calorimetry” reported first by Machesky and Anderson (1986) and de Kaizer et al. (1990).

Here after introducing an outgassed solid sample into a solution, the pH of that solution is measured, and sometimes also the concentration of other ions in the equilibrium bulk electrolyte. Then, a titration step is carried out (from the base or acid side) and the evolved heat is recorded. Depending on the reported experiments the consumption (adsorption) of protons and the ions of the inert electrolyte is monitored, accompanying the change of pH by $\Delta\mathrm{pH}$. The recorded heat effect is described by the following equation,

$$\Delta Q = \int_{\mathrm{pH}}^{\mathrm{pH}+\Delta\mathrm{pH}} \sum_i Q_i \left(\frac{\partial \theta_i}{\partial \mathrm{pH}}\right)_T d\mathrm{pH}, \qquad i = 0, +, \mathrm{A}, \mathrm{C} \tag{21}$$

where Q_i’s are the molar differential heats of the formation of the surface complexes,

$$Q_0 = -k\frac{\partial}{\partial(1/T)}\left[\frac{\mu_{\mathrm{SOH}} - \mu_{\mathrm{H}}^b}{kT}\right]_{\{\theta_{0,+,\mathrm{C},\mathrm{A}}\}} \tag{22a}$$

$$Q_+ = -k\frac{\partial}{\partial(1/T)}\left[\frac{\mu_{\mathrm{SOH}_2^+} - 2\mu_{\mathrm{H}}^b}{kT}\right]_{\{\theta_{0,+,\mathrm{C},\mathrm{A}}\}} \tag{22b}$$

$$Q_{\mathrm{C}} = -k\frac{\partial}{\partial(1/T)}\left[\frac{\mu_{\mathrm{SO}^-\mathrm{C}^+} - \mu_{\mathrm{C}^+}^b}{kT}\right]_{\{\theta_{0,+,\mathrm{C},\mathrm{A}}\}} \tag{22c}$$

$$Q_{\mathrm{A}} = -k\frac{\partial}{\partial(1/T)}\left[\frac{\mu_{\mathrm{SOH}_2^+\mathrm{A}^-} - \mu_{\mathrm{A}^-}^b - 2\mu_{\mathrm{H}}^b}{kT}\right]_{\{\theta_{0,+,\mathrm{C},\mathrm{A}}\}} \tag{22d}$$

where $\mu_{\mathrm{SO}^-\mathrm{C}^+}$, $\mu_{\mathrm{SOH}_2^+\mathrm{A}^-}$, μ_{SOH}, $\mu_{\mathrm{SOH}_2^+}$ are the chemical potentials of these surface complexes. For the particular triple-layer model accepted here, along with the assumed two-pK charging mechanism, the molar differential heats of complex formation, Q_0, Q_+, Q_C, Q_A take the following form,

$$Q_0 = Q_{a2} - e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},\mathrm{pH}} \tag{23a}$$

$$Q_+ = Q_{a2} + Q_{a1} - 2e\psi_0 - \frac{2e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},\mathrm{pH}} \tag{23b}$$

$$Q_C = Q_{aC} - e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},\mathrm{pH}} + e\frac{\delta_0}{c_1} + \frac{e\delta_0 T}{(c_1)^2}\left(\frac{\partial c_1}{\partial T}\right)_{\{\theta_i\},\mathrm{pH}} + k\left(\frac{\partial \ln a_C}{\partial(1/T)}\right)_{\mathrm{pH}} \tag{23c}$$

$$Q_A = Q_{aA} - e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},\mathrm{pH}} - e\frac{\delta_0}{c_1} - \frac{e\delta_0 T}{(c_1)^2}\left(\frac{\partial c_1}{\partial T}\right)_{\{\theta_i\},\mathrm{pH}} + k\left(\frac{\partial \ln a_A}{\partial(1/T)}\right)_{\mathrm{pH}} \tag{23d}$$

where the non-configurational heats are,

$$Q_{ai} = -k\frac{d\ln K_{ai}^{\mathrm{int}}}{d(1/T)}, \quad i = 1, 2 \tag{24a}$$

$$Q_{aC} = -k\frac{d\ln\left(K_{a2}^{\mathrm{int}}/{}^*K_C^{\mathrm{int}}\right)}{d(1/T)} \tag{24b}$$

$$Q_{aA} = -k\frac{d\ln\left(K_{a2}^{\mathrm{int}}\cdot{}^*K_A^{\mathrm{int}}\right)}{d(1/T)} \tag{24c}$$

While calculating the derivative $(\frac{\partial c_1}{\partial T})_{\{\theta_i\},\mathrm{pH}}$ we followed Blesa's recommendation (Blesa et al., 1984) to treat c_1 as the following linear functions,

$$c_1 = c_{1+} = c_{1+}^0 + \alpha_+ \cdot \Delta T, \quad \mathrm{pH} < \mathrm{PZC} \tag{25a}$$

$$c_1 = c_{1-} = c_{1-}^0 + \alpha_- \cdot \Delta T, \quad \mathrm{pH} > \mathrm{PZC} \tag{25b}$$

which may be considered as formal Taylor expansions around $T = T_0$ such that $c_{1+}(T_0) = c_{1+}^0$ and $c_{1-}(T_0) = c_{1-}^0$.

Next, we have shown that the derivatives $(\frac{\partial a_i}{\partial(1/T)})_{\{\theta_i\},\mathrm{pH}}$, i = C, A, can be expressed as follows,

$$\frac{\partial a_i}{\partial(1/T)} = -2.0172\cdot 10^{-8}\cdot T^4\, a_i\, \ln\gamma_i \qquad i = \mathrm{A, C} \tag{26}$$

whereas the derivative $(\frac{\partial\psi_0}{\partial(1/T)})_{\mathrm{pH}}$ takes the following form,

$$\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\mathrm{pH}} = -\psi_0\cdot T\left[\frac{\beta}{\beta+t} + \frac{t}{\beta+t}\cdot\frac{Q_{a2}-Q_{a1}}{2kT}\right] + 2.3\frac{kT}{e}\frac{\beta}{\beta+t}\frac{\partial\mathrm{PZC}}{\partial(1/T)} \tag{27}$$

where

$$t = \frac{1}{\sqrt{\left(\frac{e\psi_0}{\beta kT}\right)^2 + 1}} \tag{28}$$

In Eq. (27) the derivative $(\frac{\partial\mathrm{PZC}}{\partial(1/T)})$ is replaced by the term $(Q_{a1} + Q_{a2})/4.6\,k$, according to the result of the formal differentiations of PZC in Eq. (19), and the definition of Q_{a1}, Q_{a2} in Eq. (24),

$$2.3\frac{\partial\mathrm{PZC}}{\partial(1/T)} = \frac{Q_{a1}+Q_{a2}}{2k} \tag{29}$$

Equations (23) along with the expressions (25)–(29) allow to express Q_i's as functions of temperature, pH, and concentration of the inert electrolyte, provided that the other parameters are known. Having known Q_i's we may calculate the heat accompanying the change of pH by ΔpH, and monitored in the course of the potentiometric titration. The derivatives $(\frac{\partial\theta_i}{\partial\mathrm{pH}})$ appearing in Eq. (21) have been given in our previous publications (Rudziński et al., 1991a, 1991b, 1992). Here, for the reader's convenience, they are given in Appendix.

Also, for the reader's convenience, we give in Table 1 the brief description of the surface reactions, along with the corresponding equilibrium constants and the "non-configurational" heats of adsorption Q_{a1}, Q_{a2}, Q_{aC}, Q_{aA}.

Equation (29) has been known in literature for a long time, though it was developed in a somewhat different way. Now let us remark that, similarly as in Eq. (19), the same differentiation with respect to $(\frac{1}{T})$ in Eq. (20)

Table 1. Surface reactions, equilibrium constants and heats of adsorption.

No.	Reaction type	Equilibrium constants	Heat of reaction
1	$SOH^0 + H^+ \longleftrightarrow SOH_2^+$	$-pK_{a1}^{int}$	Q_{a1}
2	$SO^- + H^+ \longleftrightarrow SOH^0$	$-pK_{a2}^{int}$	Q_{a2}
3	$SOH^0 + H^+ + A^- \longleftrightarrow SOH_2^+A^-$	$-p^*K_A^{int}$	$Q_{aA} - Q_{a2}$
4	$SO^-C^+ + H^+ \longleftrightarrow SOH^0 + C^+$	$-p^*K_C^{int}$	$Q_{a2} - Q_{aC}$
5	$SO^- + 2H^+ \longleftrightarrow SOH_2^+$	$-pK_{a1}^{int} - pK_{a2}^{int}$	$Q_{a1} + Q_{a2}$
6	$SO^- + 2H^+ + A^- \longleftrightarrow SOH_2^+A^-$	$-pK_{a2}^{int} - p^*K_A^{int}$	Q_{aA}
7	$SO^- + C^+ \longleftrightarrow SO^-C^+$	$p^*K_C^{int} - pK_{a2}^{int}$	Q_{aC}
8	$SOH_2^+ + A^- \longleftrightarrow SOH_2^+A^-$	$pK_{a1}^{int} - p^*K_A^{int}$	$Q_{aA} - Q_{a1} - Q_{a2}$

leads to the following result,

$$2.3\frac{\partial \mathrm{PZC}}{\partial(1/T)} = \frac{Q_{aA} - Q_{aC}}{2k} \tag{30}$$

in view of the definitions of Q_{aC} and Q_{aA} in Eqs. (24b) and (24c). From Eqs. (29) and (30) we have,

$$Q_{aA} - (Q_{a1} + Q_{a2}) = Q_{aC} \tag{31}$$

which is surely an intriguing result.

This means that the heat effect related to the cation adsorption on an empty oxygen atom Q_{aC} is the same as the heat of the attachment of the anion to the already existing complex SOH_2^+ $Q_{aA} - (Q_{a1} + Q_{a2})$. This is a very intriguing result, as it must be true for so many different oxides and pairs of ions of the inert electrolytes, which combindly yield a large number of the adsorption systems in which the existence of CIP was reported. Looking for some rational explanation of that result, we have postulated in our previous publication (Rudziński et al., 1997) that the heat of cation adsorption Q_{aC} and the heat of anion adsorption $Q_{aA} - (Q_{a1} + Q_{a2})$ on the already formed complex SOH_2^+ are equal, because they are simply nonexistent. As a matter of fact, assumption of that kind were earlier expressed by Kosmulski (1994).

That assumption, along with Eq. (29) reduces from four to one, the number of the unknown paramerters: Q_{a1}, Q_{a2}, Q_{aC}, Q_{aA}. This is because the derivative $(\frac{\partial \mathrm{PZC}}{\partial(1/T)})$ can be experimentally determined, and was frequently reported in literature (Berube and de Bruyn, 1968; Tewari and Campbell, 1976).

The knowledge of the heats of the first and the second proton adsorption, Q_{a1} and Q_{a2} is of a great importance for fundamental studies of the charging mechanism at the oxide-electrolyte interface. However, the equations developed by us show, that the heat accompanying the titration from pH to (pH + ΔpH) carries very complex information about a number of heat effects accompanying the surface reactions taking place at the same time. Decoding that information to obtain the Q_{a1} and Q_{a2} values is possible, but requires an advanced numerical analysis of many experimental data. This may not be an attractive perspective for many researchers having at their disposal either a commercially available, or home-made experimental set for carrying out calorimetric titration.

Thus, three years ago, Kallay and coworkers (Kallay et al., 1993; Kallay and Žalac, 1994; Žalac and Kallay, 1996) started a theoretical-experimental study aimed at determining the experimental conditions, under which the obtained experimental data could be free of the coulombic contributions to the measured heats of adsorption and refer only to the nonconfigurational values Q_{a1} and Q_{a2}. This would eliminate the necessity of carrying out a complicated theoretical-numerical analysis.

In one of their papers the authors postulated that the "average" heat of proton adsorption, $\frac{Q_{a1}+Q_{a2}}{2}$, should correspond to the heat of titration from (PZC − ΔpH) to (PZC + ΔpH). So, let us consider in detail the above defined heat effect, which we denote further by Q_{0+}. Then, in terms of our theory, Q_{0+} is described by the following integral,

$$Q_{0+} = \int_{\mathrm{PZC}-\Delta\mathrm{pH}}^{\mathrm{PZC}+\Delta\mathrm{pH}} \sum_i Q_i \left(\frac{\partial\theta_i}{\partial \mathrm{pH}}\right)_T d\mathrm{pH}, \quad i = 0, +, \mathrm{A}, \mathrm{C} \tag{32}$$

The change of the pH causes the adsorption on the surface of a certain number of moles of protons,

$$N_{pr} = \int_{\mathrm{PZC}-\Delta\mathrm{pH}}^{\mathrm{PZC}+\Delta\mathrm{pH}} \left[2\left(\frac{\partial\theta_+}{\partial \mathrm{pH}}\right)_T + 2\left(\frac{\partial\theta_A}{\partial \mathrm{pH}}\right)_T + \left(\frac{\partial\theta_0}{\partial \mathrm{pH}}\right)_T\right] d\mathrm{pH} \tag{33}$$

The consumption of protons from the bulk solution was monitored in the Kallay's experiment, so, the "average" molar heat of proton adsorption, Q_{Av} is given by,

$$Q_{\mathrm{Av}} = \frac{Q_{0+}}{N_{\mathrm{pr}}} \tag{34}$$

The purpose of the present publication is to study the heat effect Q_{Av}, and to determine the experimental conditions under which the performed experiments could provide a possibly simple information about the heats of proton adsorption.

Results and Discussion

We have shown in our earlier work (Rudziński et al., 1997), that the theoretical description of the temperature dependence of ion adsorption, and of the calorimetric effects accompanying ion adsorption, involves introducing the same parameters and functions. There we have given a general theoretical interpretation of all kinds of the calorimetric experiments reported so far, along with the theoretical description of the temperature dependence of ion adsorption. However, the analysis of the available experimental data was limited to the analysis of the temperature dependence of ion adsorption at the magnetite/KNO_3 interface, studied experimentally (reported) by Blesa et al., (1984).

While fitting their experimental data by our theoretical equations, we arrived at a reasonably good agreement between the theory and experiment. The parameters found in these calculations are collected in Table 2. Some of them could be determined independently, some of them were calculated, and some of them were found by computer as best-fit parameters.

Now, we are going to use these parmeters in our model calculations to see under which conditions the data obtained in the Kallay's titration calorimetry experiment could be used to determine easily the heats of proton adsorption, Q_{a1}, Q_{a2}. We begin with studying the behavior of the function Q_{Av} defined in Eq. (34). For the parameters collected in Table 2, the behavior of the calculated functions Q_{Av} is shown in Fig. 2.

One can see that when the concentration of the inert electrolyte increases, the values of the function HQ tend to the value $\frac{Q_{a1}+Q_{a2}}{2}$, as it was assumed by Kallay and coworkers. However, our present model calculations suggest, that in order to arrive closely at the value of $\frac{Q_{a1}+Q_{a2}}{2}$, the Kallay's titration experiment has to be carried out at possibly high concentrations of the inert electrolyte. Meanwhile, Kallay proved first his

Table 2. The collection of the best-fit and calculated parameters used by us to fit our equations to the Blesa's titration curves measured at three temperatures and for three concentrations of the inert electrolyte (Rudziński et al., 1997).

N_s (sites/nm^2)	Q_{a1} (kJ/mol)	Q_{a2} (kJ/mol)	Q_{aC} (kJ/mol)	Q_{aA} (kJ/mol)
6	20.5	45.0	0.0	65.5

T (K)	$\mathrm{p}K_{a1}^{\mathrm{int}}$	$\mathrm{p}K_{a2}^{\mathrm{int}}$	$\mathrm{p}^*K_{C}^{\mathrm{int}}$	$\mathrm{p}^*K_{A}^{\mathrm{int}}$	PZC
303	4.40	9.20	6.60	7.00	6.80
323	4.18	8.72	6.12	6.78	6.45
353	3.90	8.10	5.50	6.50	6.00

c (mol/dm^3)	α_+ (F/m^{2}deg)	α_- (F/m^{2}deg)
0.1	0.003	0.0
0.01	0.005	0.0
0.001	0.060	0.0

	0.001 (mol/dm^3)		0.01 (mol/dm^3)		0.1 (mol/dm^3)	
T (K)	c_{1+} (F/m^2)	c_{1-} (F/m^2)	c_{1+} (F/m^2)	c_{1-} (F/m^2)	c_{1+} (F/m^2)	c_{1-} (F/m^2)
303	1.40	1.80	0.95	1.15	1.10	1.30
323	2.60	1.80	1.05	1.15	1.16	1.30
353	4.40	1.80	1.20	1.15	1.25	1.30

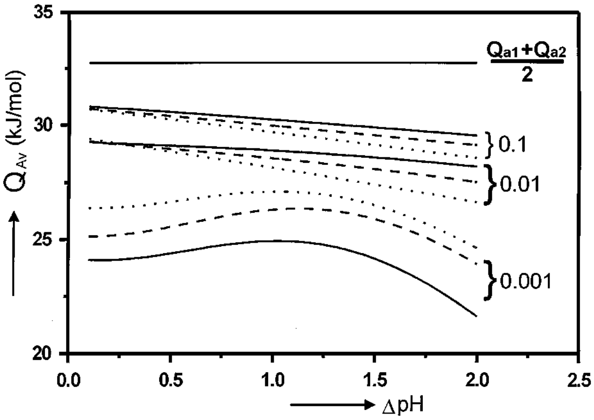

Figure 2. The behavior of the calculated functions Q_{Av}, depending on ΔpH, at three temperatures and for three concentrations of the inert electrolyte KNO_3. The solid line (——) is for the lowest temperature 303 K, the dashed line (– – –) is for the temperature 323 K, and the dotted line (· · · · · ·) is for 353 K. The numbers: 0.1, 0.01 and 0.001 at the three families of the curves (—— ; – – – ; · · · · · ·) denote the concentrations of the inert electrolyte (in mol/dm^3) for which the three functions Q_{Av} were calculated. All the calculations were done by using the parameters collected in Table 2.

hypothesis by comparing his experimental heats Q_{Av} for TiO_2 (Kallay et al., 1993), with the values of $\frac{Q_{\text{a1}}+Q_{\text{a2}}}{2}$ determined from Eq. (29). The agreement was very good.

So, trying to find out under which conditions the Kallay's calorimetric-titration experiment will yield the value $\frac{Q_{\text{a1}}+Q_{\text{a2}}}{2}$, we rewrite Eq. (34) to the following form,

$$Q_{\text{Av}} = Q_{\text{Av}}^{\text{nonc}} + Q_{\text{Av}}^{\text{el}} + Q_{\text{Av}}^{\text{act}} \tag{35}$$

where $Q_{\text{Av}}^{\text{nonc}}$ is the nonconfigurational (chemical) contribution,

$$\begin{aligned} Q_{\text{Av}}^{\text{nonc}} = \frac{1}{N_{\text{pr}}}\biggl[& Q_{\text{a2}} \int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}} \left(\frac{\partial\theta_0}{\partial\text{pH}}\right)_T d\text{pH} \\ & + (Q_{\text{a1}} + Q_{\text{a2}}) \int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}} \left(\frac{\partial\theta_+}{\partial\text{pH}}\right)_T d\text{pH} \\ & + Q_{\text{aC}} \int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}} \left(\frac{\partial\theta_{\text{C}}}{\partial\text{pH}}\right)_T d\text{pH} \\ & + Q_{\text{aA}} \int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}} \left(\frac{\partial\theta_{\text{A}}}{\partial\text{pH}}\right)_T d\text{pH} \biggr] \end{aligned} \tag{36}$$

$Q_{\text{Av}}^{\text{el}}$ is the electric (coulombic) contribution,

$$\begin{aligned} Q_{\text{Av}}^{\text{el}} = \frac{1}{N_{\text{pr}}}\Biggl[& \int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}} \Biggl(-e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},\text{pH}}\Biggr) \\ & \times \left(\frac{\partial\theta_0}{\partial\text{pH}}\right)_T d\text{pH} + \int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}} \Biggl(-2e\psi_0 \\ & - \frac{2e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},\text{pH}}\Biggr)\left(\frac{\partial\theta_+}{\partial\text{pH}}\right)_T d\text{pH} \\ & + \int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}} \Biggl(-e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},\text{pH}} \\ & + e\frac{\delta_0}{c_1} + \frac{e\delta_0 T}{(c_1)^2}\left(\frac{\partial c_1}{\partial T}\right)_{\{\theta_i\},\text{pH}}\Biggr)\left(\frac{\partial\theta_{\text{C}}}{\partial\text{pH}}\right)_T d\text{pH} \\ & + \int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}} \Biggl(-e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},\text{pH}} \\ & - e\frac{\delta_0}{c_1} - \frac{e\delta_0 T}{(c_1)^2}\left(\frac{\partial c_1}{\partial T}\right)_{\{\theta_i\},\text{pH}}\Biggr)\left(\frac{\partial\theta_{\text{A}}}{\partial\text{pH}}\right)_T d\text{pH} \Biggr] \end{aligned} \tag{37}$$

whereas $Q_{\text{Av}}^{\text{act}}$ is the contribution due to the temperature dependence of the bulk activities of ions,

$$\begin{aligned} Q_{\text{Av}}^{\text{act}} = \frac{1}{N_{\text{pr}}}\Biggl[& k\left(\frac{\partial \ln a_{\text{C}}}{\partial(1/T)}\right)_{\text{pH}} \int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}} \left(\frac{\partial\theta_{\text{C}}}{\partial\text{pH}}\right)_T d\text{pH} \\ & + k\left(\frac{\partial \ln a_{\text{A}}}{\partial(1/T)}\right)_{\text{pH}} \int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}} \left(\frac{\partial\theta_{\text{A}}}{\partial\text{pH}}\right)_T d\text{pH} \Biggr] \end{aligned} \tag{38}$$

Our numerical calculations made not only for this particular system, but also for a number of other systems showed that $Q_{\text{Av}}^{\text{act}}$ makes very small (smaller than the experimental error), thus negligible, contribution to Q_{Av}. From Eqs. (35)–(36) it follows, that the function Q_{Av} tends to $\frac{Q_{\text{a1}}+Q_{\text{a2}}}{2}$ value under the following conditions:

1. The electric contribution $Q_{\text{Av}}^{\text{el}}$ is negligible.
2. The value of Q_{aC} is zero (or very small), as it has been assumed by us.
3. The integral (39),

$$\int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}} \left(\frac{\partial\theta_0}{\partial\text{pH}}\right)_T d\text{pH} \tag{39}$$

is negligible, because Q_{a2} alone is known to take relatively high values (see Table 2).

The integral (39) tends to zero when the function $(\partial\theta_0/\partial\text{pH})$ is symmetrical with respect to PZC in such a sense that

$$-\frac{\partial\theta_0}{\partial\text{pH}}(\text{PZC} + \Delta\text{pH}) = \frac{\partial\theta_0}{\partial\text{pH}}(\text{PZC} - \Delta\text{pH}) \tag{40}$$

The function $\theta_0(\text{pH})$ was frequently calculated and shown in our theoretical papers (Rudziński et al., 1991a, 1991b, 1992, 1997) and was always highly symmetrical with respect to PZC, so the condition 40 is commonly well fulfilled. Figure 3 shows the function $(\partial\theta_0/\partial\text{pH})$ for the system magnetite/KNO_3 studied here by us, for two different concentrations of the inert electrolyte.

One can see in Fig. 3 that condition 40 is very well fulfilled in the vicinity of PZC. For the high electrolyte concentration 0.1 mol/dm^3, condition 40 is fulfilled well in the whole range of pH values. Neglecting thus the integral (39) in Eq. (36) and assuming that $Q_{\text{aC}} = 0$,

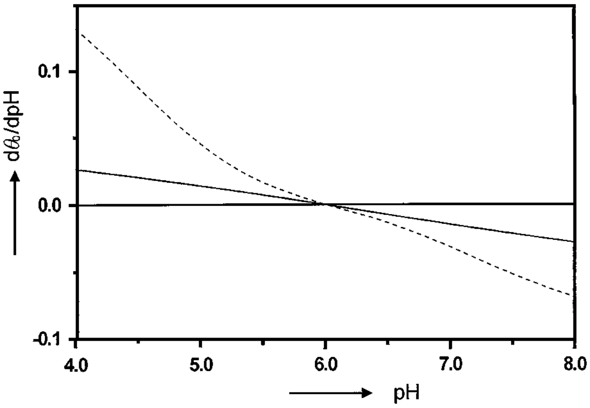

Figure 3. The shape of the function $(\partial\theta_0/\partial\text{pH})$, in the system magnetite/KNO$_3$, calculated by us for the temperature 353 K, and for two different concentrations of the inert electrolyte; 0.1 mol/dm^3 (the solid line, ——), and 0.001 mol/dm^3 (the broken line, – – –). The calculations were carried out by using the parameters collected in Table 2.

we obtain

$$Q_{\text{Av}}^{\text{nonc}} = \frac{(Q_{\text{a1}}+Q_{\text{a2}})\int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}}\left(\frac{\partial\theta_+}{\partial\text{pH}}\right)_T d\text{pH} + Q_{\text{aA}}\int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}}\left(\frac{\partial\theta_{\text{A}}}{\partial\text{pH}}\right)_T d\text{pH}}{2\int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}}\left(\frac{\partial\theta_+}{\partial\text{pH}}\right)_T d\text{pH} + 2\int_{\text{PZC}-\Delta\text{pH}}^{\text{PZC}+\Delta\text{pH}}\left(\frac{\partial\theta_{\text{A}}}{\partial\text{pH}}\right)_T d\text{pH}} \tag{41}$$

With the assumption $Q_{\text{aC}} = 0$, from Eq. (31) it follows that $Q_{\text{aA}} = Q_{\text{a1}} + Q_{\text{a2}}$, and then Eq. (41) reduces to the Kallay's equation (assumption) that $Q_{\text{Av}} = \frac{Q_{\text{a1}}+Q_{\text{a2}}}{2}$.

Now let us consider which is the condition for the electrical contribution $Q_{\text{Av}}^{\text{el}}$ to disappear. Of course, like in the case of integral (39), the condition is the following symmetry of the function $F_{\text{Av}}^{\text{el}}$,

$$-F_{\text{Av}}^{\text{el}}(\text{PZC} + \Delta\text{pH}) = F_{\text{Av}}^{\text{el}}(\text{PZC} - \Delta\text{pH}) \tag{42}$$

where $F_{\text{Av}}^{\text{el}}$ is the sum of all the functions under the integrals in the numerator of Eq. (37).

$$F_{\text{Av}}^{\text{el}} = \left(-e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},\text{pH}}\right)\left[\left(\frac{\partial\theta_0}{\partial\text{pH}}\right)_T + 2\left(\frac{\partial\theta_+}{\partial\text{pH}}\right)_T + \left(\frac{\partial\theta_{\text{C}}}{\partial\text{pH}}\right)_T + \left(\frac{\partial\theta_{\text{A}}}{\partial\text{pH}}\right)_T\right] + \left(e\frac{\delta_0}{c_1} + \frac{e\delta_0 T}{(c_1)^2}\left(\frac{\partial c_1}{\partial T}\right)_{\{\theta_i\},\text{pH}}\right) \times \left[\left(\frac{\partial\theta_{\text{C}}}{\partial\text{pH}}\right)_T - \left(\frac{\partial\theta_{\text{A}}}{\partial\text{pH}}\right)_T\right] \tag{43}$$

Figure 4 shows the function $F_{\text{Av}}^{\text{el}}(\text{pH})$ for the studied system magnetite/KNO$_3$, for the same two concentrations of the inert electrolyte, as those accepted to show the behavior of $(\partial\theta_0/\partial\text{pH})$ shown in Fig. 3.

One can see in Fig. 4 that the function $F_{\text{Av}}^{\text{el}}(\text{pH})$ is much more symmetrical for the high electrolyte concentration. Correspondingly, Fig. 2 shows that the experimental function Q_{Av} gets then closer to the value $\frac{Q_{\text{a1}}+Q_{\text{a2}}}{2}$.

Although it is difficult to prove it in a simple rigorous way, we feel, that the lack of symmetry in the electrical function $F_{\text{Av}}^{\text{el}}$, should be related to the lack of symmetry of the two branches of the titration curve,

$$-\delta_0(\text{PZC} + \Delta\text{pH}) = \delta_0(\text{PZC} - \Delta\text{pH}) \tag{44}$$

observed on the experimental titration curves reported by Blesa et al. (1984) for the system magnetite/KNO$_3$. For the two concentrations of the inert electrolyte studied in Figs. 3 and 4, Fig. 5 shows the behavior of the experimental titration curves.

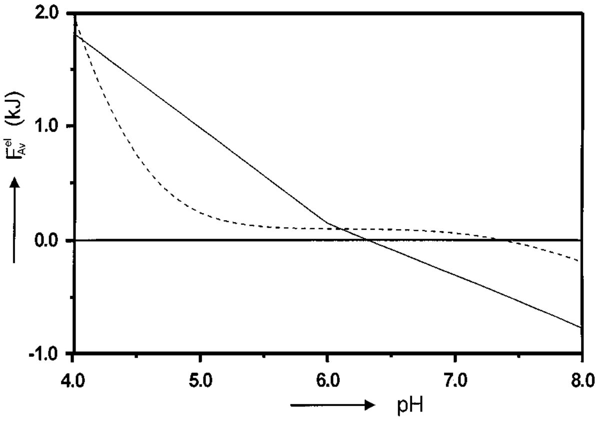

Figure 4. The shape of the function $F_{\text{Av}}^{\text{el}}(\text{pH})$, in the system magnetite/KNO$_3$, calculated by us for the temperature 353 K, and for two different concentrations of the inert electrolyte; 0.1 mol/dm^3 (the solid line, ——), and 0.001 mol/dm^3 (the broken line, – – –). The calculations were carried out by using the parameters collected in Table 2. While considering the symmetry condition 40, please note that for this temperature PZC = 6.

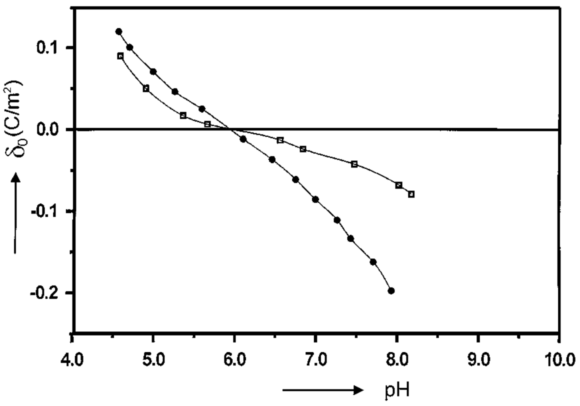

Figure 5. The experimental titration curves reported by Blesa (Blesa et al., 1984) for temperature 353 K, and the two different concentrations of the inert electrolyte (●) 0.1 mol/dm^3, (□) 0.001 mol/dm^3.

One can see that the condition (44) is much better fulfilled for the high electrolyte concentration, for which Q_{Av} values are closer to $\frac{Q_{\mathrm{a1}}+Q_{\mathrm{a2}}}{2}$. Thus, it seems that the symmetry of the titration curves may be a practical guide to a successful application of the Kallay's procedure of estimating $\frac{Q_{\mathrm{a1}}+Q_{\mathrm{a2}}}{2}$. Of course, the validity of that practical guide deserves further theoretical studies.

Such model calculations will require first a full analysis of the temperature dependence of adsorption (titration) isotherms or a full analysis of accurately determined heats of titration in a wide range of pH. Unfortunately, the small body of the experimental data reported so far in literature, and certain problems related to their accuracy create, for the moment, serious limitations for an exhaustive study of such a kind.

Appendix

The derivatives $(\frac{\partial\theta_i}{\partial(\mathrm{pH})})_T$, $(i = 0, +, \mathrm{A}, \mathrm{C})$ are to be evaluated from Eq. (3). For instance,

$$\left(\frac{\partial\theta_0}{\partial(\mathrm{pH})}\right)_T = (-1)\cdot\frac{\begin{vmatrix} \frac{\partial F_0}{\partial \mathrm{pH}} & \frac{\partial F_0}{\partial\theta_+} & \frac{\partial F_0}{\partial\theta_\mathrm{C}} & \frac{\partial F_0}{\partial\theta_\mathrm{A}} \\ \frac{\partial F_+}{\partial \mathrm{pH}} & \frac{\partial F_+}{\partial\theta_+} & \frac{\partial F_+}{\partial\theta_\mathrm{C}} & \frac{\partial F_+}{\partial\theta_\mathrm{A}} \\ \frac{\partial F_\mathrm{C}}{\partial \mathrm{pH}} & \frac{\partial F_\mathrm{C}}{\partial\theta_+} & \frac{\partial F_\mathrm{C}}{\partial\theta_\mathrm{C}} & \frac{\partial F_\mathrm{C}}{\partial\theta_\mathrm{A}} \\ \frac{\partial F_\mathrm{A}}{\partial \mathrm{pH}} & \frac{\partial F_\mathrm{A}}{\partial\theta_+} & \frac{\partial F_\mathrm{A}}{\partial\theta_\mathrm{C}} & \frac{\partial F_\mathrm{A}}{\partial\theta_\mathrm{A}} \end{vmatrix}}{\begin{vmatrix} \frac{\partial F_0}{\partial\theta_0} & \frac{\partial F_0}{\partial\theta_+} & \frac{\partial F_0}{\partial\theta_\mathrm{C}} & \frac{\partial F_0}{\partial\theta_\mathrm{A}} \\ \frac{\partial F_+}{\partial\theta_0} & \frac{\partial F_+}{\partial\theta_+} & \frac{\partial F_+}{\partial\theta_\mathrm{C}} & \frac{\partial F_+}{\partial\theta_\mathrm{A}} \\ \frac{\partial F_\mathrm{C}}{\partial\theta_0} & \frac{\partial F_\mathrm{C}}{\partial\theta_+} & \frac{\partial F_\mathrm{C}}{\partial\theta_\mathrm{C}} & \frac{\partial F_\mathrm{C}}{\partial\theta_\mathrm{A}} \\ \frac{\partial F_\mathrm{A}}{\partial\theta_0} & \frac{\partial F_\mathrm{A}}{\partial\theta_+} & \frac{\partial F_\mathrm{A}}{\partial\theta_\mathrm{C}} & \frac{\partial F_\mathrm{A}}{\partial\theta_\mathrm{A}} \end{vmatrix}} \qquad (\mathrm{A.1})$$

where

$$F_0 = -\ln K_{\mathrm{a2}}^{\mathrm{int}} - \frac{e\psi_0}{kT} - 2.3\,\mathrm{pH} - \ln\frac{\theta_0}{\theta_-} = 0 \qquad (\mathrm{A.2a})$$

$$F_+ = -\ln\left(K_{\mathrm{a1}}^{\mathrm{int}}\cdot K_{\mathrm{a2}}^{\mathrm{int}}\right) - \frac{2e\psi_0}{kT} - 4.6\,\mathrm{pH} - \ln\frac{\theta_+}{\theta_-} = 0 \qquad (\mathrm{A.2b})$$

$$F_\mathrm{C} = -\ln\left(K_{\mathrm{a2}}^{\mathrm{int}}/{}^*K_{\mathrm{C}}^{\mathrm{int}}\right) - \frac{e\psi_0}{kT} + \frac{e\delta_0}{kTc_1} + \ln a_\mathrm{C} - \ln\frac{\theta_\mathrm{C}}{\theta_-} = 0 \qquad (\mathrm{A.2c})$$

$$F_\mathrm{A} = -\ln\left(K_{\mathrm{a2}}^{\mathrm{int}}\cdot{}^*K_{\mathrm{A}}^{\mathrm{int}}\right) - \frac{e\psi_0}{kT} - \frac{e\delta_0}{kTc_1} + \ln a_\mathrm{A} - 4.6\,\mathrm{pH} - \ln\frac{\theta_\mathrm{A}}{\theta_-} = 0 \qquad (\mathrm{A.2d})$$

While evaluating the partial derivatives $(\frac{\partial F_i}{\partial \mathrm{pH}})$ occurring in the numerator of Eq. (A.1), one has to consider ψ_0 as a function of pH defined in Eq. (8). Then,

$$\frac{\partial F_0}{\partial \mathrm{pH}} = -2.3\frac{t}{t+\beta} \quad \frac{\partial F_+}{\partial \mathrm{pH}} = -4.6\frac{t}{t+\beta}$$
$$\frac{\partial F_\mathrm{C}}{\partial \mathrm{pH}} = 2.3\frac{\beta}{t+\beta} \quad \frac{\partial F_\mathrm{A}}{\partial \mathrm{pH}} = -2.3\frac{2t+\beta}{t+\beta} \qquad (\mathrm{A.3})$$

Further, while, evaluating the derivatives: $(\frac{\partial F_i}{\partial\theta_i})$, $(i, j = 0, +, \mathrm{A}, \mathrm{C})$ one has to consider the equation,

$$\delta_0 = B(2\theta_+ + 2\theta_\mathrm{A} + \theta_0 - 1) \qquad (\mathrm{A.4})$$

to obtain:

$$\frac{\partial F_0}{\partial\theta_0} = -\frac{\theta_0+\theta_-}{\theta_0\theta_-} \quad \frac{\partial F_+}{\partial\theta_+} = -\frac{\theta_+ + \theta_-}{\theta_+\theta_-}$$
$$\frac{\partial F_\mathrm{C}}{\partial\theta_\mathrm{C}} = -\frac{\theta_\mathrm{C}+\theta_-}{\theta_\mathrm{C}\theta_-} \quad \frac{\partial F_\mathrm{A}}{\partial\theta_\mathrm{A}} = -\frac{\theta_\mathrm{A}+\theta_-}{\theta_\mathrm{A}\theta_-} - 2w$$
$$\frac{\partial F_0}{\partial\theta_+} = \frac{\partial F_0}{\partial\theta_\mathrm{C}} = \frac{\partial F_0}{\partial\theta_\mathrm{A}} = \frac{\partial F_+}{\partial\theta_0} = \frac{\partial F_+}{\partial\theta_\mathrm{C}} = \frac{\partial F_+}{\partial\theta_\mathrm{A}} = \frac{\partial F_\mathrm{A}}{\partial\theta_\mathrm{C}} = -\frac{1}{\theta_-} \qquad (\mathrm{A.5})$$
$$\frac{\partial F_\mathrm{C}}{\partial\theta_0} = -\frac{1}{\theta_0} + w \quad \frac{\partial F_\mathrm{C}}{\partial\theta_+} = \frac{\partial F_\mathrm{C}}{\partial\theta_\mathrm{A}} = -\frac{1}{\theta_-} + 2w$$
$$\frac{\partial F_\mathrm{A}}{\partial\theta_0} = -\frac{1}{\theta_0} - w \quad \frac{\partial F_\mathrm{A}}{\partial\theta_+} = -\frac{1}{\theta_-} - 2w$$

where

$$w = \frac{eB}{kTc_1} \tag{A.6}$$

After solving the determinants, we arrive at the following explicit form of the derivatives $\frac{\partial\theta_i}{\partial \mathrm{pH}}$,

$$\frac{\partial\theta_i}{\partial \mathrm{pH}} = -\frac{2.3\theta_i}{t+\beta}\cdot\frac{X_i}{Y}, \quad i = 0, +, \mathrm{A}, \mathrm{C} \tag{A.7}$$

where

$$\begin{aligned}
X_0 &= t[\theta_- + \theta_\mathrm{C} - \theta_+ - \theta_\mathrm{A}] + 2wt[\theta_-\theta_\mathrm{A} - \theta_+\theta_\mathrm{C}]\\
&\quad + \beta[\theta_\mathrm{C} - \theta_\mathrm{A}]\\
X_+ &= t[\theta_0 + 2\theta_- + 2\theta_\mathrm{C}]\\
&\quad + wt[\theta_0\theta_\mathrm{C} + \theta_\mathrm{A}\theta_0 + 4\theta_\mathrm{A}\theta_- + 4\theta_\mathrm{A}\theta_\mathrm{C}]\\
&\quad + \beta[\theta_\mathrm{C} - \theta_\mathrm{A}]\\
X_\mathrm{C} &= -t[\theta_0 + 2\theta_+ + 2\theta_\mathrm{A}]\\
&\quad + wt[\theta_0\theta_+ + \theta_-\theta_0 + 4\theta_-\theta_+ + 4\theta_-\theta_\mathrm{A}]\\
&\quad - \beta[\theta_0 + \theta_+ + \theta_- + 2\theta_\mathrm{A}]\\
X_\mathrm{A} &= t[\theta_0 + 2\theta_- + 2\theta_\mathrm{C}]\\
&\quad - wt[\theta_0\theta_+ + \theta_-\theta_0 + 4\theta_-\theta_+ + 4\theta_+\theta_\mathrm{C}]\\
&\quad + \beta[\theta_0 + \theta_+ + \theta_- + 2\theta_\mathrm{C}]\\
Y &= 1 + w[\theta_\mathrm{A}(2\theta_- + 2\theta_\mathrm{C} + \theta_0)\\
&\qquad + \theta_\mathrm{C}(2\theta_+ + 2\theta_\mathrm{A} + \theta_0)]
\end{aligned} \tag{A.8}$$

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