Four-Layer Model for Simple Ion Adsorption at Energetically Heterogeneous Metal Oxide/Electrolyte Interfaces: Quantitative Thermodynamic Description Including Related Calorimetric Effects

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Equations that are developed describe enthalpic effects of ion adsorption, which is predicted by the four-layer model assuming that the anions and cations of the inert electrolyte (1:1) are adsorbed in two distinct layers located different distances from the surface. The theoretical development has been based on the 2-pK charging mechanism. Furthermore, the expressions that are developed for the four-layer model take into account the energetic heterogeneity of the surface, assuming small correlations exist between adsorption energies of different surface complexes.

Introduction

It has long been realized that knowledge of the enthalpic effects accompanying the adsorption of ions may shed more light onto the fundamental features of ion adsorption at the oxide/electrolyte interface. The enthalpic effects were first elucidated from the temperature dependence of ion adsorption[1−13], but now they are more frequently measured directly in appropriate calorimetric experiments[14−23]. Until very recently, interpretation of the experimental data was carried out mostly on a qualitative level. The reason, as Kallay and Zalac have emphasized in their recent review[24], was that the measured heat effects contain very complicated information that needs an advanced theoretical analysis. The first attempts to carry out a quantitative analysis were reported by de Keizer et al.[19] in 1990 and by Rudzinski and co-workers[25,26] in 1991. Their analyses have recently been extended[27−30] to new types of calorimetric experiments. We have also shown that the description of the temperature dependence of the adsorption isotherms of ions[31] introduces essentially the same functions and parameters that appear in the theoretical description of the directly measured enthalpic effects and in the temperature dependence of the individual adsorption isotherms of simple ions.[32]

The most commonly used models of surface complexation represent ion adsorption at oxide/electrolyte interfaces. A variety of such models have been employed. Their construction can differ in the modeling of the surface (charging mechanism of surface sites) and interfacial region (distribution of ions).[33−36]

Of all the published models, the one that is most frequently used is the so-called triple layer model (TLM)[37−40] along with the 2-pK charging mechanism. All of the assumptions accompanying the construction of the TLM were discussed by Robertson and Leckie[36] and by Sverjensky and Sahai.[41−43] However, despite the great success of TLM in explaining many features of the actual adsorption systems, some feel that this popular model needs significant improvement.

The modifications of TLM were carried out in three directions. One group of scientists has challenged the charging mechanism of the surface oxygens. That hypothesis is commonly called the 1-pK charging mechanism[44], and its refinement is the multisite complexation model (MUSIC) of the oxide electrolyte interface.[45−48] Another group of scientists has accepted the classical 2-pK charging mechanism but has emphasized the importance of a small degree of crystallographic organization of the surface oxygens compared to the situation found in the interior of an oxide crystal. That smaller degree of surface organization should lead to a different status of the surface oxygens, resulting in surface energetic heterogeneity.[25,26,49−53]

The third refinement of the classical 2-pK TLM is the four-layer model (FLM). It was introduced by Barrow et al.[54] A new layer, (actually the fourth layer, as the name indicates, but situated as the second layer, next to the surface layer "0" where protons are adsorbed) was reserved first for the bivalent metal ions or anions of multiproton oxyacids. Cations and anions of a basic electrolyte were placed in the same layer as in the TLM. Another kind of FLM was suggested by Bousse et al.,[55] who presented a diagram of FLM in which there are only ions of a basic electrolyte and the potential-determining ions H$^+$. They argued that anions and cations of the basic electrolyte are not located in the same layer (as in TLM) but in two separate layers. A schematic picture of such a FLM is shown in Figure 1. The first rigorous thermodynamic description that is based on that physical model and provides theoretical expressions for all of the experimentally measured physicochemical quantities has recently been published.[56−58]

Recently, I have made further improvements to FLM (the improved version is het-FLM), taking into account the energetic heterogeneity of the actual oxide surfaces.[59] Distinguishing four layers instead of three, in the adsorbed phase, does not introduce any new parameters. However, as expected, the higher complexity of the refined model results in a higher complexity of the related theoretical description. Thus, to keep the size of the previous publication[59] within reasonable limits, the related discussion of the enthalpic effects was postponed for this publication. The present work, which is a continuation of that

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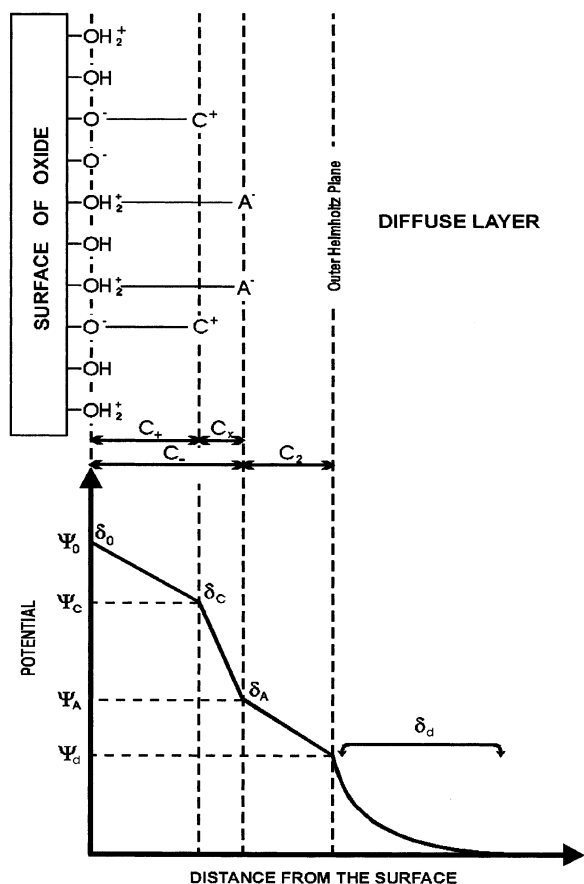
Figure 1. Diagramatic presentation of the four-layer model (FLM). ψ_0, δ_0 are the surface potential and the surface charge density in the 0 plane, respectively; ψ_d and δ_d are the diffuse layer potential and its charge, respectively; ψ_C, δ_C, ψ_A, δ_A are the potentials and the charges, respectively from the specifically adsorbed ions (cations C^+ and anions A^- of the inert electrolyte: C_+, C_-, C_x, and C_2 are the electrical capacitances, which are constant in the regions between the planes).

paper, was carried out to arrive at a complete thermodynamic description (including the description of the enthalpic effects equations).

Theory

1. Charging Mechanism and Assumed Structure of the Interfacial Region in the Four-Layer Model. The potential-determining ions H^+, cations C^+, and anions A^- of the basic electrolyte form the following surfaces complexes according to the 2-pK charging mechanism: SOH^0, SOH_2^+, SO^-C^+, and $SOH_2^+A^-$, where S is the surface metal atom. The concentrations of these complexes on the surface are denoted by $[SOH^0]$, $[SOH_2^+]$, $[SO^-C^+]$, and $[SOH_2^+A^-]$. $[SO^-]$ is the surface concentration of the "unoccupied" surface oxygens that are, in fact, engaged in adsorption of nondissociated water molecules. The first rigorous thermodynamic description of the FLM has been described[56−58]. Here, only the basic definitions will be repeated for the readers' convenience.

The total number of sites capable of forming surface complexes, N_s, is given by

$$N_s = [SO^-] + [SOH^0] + [SOH_2^+] + [SOH_2^+A^-] + [SO^-C^+] \quad (1)$$

The surface coverage values θ_i of the individual surface

complexes ($i = 0, +, C, A$) and free sites ($i = -$) are defined as follows:

$$\theta_0 = \frac{[SOH^0]}{N_s} \qquad \theta_+ = \frac{[SOH_2^+]}{N_s} \qquad \theta_C = \frac{[SO^-C^+]}{N_s}$$

$$\theta_A = \frac{[SOH_2^+A^-]}{N_s} \qquad \theta_- = \frac{[SO^-]}{N_s} \quad (2)$$

The surface charge density, δ_0, that is monitored in the titration experiments is given by

$$\delta_0 = B_s(\theta_+ + \theta_A - \theta_- - \theta_C) \qquad B_s = N_s e \quad (3)$$

The charges of the specifically adsorbed ions (forming the ion-pair surface complexes), which are cations and anions of the basic electrolyte in their planes, are respectively given by
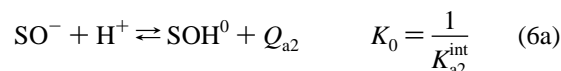
$$\theta_C = B_s\theta_C \qquad \text{and} \qquad \delta_A = -B_s\theta_A \quad (4)$$

For the entire compact layer, the electroneutrality condition must be fulfilled (i.e., the sum of all charges must be equal to zero), so the diffuse-layer charge, δ_d, is given by the expression
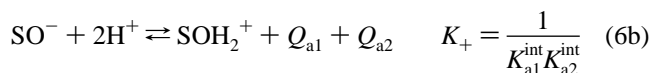
$$\delta_d = B_s(\theta_- - \theta_+) \quad (5)$$

The relationships between the capacitances, the potentials, and the charges within the individual electric layers were developed previously.[56−58]
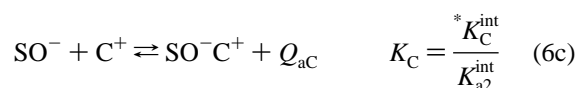
2. Expressions for the Individual Adsorption Isotherms of Ions. To arrive at the adsorption isotherm equations, we consider the reactions leading to the adsorption of ions onto the "free" sites (SO^-). The surface reactions, the related intrinsic equilibrium constants, and the heats of these reactions (Q_{ai}, $i = 1, 2, C, A$) are given by the following equations:[30,56]
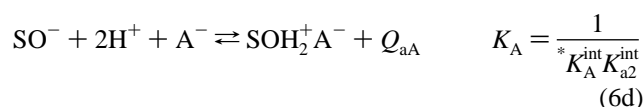
$$SO^- + H^+ \rightleftharpoons SOH^0 + Q_{a2} \qquad K_0 = \frac{1}{K_{a2}^{int}} \quad (6a)$$

$$K_{a2}^{int} \exp\left\{\frac{e\psi_0}{kT}\right\} = \frac{(a_H)\theta_-}{\theta_0}$$

$$SO^- + 2H^+ \rightleftharpoons SOH_2^+ + Q_{a1} + Q_{a2} \qquad K_+ = \frac{1}{K_{a1}^{int}K_{a2}^{int}} \quad (6b)$$

$$K_{a1}^{int}K_{a2}^{int} \exp\left\{\frac{2e\psi_0}{kT}\right\} = \frac{(a_H)^2\theta_-}{\theta_+}$$

$$SO^- + C^+ \rightleftharpoons SO^-C^+ + Q_{aC} \qquad K_C = \frac{^*K_C^{int}}{K_{a2}^{int}} \quad (6c)$$

$$K_{a2}^{int}/^*K_C^{int} \exp\left\{\frac{e\psi_C}{kT}\right\} = \frac{(a_C)\theta_-}{\theta_C}$$

$$SO^- + 2H^+ + A^- \rightleftharpoons SOH_2^+A^- + Q_{aA} \qquad K_A = \frac{1}{^*K_A^{int}K_{a2}^{int}} \quad (6d)$$

$$K_{a2}^{int} {}^*K_A^{int} \exp\left\{\frac{e(2\psi_0 - \psi_A)}{kT}\right\} = \frac{(a_H)^2(a_A)\theta_-}{\theta_A}$$

K_{a1}^{int}, K_{a2}^{int}, $^*K_C^{int}$, and $^*K_A^{int}$ are the commonly used symbols in the

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literature[37,38] for intrinsic equilibrium constants of the following reactions:

$$SOH_2^+ \xrightarrow{K_{a1}^{int}} SOH^0 + H^+ \tag{7a}$$

$$SOH^0 \xrightarrow{K_{a2}^{int}} SO^- + H^+ \tag{7b}$$

$$SOH^0 + C^+ \xrightarrow{{}^*K_C^{int}} SO^-C^+ + H^+ \tag{7c}$$

$$SOH_2^+A^- \xrightarrow{{}^*K_A^{int}} SOH^0 + H^+ + A^- \tag{7d}$$
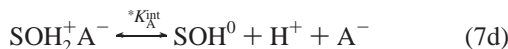
In eqs 6, a_C, a_A, and a_H are the activities of cations, anions, and protons, respectively.

The set of the nonlinear eqs 6a–d can be transformed into an equation having the form of multicomponent Langmuir-like adsorption isotherms of ions θ_i ($i = 0, +, A, C$):

$$\theta_i = \frac{K f_i}{1 + \sum_i K f_i} \qquad i = 0, +, A, C \tag{8}$$

The K_i's are the equilibrium constants defined for eqs 6, and the f_i's are the functions of the activity of protons and salt ions in the equilibrium bulk electrolyte having the following forms:[56]

$$f_0 = \exp\left\{-\frac{e\psi_0}{kT} - 2.3\,\mathrm{pH}\right\}$$

$$f_+ = \exp\left\{-\frac{2e\psi_0}{kT} - 4.6\,\mathrm{pH}\right\} \tag{9ab}$$

$$f_C = a_C \exp\left\{-\frac{e\psi_0}{kT} + \frac{e\delta_0}{kTC_+}\right\} \tag{9c}$$

$$f_A = a_A \exp\left\{-\frac{e\psi_0}{kT} - \frac{e\delta_0}{kTC_+} - \frac{e\delta^*}{kTC_+} + \frac{e\delta^*}{kTC_-} - 4.6\,\mathrm{pH}\right\} \tag{9d}$$

where

$$\delta^* = \delta_A + \delta_d = B_S(\theta_- - \theta_+ - \theta_A) \tag{9e}$$

The surface potential in eqs 6 can be calculated as $\psi_0(\mathrm{pH})$ from the equation developed by Bousse et al.,[60,61]

$$2.303(\mathrm{PZC} - \mathrm{pH}) = \frac{e\psi_0}{kT} + \sinh^{-1}\left(\frac{e\psi_0}{\beta kT}\right) \tag{10}$$

where the dimensionless quantity β has the form[60]

$$\beta = \frac{2e^2 N_s}{C_t kT}\left(\frac{K_{a2}^{int}}{K_{a1}^{int}}\right)^{1/2}$$

and where C_t is the linear capacitance of the double electrical layer that can be calculated in the way proposed by Bousse et al.[60,61] Note that the quantity β is not a best-fit parameter but rather a function of the equilibrium constant describing proton adsorption onto the surface.

Equations 8–10 may be solved by calculating the individual adsorption isotherms θ_i and the surface charge δ_0 as a function of pH, as was shown in our previous papers.[56–59]

In our recent theoretical investigations,[52,53,62] we modified the model of a homogeneous surface by taking into account

the smaller degree of crystallographic organization of the surface oxygens compared to the situation in the interior of a crystal. That smaller degree of surface organization leads to a diversity in the features of the surface oxygens, resulting in "surface energetic heterogeneity".[63] That surface heterogeneity causes the free energy of complex formation to change from one surface oxygen to another.

We took into account two physical situations: the case of high correlations between the adsorption energies of different surface complexes when going from one oxygen to another and the case of small correlations between those energies. Our analysis showed, however, that the most realistic model seems to be the one that assumes that small correlations exist between the adsorption energies of different complexes formed on various surface oxygens. This was proved by analyses of the behavior of potentiometric, electrokinetic, and radiometric data[62], bivalent ion adsorption at low ion concentrations[52], and calorimetric effects accompanying ion adsorption.[29] Thus, while developing the expressions for the enthalpic effects for the het-FLM, we will consider only the case of small correlations between adsorption energies of different surface complexes.

With the assumption of such small correlations, one arrives at the following system of nonlinear equations describing the adsorption isotherms of ions:[62]

$$\theta_{it} = \frac{[\sum_i K_i f_i]^{kT/c_i}}{1 + [\sum_i K_i f_i]^{kT/c_i}} \qquad i = 0, +, A, C \tag{11}$$

f_i values ($i = 0, +, A, C$) are given by eqs 9a–9e.

In eq 11, c_i ($i = 0, +, A, C$) represents the heterogeneity parameters that are proportional to the variance $\pi^2 c_i^2/3$ of a Gaussian-like, fully symmetrical function describing the dispersion of adsorption energies of complex i on different surface oxygens.[62]

The method of solving the set of eqs 11 and 9 is similar to that described in the homogeneous FLM.[57] At first, an attempt is made to reduce the number of nonlinear equations (four) in system 11. The starting point in calculating the function θ_{it} is to solve the set of two nonlinear equations obtained from eqs 3 and 9e and to take account eq 11 into account:

$$F_1(\delta_0, \delta^*) = B_s \frac{1 - [K_+ f_+]^{kT/c_+} - [K_A f_A]^{kT/c_A}}{1 + \sum_i [K_i f_i]^{kT/c_i}} - \delta^* = 0$$

$$i = 0, +, A, C \tag{12a}$$

$$F_2(\delta_0, \delta^*) = $$
$$B_s \frac{[K_+ f_+]^{kT/c_+} + [K_A f_A]^{kT/c_A} - [K_C f_C]^{kT/c_C} - 1}{1 + \sum_i [K_i f_i]^{kT/c_i}} - \delta_0 = 0$$

$$i = 0, +, A, C \tag{12b}$$

$f_C = f_C(\delta_0)$ and $f_A = f_A(\delta_0, \delta^*)$ were used to calculate δ^* and δ_0 for each value of pH. Further transformations (for details, see ref 59) lead to the following equation for $\delta^* = \delta^*(\delta_0)$:

$$\delta^* = \frac{\delta_0(2 + [K_0 f_0]^{kT/c_0} + [K_C f_C]^{kT/c_C}) + B_S[K_C f_C]^{kT/c_C}}{2 + [K_0 f_0]^{kT/c_0} + 2[K_C f_C]^{kT/c_C}} \tag{13}$$

After substituting the above relation into eq 12b (the variable δ^* appears in eq 12b only inside the function f_A), the resulting expression is implicit only with respect to the variable δ_0. Then, eq 12b can be solved numerically using one of the iteration methods to obtain δ_0 values for each pH. Finally, having calculated the values of surface charge δ_0, we calculate individual isotherms of ions (θ_i values) from eq 11.

The experimental titration curves corresponding to different concentrations of the inert electrolyte usually have a common intersection point (CIP) at the point of zero charge (PZC) (which is the concentration of potential-determining ions (PDI) at which the surface charge is equal to zero), so PZC = pH when δ_0 = 0. This means that the PZC value for a given system of oxide and electrolyte does not depend practically on salt concentration in the bulk solution.

Rudzinski et al.[62] were the first to draw attention to the fact that such PZC independence of salt concentration can be formally expressed by the following two equations:

$$\delta_0(\text{pH} = \text{PZC}) = 0 \quad \text{and} \quad \frac{\partial \delta_0(\text{pH} = \text{PZC})}{\partial a = a_C = a_A} = 0 \quad (14)$$

Drawing formal mathematical consequences from the above formal criterion[56,62] decreases the number of the equilibrium constants K_{a1}^{int}, K_{a2}^{int}, $^*K_C^{int}$, and $^*K_A^{int}$ (best fit parameters) determined by fitting suitable experimental data by two. In doing so,[52,56,62] we obtain two equations for the het-FLM:[59]

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

$$(15a)$$

$$\frac{kT}{c_A}\left(\frac{H^2 a P^*}{K_{a2}^{int*}K_A^{int}}\right)^{kT/c_A}\left(1+\frac{a}{P^*}\frac{\partial P^*}{\partial a}\right) - \frac{kT}{c_C}\left(\frac{^*K_C^{int}a}{K_{a2}^{int}}\right)^{kT/c_C} = 0$$

$$(15b)$$

where $H = 10^{-\text{PZC}}$ and

$$P^* = \exp\left\{\frac{e\delta^*}{kT}\left(\frac{1}{C_-}-\frac{1}{C_+}\right)\right\} \quad (16a)$$

$$\delta^* = -B_s\frac{(K_C a)^{kT/c_C}}{2+(K_0H)^{kT/c_0}+2(K_C a)^{kT/c_C}} \quad (16b)$$

$$\frac{\partial P^*}{\partial a} = P^* \ln P^*\left(\frac{\frac{kT}{c_C}}{a}\frac{2+(K_0H)^{kT/c_0}}{2+(K_0H)^{kT/c_0}+2(K_C a)^{kT/c_C}} + \frac{d\ln(1/C_- - 1/C_+)}{da}\right) \quad (16c)$$

To calculate the equilibrium constant values from eq 15 for a given set of heterogeneity parameters kT/c_i (i = 0, +, A, C) , we assume K_{a2}^{int} and $^*K_C^{int}$ to be the starting values and then calculate K_{a1}^{int} from eq 15a and $^*K_A^{int}$ from eq 15b.

Because the het-FLM is the most complex model we used (it has more general assumptions), for certain parameter values, it should reduce to the triple layer model (TLM) and the four-layer model (FLM), assuming the surface is energetically homogeneous, and the het-TLM−triple layer model, assuming the oxide surface is energetically heterogeneous. These reduction
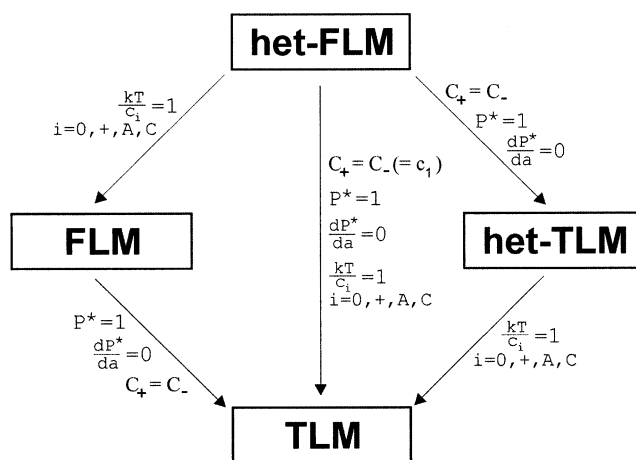
Figure 2. Schematic picture of the reduction conditions for the investigated models.

conditions are presented in Figure 2. We find that eqs 15 can also be used also as a general set of equations to calculate the equilibrium constant parameters for models that are simpler than the het-FLM.

3. Theoretical Expressions for the Heats of Adsorption Developed by Applying the Four-Layer Model While Taking into Account Energetic Surface Heterogeneity. The accompanying heat effects in the titration calorimetry experiment are measured upon the addition of an acid or base. After introducing an outgassed solid sample into a solution, the pH of that solution is measured. Then, a titration is carried out (from the basic or acidic side), and the evolved heat is recorded. Depending on the reported experiments, the consumption (adsorption) of protons and ions of the inert electrolyte, which is accompanied by a change in pH of ΔpH, is monitored. We have shown in our previous publications[27−29] that the heat data reported by Machesky et al.[17,20,21] for the goethite/NaNO3 and alumina/NaCl interfaces, by Mehr et al.[18] for the TiO2/NaCl interface, and by Casey[23] for the silica/different electrolyte interfaces are described by the following equation:

$$Q_{pr} = \frac{\int_{pH}^{pH+\Delta pH}\sum_i Q_i\left(\frac{\partial\theta_i}{\partial pH}\right)_T dpH}{\int_{pH}^{pH+\Delta pH}\left[2\left(\frac{\partial\theta_+}{\partial pH}\right)_T + 2\left(\frac{\partial\theta_A}{\partial pH}\right)_T + \left(\frac{\partial\theta_0}{\partial pH}\right)_T\right]dpH}$$

$$i = 0, +, C, A \quad (17)$$

Q_0, Q_+, Q_C, and Q_A are the molar differential heats accompanying the formation of the SOH, SOH$_2^+$, SO$^-$C$^+$, and SOH$_2^+$A$^-$ surface complexes, respectively. The derivatives $(\partial\theta_i/\partial pH)_T$ with i = 0, +, A, C in eq 17, which correspond to het-FLM, are given in Appendix A.

Rudzinski et al.[27−29] subjected these experimental Q_{pr} data to quantitative analysis based on TLM models. Very recently, I adopted the FLM approach for this purpose.[30] That attempt, however, was based on the simpler FLM approach that ignores the energetic heterogeneity of the surface oxygens because of the complexity of the theoretical expressions obtained when FLM is applied. The surface energetic heterogeneity may play a smaller role in the system that was subjected to quantitative analysis.[30] In general, however, this surface energetic heterogeneity cannot be ignored no matter how many complicated expressions must be used.

TABLE 1: Surface Reactions, Equilibrium Constants, and Heats of Reactions

reaction type	equilibrium constant[a]	heat of reaction
$SOH^0 + H^+ \leftrightarrow SOH_2^+$	$-pK_{a1}^{int}$	Q_{a1}
$SO^- + H^+ \leftrightarrow SOH^0$	$-pK_{a2}^{int}$	Q_{a2}
$SOH^0 + H^+ + A^- \leftrightarrow SOH_2^+A^-$	$-p^*K_A^{int}$	$Q_{aA} - Q_{a2}$
$SO^-C^+ + H^+ \leftrightarrow SOH^0 + C^+$	$-p^*K_C^{int}$	$Q_{a2} - Q_{aC}$
$SO^- + 2H^+ \leftrightarrow SOH_2^+$	$-pK_{a1}^{int} - pK_{a2}^{int}$	$Q_{a1} + Q_{a2}$
$SO^- + 2H^+ + A^- \leftrightarrow SOH_2^+A^-$	$-pK_{a2}^{int} - p^*K_A^{int}$	Q_{aA}
$SO^- + C^+ \leftrightarrow SO^-C^+$	$-p^*K_C^{int} - pK_{a2}^{int}$	Q_{aC}
$SOH_2^+ + A^- \leftrightarrow SOH_2^+A^-$	$-pK_{a1}^{int} - p^*K_A^{int}$	$Q_{aA} - Q_{a1} - Q_{a2}$

[a] $pK = -\log K$.

For the heterogeneous FLM model, assuming that there are small correlations between the adsorption energies of various surface complexes, the Q_i's take the following form:

$$Q_i = Q_i^{hom} - c_i \ln \frac{\theta_i}{\theta_-} \qquad i = 0, +, A, C \qquad (18)$$

The Q_i^{hom} terms are the expressions for the homogeneous FLM[30],

$$Q_0^{hom} = Q_{a2} - e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},pH} \qquad (19a)$$

$$Q_+^{hom} = Q_{a1} + Q_{a2} - 2e\psi_0 - \frac{2e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},pH} \qquad (19b)$$

$$Q_C^{hom} = Q_{aC} - e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},pH} + \\ e\frac{\delta_0}{C_+} + \frac{e\delta_0 T}{(C_+)^2}\left(\frac{\partial C_+}{\partial T}\right)_{\{\theta_i\},pH} + k\left(\frac{\partial \ln a_C}{\partial(1/T)}\right)_{pH} \qquad (19c)$$

$$Q_A^{hom} = Q_{aA} - e\psi_0 - \frac{e}{T}\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{\{\theta_i\},pH} - e\frac{\delta_0 + \delta^*}{C_+} - \\ \frac{e(\delta_0 + \delta^*)T}{(C_+)^2}\left(\frac{\partial C_+}{\partial T}\right)_{\{\theta_i\},pH} + e\frac{\delta^*}{C_-} + \frac{e\delta^* T}{(C_-)^2}\left(\frac{\partial C_-}{\partial T}\right)_{\{\theta_i\},pH} + \\ k\left(\frac{\partial \ln a_A}{\partial(1/T)}\right)_{pH} \qquad (19d)$$

where Q_{a1}, Q_{a2}, Q_{aC}, and Q_{aA} are the are the heats of the reactions 1a, 1b, 7c, and 7d, respectively,

$$Q_{ai} = -k\frac{d \ln K_{ai}^{int}}{d(1/T)}, \qquad i = 1, 2$$

$$Q_{aC} = -k\frac{d \ln(K_{a2}^{int}/^*K_C^{int})}{d(1/T)}$$

$$Q_{aA} = -k\frac{d \ln(K_{a2}^{int*}K_A^{int})}{d(1/T)} \qquad (20)$$

Surface reactions, equilibrium constants, and heats of reactions are collected in Table 1.

As in our previous publication,[30] while calculating the derivatives $(\partial C_+/\partial T)_{\{\theta_i\},pH}$ and $(\partial C_-/\partial T)_{\{\theta_i\},pH}$, we followed

Blesa's recommendation[8] that C_+ and C_- be treated as linear functions of temperature:

$$C_+ = C_+^0 + \alpha_+\Delta T \qquad \text{and} \qquad C_- = C_-^0 + \alpha_-\Delta T \qquad (21)$$

These linear functions may be considered to be formal Taylor expansions around $T = T_0$ such that $C_+(T_0) = C_+^0$ and $C_-(T_0) = C_-^0$.

We have shown[25] that the derivatives $(\partial \ln a_i/\partial(1/T))_{\{\theta_i\},pH}$ $(i = C, A)$ in eqs 19 can be well approximated by the equation

$$\frac{\partial \ln a_i}{\partial(1/T)} = -2.0172 \times 10^{-8}T^4 \ln \gamma_i \qquad i = A, C \qquad (22)$$

Finally, the derivatives $(\partial\psi_0/\partial(1/T))_{\{\theta_i\},pH}$ in eqs 19 are evaluated from eq 10 and take the form

$$\left(\frac{\partial\psi_0}{\partial(1/T)}\right)_{pH} = -\psi_0 T\left[\frac{\beta}{\beta + t} + \frac{t}{\beta + t}\frac{Q_{a2} - Q_{a1}}{2kT}\right] + \\ 2.3\frac{kT}{e}\frac{\beta}{\beta + t}\frac{\partial PZC}{\partial(1/T)} \qquad (23)$$

where

$$t = \left[\left(\frac{e\psi_0}{\beta kT}\right)^2 + 1\right]^{-1/2} \qquad (23a)$$

In eq 23, the derivative $\partial PZC/\partial(1/T)$ should be replaced by the terms resulting from the formal differentiation of PZC with respect to $(1/T)$ in eqs 15a and 15b following the definitions of Q_{a1}, Q_{a2}, Q_{aC}, and Q_{aA} in eq 20. Therefore, we take the advantage of having two expressions for PZC(T) with which to develop interrelations betweem some temperature derivatives of interest. Thus, we calculate $\partial PZC/\partial(1/T)$ from the two equation systems (15a,16) and (15b,16):

$$\frac{\partial PZC}{\partial(1/T)} = -\frac{\left(\frac{\partial F_{PZC}^{(1)}}{\partial(1/T)}\right)_{PZC}}{\left(\frac{\partial F_{PZC}^{(1)}}{\partial PZC}\right)_{1/T}} \qquad (24a)$$

$$\frac{\partial PZC}{\partial(1/T)} = -\frac{\left(\frac{\partial F_{PZC}^{(2)}}{\partial(1/T)}\right)_{PZC}}{\left(\frac{\partial F_{PZC}^{(2)}}{\partial PZC}\right)_{1/T}} \qquad (24b)$$

$F_{PZC}^{(1)}$ and $F_{PZC}^{(2)}$ are eqs 15a and 15b, respectively. One must remember that the derivatives $(\partial F_{PZC}^{(i)}/\partial PZC)_{1/T}$ $(i = 1, 2)$ are equal to $-2.3H(\partial F_{PZC}^{(i)}/\partial H)_{1/T}$. After some algebra, one arrives at the complicated, explicit forms of eqs 24 given in Appendix B.

Finally, by solving eqs 24a and 24b, one arrives at the interrelation of the nonconfigurational heats of adsorption: Q_{a1}, Q_{a2}, Q_{aC}, and Q_{aA}.

Results and Discussion

While summarizing the theoretical considerations devoted to the four-layer model and assuming that small correlations exist between adsorption energies of different surface complexes (het-FLM), we have generated the following set of parameters that should be determined by fitting suitable experimental data:

(1) Two equilibrium constants. Application of the criterion in ref 14 yields eqs 15a and 15b, which allow us to decrease the number of free (to be fitted) equilibrium constants (K_{a1}^{int}, K_{a2}^{int}, $^*K_C^{int}$, $^*K_A^{int}$) by two.

(2) Two electrical capacitance parameters C_+ and C_- and their derivative $dln(1/C_- - 1/C_+)/da$.

(3) Two heterogeneity parameters. While assuming that small correlations exist between adsorption energies of various surface complexes for het-TLM,[29] we may treat kT/c_0, kT/c_+, kT/c_C, and kT/c_A as independent free parameters. However, we also realize that decreasing the number of such freely chosen parameters would result in increasing confidence in our numerical exercises, so we decreased the number of the free parameters from four to two according to the following rationalization. The energetic heterogeneity of surface oxygens should affect the surface complexes containing two protons in a similar way; therefore, we included $kT/c_+ = kT/c_A$ in our calculations. We also assumed that the energetic heterogeneity will similarly affect the adsorption of the first proton and the adsorption of cations carrying the same charge, so we used $kT/c_0 = kT/c_C$. In that way, we reduced the number of freely chosen heterogeneity parameters from four to two.

(4) Two nonconfigurational heats of adsorption Q_{a1} and Q_{a2}. In a previous publication,[29] we hypothesized that the enthalpic effects accompanying the purely Coulombic adsorption of alkali cations on the SO^- are negligible, so we used $Q_{aC} = 0$. Such a conclusion was, in fact, drawn by Kosmulski[10], who used radiometric methods to study the individual adsorption isotherms of ions of the inert electrolyte. The other heat of adsorption Q_{aA} can be calculated from eqs 24a and 24b.

(5) Two derivatives α_+ and α_-, which are defined from eqs 21 by dC_+/dT and dC_-/dT, respectively.

Because of the large number of parameters in the het-FLM equations describing the oxide/electrolyte interface, a reliable estimation of these parameters requires the consideration of a set of experiments differing in the methodology of the measurements and providing independent information about the electrolyte/metal oxide system under investigation. Such a set may be composed of potentiometric titration curves, individual adsorption isotherms of cations and anions of the inert electrolyte, electrokinetic curves, and results of calorimetric experiments (which is the aim of this paper). Such a system has not been published in the literature.

When there are such a large number of parameters, the best-fit procedure should be applied, and the numerical program must allow for model investigations. Then it is possible to change parameters, generate theoretical curves for various experiments, and become familiar with the influence of the values of these parameters on the shape and course of the curves describing these experiments. This allows for a narrowing of the physical boundaries of variability of the parameters whose values are obtained from the best-fit procedure.

As I showed in previous papers on the FLM model, there is some correlation between the parameters (e.g., different values of heterogeneity parameters kT/c_i ($i = 0, +, A, C$) (Table 5[59])); also, different values of the derivative $dln(1/C_- - 1/C_+)$ (Figure 6[56]) predict similar differences between the PZC values and the isoelectric point (IEP) (mathematical relations between the PZC and IEP values have been discussed[59]). There is a compensation effect (i.e., for different values of these parameters, we obtain the same results). This effect can be eliminated only analyzing a complete experimental set; different parameters
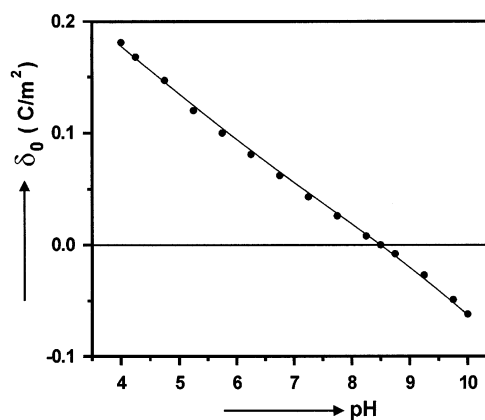
Figure 3. Comparison of the experimental potentiometric titration data $\delta_0(pH)$ reported by Machesky and Jacobs[20] for the system alumina/0.1 mol/dm³ NaCl (•) with the theoretical data calculated by using the parameters collected in Table 1. Lines indicating het-FLM (—) and het-TLM (− − −) overlap each other.

have different effects on curves obtained in different kinds of experiments.

Because of these problems, the aim of this paper is not to obtain real values of parameters but to present possible calculations of calorimetric effects by means of the het-FLM model using the equations derived here.

While selecting the experimental data for analysis, we tried to determine which of the adsorption systems that had been studied by titration calorimetry might exhibit the strongest heterogeneity effects. The experimental data reported by Machesky and Jacobs,[20,21] who used titration calorimetry to study heats of proton adsorption in the γ-alumina/NaCl electrolyte system, were selected. These data were also studied by us[29] when we used the triple-layer model with the assumption that the heterogeneity effects describe adsorption of ions at the oxide/electrolyte interface. On the alumina surfaces, five isolated $-OH$ group stretching frequencies have been identified, in addition to a band associated with the hydrogen-bonded SOH groups[21]. Of course, the proton (ion) binding constants of the various groups should vary. Moreover, even for one kind of $-OH$ group, a certain dispersion of adsorption properties is to be expected. All of these factors may suggest that alumina is a good candidate for the study of the effects of the energetic heterogeneity of surface oxygens on proton adsorption-accompanying heats.

For theoretical studies, such as the one in ref 29, calorimetric data for the sample γ-Al$_2$O$_3$, called Alumina II, in contact with a 0.1 mol/dm³ NaCl solution (the value of PZC for this oxide was determined to be 8.5[20]) were chosen. These data were chosen from among other data sets[29] because Machesky and Jacobs[20] reported heat effects and gave the results of potentiometric titrations for this system. Moreover, for this system, hysteresis of both potentiometric and calorimetric titration curves is the smallest. The theoretical analysis also included data from the radiometric measurements of individual isotherms of Na$^+$ and Cl$^-$ ion adsorptions obtained by Sprycha.[64,65] These data[65] can be very helpful in monitoring the behavior of theoretical individual isotherms of Na$^+$ and Cl$^-$ ion adsorptions corresponding to the calculated heats of adsorption, though they were not measured on the same samples of aluminum oxide as were heat effects.

Because there was no information about the IEP values (no measurements of the electrophoretic mobility of this adsorption system), the calculations were made for the het-FLM model by assuming that the IEP value was equal to that obtained from

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TABLE 2: Parameters Used to Calculate the Theoretical Values Presented in Figures 3−5

het-TLM[a]

best-fit parameters

kT/c_i $i = +$, A	kT/c_i $i = 0$, C	pK_{a2}^{int}	$p^*K_{aC}^{int}$	c_1^L F/m²	c_1^R F/m²	Q_{a1} kJ/mol	Q_{a1} kJ/mol	α_1^L F/m²/deg	α_1^L F/m²/deg
0.7	0.8	11.47	9.60	0.90	0.90	17.0	73.0	-0.0040	-0.0040

calculated parameters

		pK_{a1}^{int}	$p^*K_A^{int}$	Q_{aA} kJ/mol					
		5.00	7.59	87.3					

het-FLM[b]

best-fit parameters

kT/c_i $i = +$, A	kT/c_i $i = 0$, C	pK_{a2}^{int}	$p^*K_{aC}^{int}$	C_- F/m²	C_+ F/m²	Q_{a1} kJ/mol	Q_{a2} kJ/mol	α_- F/m²/deg	α_+ F/m²/deg
0.7	0.8	11.47	9.60	0.87	0.92	17.5	71.0	-0.0040	-0.0040

calculated parameters

		pK_{a1}^{int}	$p^*K_A^{int}$	Q_{aA} kJ/mol					
		5.03	7.62	84.1					

[a] Het-TLM: c_1^L and c_1^R are two different values of the electrical capacitance c_1, depending on the pH—one for the acidic region (pH < PZC) and the other for the basic region (pH > PZC).[29] α_1^L and α_1^L are the temperature derivatives dc_1^L/dT and dc_1^L/dT, respectively.[29] [b] Het-FLM: The value of the derivative $d\ln(1/C_- - 1/C_+)/da$ is assumed to be equal to -11.0 dm³/mol to obtain the IEP value equal to that obtained for het-TLM (see appropriate eqs in ref 59).
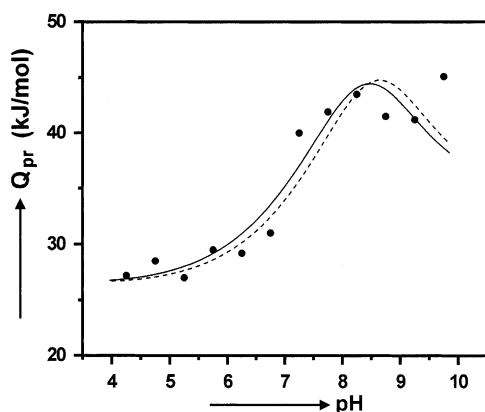
Figure 4. Comparison of the experimental data (•), reported by Machesky and Jacobs[20] for the system alumina/0.1 mol/dm³ NaCl, and the theoretical heats of proton adsorption Q_{pr}(pH) calculated for the sets of parameters collected in Table 1. Lines indicate het-FLM(—) and het-TLM (− − −).

Figure 5. Comparison of the individual adsorption isotherms of Na⁺ (•) and Cl⁻ (■) reported by Sprycha[65] for the system alumina/0.1 mol/dm³ NaCl and the theoretical isotherms calculated by using the same sets of parameters as those used to prepare Figures 2 and 3. The meanings of the solid (—) and dashed (− − −) theoretical lines are the same.

the best-fit calculations for the het-TLM model in ref 29. Using the appropriate interrelation between PZC, IEP, and the best-fit parameters for het-TLM from Table 3[59], I obtained IEP = 8.1. Figures 3−5 present the results of calculations assuming that $kT/c_0 = kT/c_C$ and $kT/c_+ = kT/c_A$. The behavior of the het-FLM model was compared in these Figures with the calculations for the best-fit parameters for the het-TLM model[29]. As a result of the best fit presented in Figure 4, better agreement was obtained for the het-FLM of the theoretical curve (solid line) and the experimental data of proton adsorption heat than that for the het-TLM model (broken line). I stress that the same calculated effect for the het-FLM can be achieved with a different set of best-fit parameters when IEP has a different value. One can draw the conclusion that actual parameters values can be obtained only when a complex theoretical analysis of a full set of experimental data can be made. Theoretical and experimental studies should be complementary, which leads to

the complete representation of the adsorption system under investigation.

Figure 3 shows the agreement between the experimental δ_0(pH) and the theoretically calculated curves for both the het-TLM and het-FLM models using the various sets of parameters included in Table 2. The theoretically calculated curves δ_0(pH) overlap so much that it is impossible to present them as the lines separated from one another, even in a much larger figure. This again confirms the fact, which has long been discussed in the literature, that the experimental titration curves can be reproduced using various adsorption models and different sets of parameters.[25,29] As long as other experimental data (individual isotherms of ions adsorption, heats of adsorption) are not taken into consideration, titration curves alone are not a reliable source of information.

A compromise between the correct behavior of the calculated heats of proton adsorption and the calculated individual isotherms of ion adsorption was obtained for het-TLM[29] by assuming that $kT/c_0 = kT/c_C = 0.8$ and $kT/c_+ = kT/c_A = 0.7$, which is marked with a broken line in Figures 4 and 5. This case is similar to that of het-FLM. Even if individual isotherms of ions adsorption, which were measured by Sprycha[65] on another sample of aluminum oxide, are treated with less reliability, optimal results are obtained by assuming that the values of the heterogeneity parameters are close to the previous values.

Reference 29 also presents vast model investigations. The theoretical curves were generated for many sets of parameters to show the full influence of their values on the course of these curves. These parameters have a similar effect on the curves generated using the het-FLM model studied in this paper.

This paper, along with ref 59, presents the most general version of the FLM model, assuming that the surface energetic heterogeneity of oxide with the heat effects of ion adsorption at the metal oxide/electrolyte solution is described theoretically.

Appendix A

The derivatives $(\partial\theta_i/\partial pH)_T$, $(i = 0, +, A, C)$ in eqs 17 are to be evaluated from the following equation system, which is obtained from eqs 11 in the same way as in refs 25 and 30:

$$F_0 = -\ln K_{a2}^{int} - \frac{e\psi_0}{kT} - 2.3\,pH - \frac{c_0}{kT}\ln\frac{\theta_0}{\theta_-} = 0 \quad (A.1a)$$

$$F_+ = -\ln(K_{a1}^{int}K_{a2}^{int}) - \frac{2e\psi_0}{kT} - 4.6\,pH - \frac{c_+}{kT}\ln\frac{\theta_+}{\theta_-} = 0 \quad (A.1b)$$

$$F_C = -\ln(K_{a2}^{int}/\,^*K_C^{int}) - \frac{e\psi_0}{kT} + \frac{e\delta_0}{kT} + \ln a_C - \frac{c_C}{kT}\ln\frac{\theta_C}{\theta_-} = 0 \quad (A.1c)$$

$$F_A = -\ln(K_{a2}^{int}/\,^*K_A^{int}) - \frac{e\psi_0}{kT} - \frac{e\delta_0}{kTC_+} - \frac{e\delta^*}{kTC_+} + \frac{e\delta^*}{kTC_-} +$$
$$\ln a_A - 4.6\,pH - \frac{c_A}{kT}\ln\frac{\theta_A}{\theta_-} = 0 \quad (A.1d)$$

Then, for instance,

$$\left(\frac{\partial\theta_0}{\partial pH}\right)_T = (-1)\frac{\begin{vmatrix} \partial F_0/\partial pH & \partial F_0/\partial\theta_+ & \partial F_0/\partial\theta_C & \partial F_0/\partial\theta_A \\ \partial F_+/\partial pH & \partial F_+/\partial\theta_+ & \partial F_+/\partial\theta_C & \partial F_+/\partial\theta_A \\ \partial F_C/\partial pH & \partial F_C/\partial\theta_+ & \partial F_C/\partial\theta_C & \partial F_C/\partial\theta_A \\ \partial F_A/\partial pH & \partial F_A/\partial\theta_+ & \partial F_A/\partial\theta_C & \partial F_A/\partial\theta_A \end{vmatrix}}{\begin{vmatrix} \partial F_0/\partial\theta_0 & \partial F_0/\partial\theta_+ & \partial F_0/\partial\theta_C & \partial F_0/\partial\theta_A \\ \partial F_+/\partial\theta_0 & \partial F_+/\partial\theta_+ & \partial F_+/\partial\theta_C & \partial F_+/\partial\theta_A \\ \partial F_C/\partial\theta_0 & \partial F_C/\partial\theta_+ & \partial F_C/\partial\theta_C & \partial F_C/\partial\theta_A \\ \partial F_A/\partial\theta_0 & \partial F_A/\partial\theta_+ & \partial F_A/\partial\theta_C & \partial F_A/\partial\theta_A \end{vmatrix}}$$
$$(A.2)$$

When evaluating the partial derivatives $(\partial F_i/\partial pH)_T$ in the numerator of eq A.2, one must consider ψ_0 to be a function of pH as defined in eq 10. Then,

$$\frac{\partial F_0}{\partial pH} = -2.3\frac{t}{t+\beta} \qquad \frac{\partial F_+}{\partial pH} = -4.6\frac{t}{t+\beta}$$

$$\frac{\partial F_C}{\partial pH} = -2.3\frac{\beta}{t+\beta} \qquad \frac{\partial F_A}{\partial pH} = -2.3\frac{2t+\beta}{t+\beta} \quad (A.3)$$

For the FLM with small correlations between the adsorption energies of different surface complexes (het-FLM), the derivatives $\partial F_i/\partial\theta_j$ $(i, j = 0, +, A, C)$ in the determinants of eq A.2 will have the following form,

$$\frac{\partial F_0}{\partial\theta_0} = -\frac{c_0}{kT}\frac{\theta_0 + \theta_-}{\theta_0\theta_-} \qquad \frac{\partial F_0}{\partial\theta_+} = -\frac{c_0}{kT}\frac{1}{\theta_-}$$

$$\frac{\partial F_+}{\partial\theta_0} = -\frac{c_+}{kT}\frac{1}{\theta_-} \qquad \frac{\partial F_+}{\partial\theta_+} = -\frac{c_+}{kT}\frac{\theta_+ + \theta_-}{\theta_+\theta_-}$$

$$\frac{\partial F_C}{\partial\theta_0} = -\frac{c_C}{kT}\frac{1}{\theta_-} + w_+ \qquad \frac{\partial F_C}{\partial\theta_+} = -\frac{c_C}{kT}\frac{1}{\theta_-} + 2w_+$$

$$\frac{\partial F_A}{\partial\theta_0} = -\frac{c_A}{kT}\frac{1}{\theta_-} - w_- \qquad \frac{\partial F_A}{\partial\theta_+} = -\frac{c_A}{kT}\frac{1}{\theta_-} - 2w_-$$

$$\frac{\partial F_0}{\partial\theta_C} = -\frac{c_0}{kT}\frac{1}{\theta_-} \qquad \frac{\partial F_0}{\partial\theta_A} = -\frac{c_0}{kT}\frac{1}{\theta_-}$$

$$\frac{\partial F_+}{\partial\theta_C} = -\frac{c_+}{kT}\frac{1}{\theta_-} \qquad \frac{\partial F_+}{\partial\theta_A} = -\frac{c_+}{kT}\frac{1}{\theta_-}$$

$$\frac{\partial F_C}{\partial\theta_C} = -\frac{c_C}{kT}\frac{\theta_C + \theta_-}{\theta_C\theta_-} \qquad \frac{\partial F_C}{\partial\theta_A} = -\frac{c_C}{kT}\frac{1}{\theta_-} + 2w_+$$

$$\frac{\partial F_A}{\partial\theta_C} = -\frac{c_A}{kT}\frac{1}{\theta_-} + w_+ - w_- \qquad \frac{\partial F_A}{\partial\theta_A} = -\frac{c_A}{kT}\frac{\theta_A + \theta_-}{\theta_A\theta_-} - 2w_-$$
$$(A.4)$$

where

$$w_+ = \frac{eB_S}{kTC_+} \qquad \text{and} \qquad w_- = \frac{eB_S}{kTC_-} \quad (A.5)$$

When calculating these derivatives, one must consider eq 3 and the condition $\sum_i \theta_i = 1$ $(i = 0, +, A, C, -)$. δ_0 will have the following form:

$$\delta_0 = B_S(2\theta_+ + 2\theta_A + \theta_0 - 1) \quad (A.6)$$

A special computer subroutine was used to find the analytical form of the derivatives $(\partial\theta_i/\partial pH)_T$,

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

and

$$X_0 = t\frac{c_C}{kT}\left[\frac{c_+}{kT}\frac{c_A}{kT}(\theta_- + \theta_C) - \frac{c_A}{kT}\left(2\frac{c_0}{kT} - \frac{c_+}{kT}\right)\theta_+ - \right.$$
$$\left. \frac{c_+}{kT}\left(2\frac{c_0}{kT} - \frac{c_A}{kT}\right)\theta_A\right] + w_- t\frac{c_+}{kT}\frac{c_C}{kT}\theta_A(\theta_C + 2\theta_-) -$$
$$w_+ t\theta_C\left[\frac{c_+}{kT}\left(4\frac{c_0}{kT} - \frac{c_C}{kT} - 2\frac{c_A}{kT}\right)\theta_A + 2\frac{c_A}{kT}\left(2\frac{c_0}{kT} - \frac{c_+}{kT}\right)\theta_+\right] +$$
$$(w_- - w_+)\frac{c_+}{kT}\theta_C\theta_A\left[\beta\frac{c_0}{kT} + 2w_+ t\theta_-\right] + \beta\frac{c_0}{kT}\frac{c_+}{kT}\left[\frac{c_A}{kT}\theta_C - \right.$$
$$\left. \frac{c_C}{kT}\theta_A\right]$$

$$X_+ = t\frac{c_C}{kT}\left[2\frac{c_0}{kT}\frac{c_A}{kT}(\theta_- + \theta_C) + \frac{c_A}{kT}\left(2\frac{c_0}{kT} - \frac{c_+}{kT}\right)\theta_0 - 2\frac{c_0}{kT}\left(\frac{c_A}{kT} - \right.\right.$$
$$\left.\left. \frac{c_+}{kT}\right)\theta_A\right] + w_- t\theta_A\left[\frac{c_C}{kT}\left(2\frac{c_0}{kT} - \frac{c_+}{kT}\right)\theta_0 + 2\frac{c_0}{kT}\frac{c_C}{kT}(2\theta_- + \theta_C)\right] +$$
$$w_+ t\theta_C\left[\frac{c_A}{kT}\left(2\frac{c_0}{kT} - \frac{c_+}{kT}\right)\theta_0 + 2\frac{c_0}{kT}\left(\frac{c_C}{kT} + 2\frac{c_A}{kT} - 2\frac{c_+}{kT}\right)\theta_A\right] +$$
$$(w_- - w_+)\theta_C\theta_A\left[\beta\frac{c_0}{kT}\frac{c_+}{kT} + w_+ t\left(4\frac{c_0}{kT}\theta_- - \frac{c_+}{kT}\theta_0 + 2\frac{c_0}{kT}\theta_0\right)\right] +$$
$$\beta\frac{c_0}{kT}\frac{c_+}{kT}\left[\frac{c_A}{kT}\theta_C - \frac{c_C}{kT}\theta_A\right]$$

$$X_C = -t\frac{c_C}{kT}\left[\frac{c_+}{kT}\frac{c_A}{kT}\theta_0 + 2\frac{c_0}{kT}\frac{c_A}{kT}\theta_+ + 2\frac{c_0}{kT}\frac{c_+}{kT}\theta_A\right] +$$
$$w_- t\frac{c_+ c_C}{kTkT}\theta_0\theta_A + w_+ t\left[\frac{c_A}{kT}\left(2\frac{c_0}{kT} - \frac{c_+}{kT}\right)\theta_0\theta_+ + \frac{c_+}{kT}\frac{c_A}{kT}\theta_-\theta_0 +\right.$$
$$\left. 4\frac{c_0}{kT}\frac{c_A}{kT}\theta_-\theta_+ + 4\frac{c_0}{kT}\frac{c_+}{kT}\theta_-\theta_A + \frac{c_+}{kT}\left(2\frac{c_0}{kT} - \frac{c_A}{kT}\right)\theta_0\theta_A\right] -$$
$$(w_- - w_+)\frac{c_0}{kT}\frac{c_+}{kT}\beta\theta_A(2\theta_- + \theta_0) - \beta\frac{c_0}{kT}\frac{c_+}{kT}\left[\frac{c_A}{kT}(\theta_0 + \theta_+ + \right.$$
$$\left. \theta_-) + \left(\frac{c_C}{kT} + \frac{c_A}{kT}\right)\theta_A\right]$$

$$X_A = t\frac{c_C}{kT}\left[\frac{c_+}{kT}\left(2\frac{c_0}{kT} - \frac{c_A}{kT}\right)\theta_0 + 2\frac{c_0 c_+}{kTkT}(\theta_- + \theta_C) - \right.$$
$$\left. 2\frac{c_0}{kT}\left(\frac{c_+}{kT} - \frac{c_A}{kT}\right)\theta_+\right] - w_- t\left[\frac{c_C}{kT}\left(2\frac{c_0}{kT} - \frac{c_+}{kT}\right)\theta_0\theta_+ +\right.$$
$$\left. \frac{c_+}{kT}\frac{c_C}{kT}\theta_-\theta_0 + 4\frac{c_0}{kT}\frac{c_C}{kT}\theta_-\theta_+ + 2\frac{c_0}{kT}\frac{c_C}{kT}\theta_+\theta_C\right] -$$
$$w_+ t\left[2\frac{c_0}{kT}\left(2\frac{c_A}{kT} + \frac{c_C}{kT} - 2\frac{c_+}{kT}\right)\theta_+\theta_C + \frac{c_+}{kT}\left(\frac{c_C}{kT} + \frac{c_A}{kT} - \right.\right.$$
$$\left.\left. 2\frac{c_0}{kT}\right)\theta_0\theta_C\right] + (w_- - w_+)\theta_C\left[\beta\frac{c_0}{kT}\frac{c_+}{kT}(\theta_- - \theta_+) - \right.$$
$$\left. w_+ t\left(4\frac{c_0}{kT}\theta_+\theta_- + 2\frac{c_0}{kT}\theta_+\theta_0 + \frac{c_+}{kT}\theta_0\theta_- - \frac{c_+}{kT}\theta_0\theta_+\right)\right] +$$
$$\beta\frac{c_0}{kT}\frac{c_+}{kT}\left[\frac{c_C}{kT}(\theta_0 + \theta_+ + \theta_-) + \left(\frac{c_C}{kT} + \frac{c_A}{kT}\right)\theta_C\right]$$

$$Y = \frac{c_0 c_+ c_C c_A}{(kT)^4} + \frac{c_0 c_+}{(kT)^2}\left[w_+\left(\frac{c_C}{kT} + 2\frac{c_A}{kT}\right)\theta_C\theta_A + \right.$$
$$w_+\frac{c_A}{kT}\theta_C(2\theta_+ + \theta_0) + w_-\frac{c_C}{kT}\theta_A(\theta_C + 2\theta_- + \theta_0) + w_+(w_- -$$
$$\left. w_+)\theta_C\theta_A(2\theta_- + \theta_0)\right]$$

where t is defined in eq 23a and w_+ and w_- are defined in eq A.5. When $kT/c_0 = kT/c_+ = kT/c_C = kT/c_A = 1$, eqs A.7 reduce to those developed for the homogeneous four-layer model FLM, which were presented in the Appendix of ref 30. When $w_+ = w_- = w$, these equations reduce to those of the heterogeneous

triple-layer model, which were presented in the Appendix of ref 29.

Appendix B

The derivatives $(\partial F_{PZC}^{(1)}/\partial PZC)_{1/T}$ and $(\partial F_{PZC}^{(2)}/\partial PZC)_{1/T}$ in eqs 24 have the following form:

$$\left(\frac{\partial F_{PZC}^{(1)}}{\partial PZC}\right)_{1/T} = -4.6\frac{kT}{c_+}\left(\frac{H^2}{K_{a1}^{int}K_{a2}^{int}}\right)^{kT/c_+} +$$
$$2.3\frac{\frac{kT}{c_C}}{\frac{kT}{c_A}}\left(\frac{^*K_C^{int}a}{K_{a2}^{int}}\right)^{kT/c_C}\frac{aH\left(\frac{\partial^2 P^*}{\partial a\partial H} - \frac{1}{P^*}\frac{\partial P^*}{\partial a}\frac{\partial P^*}{\partial H}\right)}{P^*\left(1 + \frac{a}{P^*}\frac{\partial P^*}{\partial a}\right)^2} \quad \text{(B.1a)}$$

$$\left(\frac{\partial F_{PZC}^{(2)}}{\partial PZC}\right)_{1/T} = -2.3\frac{kT}{c_A}\left(\frac{H^2 aP^*}{K_{a2}^{int*}K_A^{int}}\right)^{kT/c_A}\left[\frac{kT}{c_A}\left(2 + \frac{H}{P^*}\frac{\partial P^*}{\partial H}\right)\left(1 + \right.\right.$$
$$\left.\left. \frac{a}{P^*}\frac{\partial P^*}{\partial a}\right) + \frac{aH}{P^*}\left(\frac{\partial^2 P^*}{\partial a\partial H} - \frac{1}{P^*}\frac{\partial P^*}{\partial a}\frac{\partial P^*}{\partial H}\right)\right] \quad \text{(B.1b)}$$

where

$$\frac{\partial P^*}{\partial H} = -\frac{P^* \ln P^*}{H}\frac{\frac{kT}{c_0}(K_0 H)^{kT/c_0}}{2 + (K_0 H)^{kT/c_0} + 2(K_C a)^{kT/c_C}} \quad \text{(B.2a)}$$

$$\frac{\partial P^*}{\partial a\partial H} = \frac{\ln P^* + 1}{P^* \ln P^*}\frac{\partial P^*}{\partial a}\frac{\partial P^*}{\partial H} +$$
$$P^* \ln P^*\frac{\frac{kT}{c_0}(K_0 H)^{kT/c_0}\frac{kT}{c_C}(K_C a)^{kT/c_C}}{aH[2 + (K_0 H)^{kT/c_0} + 2(K_C a)^{kT/c_C}]^2} \quad \text{(B.2b)}$$

The derivatives $(\partial F_{PZC}^{(1)}/\partial^1/_T)PZC$ and $(\partial F_{PZC}^{(2)}/\partial^1/_T)PZC$ in eqs 24 can be written in the following way:

$$\left(\frac{\partial F_{PZC}^{(1)}}{\partial(1/T)}\right)_{PZC} =$$
$$-\frac{\partial\left[\left(\frac{H^2}{K_{a1}^{int}K_{a2}^{int}}\right)^{kT/c_+}\right]}{\partial(1/T)} + \left(\frac{\frac{kT}{c_C}}{\frac{kT}{c_A}}\frac{1}{1 + \frac{a}{P^*}\frac{\partial P^*}{\partial a}} - 1\right)\frac{\partial\left[\left(\frac{^*K_C^{int}a}{K_{a2}^{int}}\right)^{kT/c_C}\right]}{\partial(1/T)} -$$
$$\frac{\frac{kT}{c_C}}{\frac{kT}{c_A}}\left(\frac{^*K_C^{int}a}{K_{a2}^{int}}\right)^{kT/c_C}\frac{a\left[\frac{\partial^2 P^*}{\partial a\partial(1/T)} + \frac{\partial P^*}{\partial a}\left(\frac{\partial \ln a}{\partial(1/T)} - \frac{1}{P^*}\frac{\partial P^*}{\partial(1/T)}\right)\right]}{P^*\left(1 + \frac{a}{P^*}\frac{\partial P^*}{\partial a}\right)^2} \quad \text{(B.3a)}$$

$$\left(\frac{\partial F_{PZC}^{(2)}}{\partial(1/T)}\right)_{PZC} = -\frac{kT}{c_A}\left(1 + \frac{a}{P^*}\frac{\partial P^*}{\partial a}\right)\left[\frac{\partial\left[\left(\frac{H^2 aP^*}{K_{a2}^{int*}K_A^{int}}\right)^{kT/c_A}\right]}{\partial(1/T)} - \right.$$
$$T\left(\frac{H^2 aP^*}{K_{a2}^{int*}K_A^{int}}\right)^{kT/c_A} + \frac{kT}{c_C}T\left(\frac{^*K_C^{int}a}{K_{a2}^{int}}\right)^{kT/c_C} - \frac{kT}{c_C}\frac{\partial\left[\left(\frac{^*K_C^{int}a}{K_{a2}^{int}}\right)^{kT/c_C}\right]}{\partial(1/T)} +$$
$$\left. \frac{kT}{c_A}\left(\frac{H^2 aP^*}{K_{a2}^{int*}K_A^{int}}\right)^{kT/c_A}\frac{a}{P^*}\left[\frac{\partial^2 P^*}{\partial a\,\partial(1/T)} + \frac{\partial P^*}{\partial a}\left(\frac{\partial \ln a}{\partial(1/T)} - \frac{1}{P^*}\frac{\partial P^*}{\partial(1/T)}\right)\right]\right] \quad \text{(B.3b)}$$

where

$$\frac{\partial P^*}{\partial (1/T)} = P^* \ln P^* \left[T + \frac{1}{\delta^*} \frac{\partial \delta^*}{\partial (1/T)} + T^2 \frac{\frac{\alpha_-}{(C_-)^2} - \frac{\alpha_+}{(C_+)^2}}{\frac{1}{C_-} - \frac{1}{C_+}} \right] \quad (B.4a)$$

$$\frac{\partial \delta^*}{\partial (1/T)} = -B_S \left[\frac{\frac{\partial [(K_C a)^{kT/c_C}]}{\partial (1/T)} (2 + (K_0 H)^{kT/c_0} + 2(K_C a)^{kT/c_C})}{[2 + (K_0 H)^{kT/c_0} + 2(K_C a)^{kT/c_C}]^2} - \right.$$
$$\left. \frac{\left(\frac{\partial [(K_0 H)^{kT/c_0}]}{\partial (1/T)} + 2\frac{\partial [(K_C a)^{kT/c_C}]}{\partial (1/T)}\right)(K_C a)^{kT/c_C}}{[2 + (K_0 H)^{kT/c_0} + 2(K_C a)^{kT/c_C}]^2} \right] \quad (B.4b)$$

$$\frac{\partial P^*}{\partial a \, \partial (1/T)} = \frac{\ln P^* + 1}{P^* \ln P^*} \frac{\partial P^*}{\partial a} \frac{\partial P^*}{\partial (1/T)} + P^* \ln P^*$$

$$\left[\frac{d^2 \ln \left(\frac{1}{C_-} - \frac{1}{C_+}\right)}{da \, d(1/T)} - \frac{kT}{c_C} \frac{1}{a}\left(T + \frac{\partial \ln a}{\partial (1/T)}\right) \frac{2 + (K_0 H)^{kT/c_0}}{2 + (K_0 H)^{kT/c_0} + 2(K_C a)^{kT/c_C}} + \right.$$
$$\frac{kT}{c_C} \frac{1}{a} \left\{ \frac{\frac{\partial [(K_0 H)^{kT/c_0}]}{\partial (1/T)}(2 + (K_0 H)^{kT/c_0} + 2(K_C a)^{kT/c_C})}{(2 + (K_0 H)^{kT/c_0} + 2(K_C a)^{kT/c_C})^2} - \right.$$
$$\left.\left. \frac{\left(\frac{\partial [(K_0 H)^{kT/c_0}]}{\partial (1/T)} + 2\frac{\partial [(K_C a)^{kT/c_C}]}{\partial (1/T)}\right)(2 + (K_0 H)^{kT/c_0})}{(2 + (K_0 H)^{kT/c_0} + 2(K_C a)^{kT/c_C})^2} \right\} \right] \quad (B.4c)$$

and where

$$\frac{\partial [(K_0 H)^{kT/c_0}]}{\partial (1/T)} = \frac{\partial \left[\left(\frac{H}{K_{a2}^{int}}\right)^{kT/c_0}\right]}{\partial (1/T)} =$$
$$\frac{kT}{c_0}\left(\frac{H}{K_{a2}^{int}}\right)^{kT/c_0}\left[-T \ln\left(\frac{H}{K_{a2}^{int}}\right) + \frac{Q_{a2}}{k}\right] \quad (B.5a)$$

$$\frac{\partial \left[\left(\frac{H}{K_{a1}^{int} K_{a2}^{int}}\right)^{kT/c_+}\right]}{\partial (1/T)} =$$
$$\frac{kT}{c_+}\left(\frac{H^2}{K_{a1}^{int} K_{a2}^{int}}\right)^{kT/c_+}\left[-T \ln\left(\frac{H^2}{K_{a1}^{int} K_{a2}^{int}}\right) + \frac{Q_{a1} + Q_{a2}}{k}\right] \quad (B.5b)$$

$$\frac{\partial [(K_C a)^{kT/c_C}]}{\partial (1/T)} = \frac{\partial \left[\left(\frac{{}^*K_C^{int} a}{K_{a2}^{int}}\right)^{kT/c_C}\right]}{\partial (1/T)} =$$
$$\frac{kT}{c_C}\left(\frac{{}^*K_C^{int} a}{K_{a2}^{int}}\right)^{kT/c_C}\left[\frac{\partial \ln a}{\partial (1/T)} - T \ln\left(\frac{{}^*K_C^{int} a}{K_{a2}^{int}}\right) + \frac{Q_{aC}}{k}\right] \quad (B.5c)$$

$$\frac{\partial \left[\left(\frac{H^2 a P^*}{K_{a1}^{int *} K_A^{int}}\right)^{kT/c_A}\right]}{\partial (1/T)} = \frac{kT}{c_A}\left(\frac{H^2 a P^*}{K_{a2}^{int *} K_A^{int}}\right)^{kT/c_A}\left[\frac{\partial \ln a}{\partial (1/T)} + \frac{1}{P^*}\frac{\partial P^*}{\partial (1/T)} - \right.$$
$$\left. T \ln\left(\frac{H^2 a P^*}{K_{a2}^{int *} K_A^{int}}\right) + \frac{Q_{aA}}{k}\right] \quad (B.5d)$$

Thus, in eq B.4c, one new parameter appears: $d^2 \ln(1/C_- - 1/C_+)/da \, d(1/T)$. However, the numerical exercises showed that this parameter does not affect the theoretical calculated functions, so its value is zero.

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