

Activity Coefficients and Coulombic Correction Factor for Surface Complexation Modeling

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Abstract Surface complexation models employ mass law equations to describe the reaction of surface functional groups with ions in the solution and also Gouy-Chapman theory to consider the electrostatic effects in the surface reactions. In current surface complexation models, however, the coulombic factors used are not wholly consistent with the Gouy-Chapman model of the surface. This study was to provide the derivation of the coulombic term usually employed and then a revised coulombic term completely consistent with Gouy-Chapman Theory. The electrical potential energy, $zF\psi$, in current surface complexation models is not consistent with the Gouy-Chapman theory with the potential gradient close to the charged surface but with the Donnan model with the uniform potential. Even though the new coulombic factor yielded lower surface potential, it provided worse fits for acid-base titration data of the goethite suspensions.

Key Words : Surface complexation models, Gouy-Chapman theory, Coulombic term, Electrical potential energy, Donnan model

1. INTRODUCTION

Surface complexation models employ mass law equations to describe the reaction of surface functional groups with ions in solution [1]. The extent of specific adsorption of ions on charged surfaces is influenced by the change on the surface, and this effect is represented in surface complexation models by including a coulombic correction term in the mass law equations for surface reactions. The electrostatic effects on ion adsorption vary with surface change, which is affected by the extent of specific adsorption.

The Gouy-Chapman theory is usually invoked to describe the relationship between surface charge and potential, the latter of which is used in the coulombic correction term employed in surface complexation mass law equations. In current surface complexation models, however, the coulombic factors used are not wholly consistent with the Gouy-Chapman model of the interface.

In this study, derivation of the coulombic term

usually employed in surface complexation models is presented, and the nature of its inconsistency with Gouy-Chapman theory is explained. A revised coulombic term that is completely consistent with Gouy-Chapman theory is then described. Finally, the current and revised coulombic factors are compared quantitatively and tested against some experimental data for proton adsorption on goethite, an iron oxide.

2. BACKGROUND

A surface complexation reaction describes the reaction between a functional group on the surface and an ion near the charged site. For the specific adsorption of Na^+ on a permanent surface site ($\equiv S_p^-$), the chemical reaction can be written by



where the subscript s stands for the species present close to the surface, i.e., in the diffuse layer but immediately adjacent for the surface. The corresponding equation of mass action expression is

$$K_{\equiv S_p Na}^{int} = \frac{\{\equiv S_p Na^o\}}{\{\equiv S_p^-\}\{Na_s^+\}} \quad (2)$$

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where $\{ \}$ represents activity and $K_{\equiv S_p Na}^{int}$ is the intrinsic (thermodynamic) equilibrium constant. Na^+ activity in the solution can be substituted for that close to the surface, with consideration of the energy required to bring an ion from the bulk solution through the electrical field to the charged surface. The mass law expression for the equilibrium constant, which varies with surface charge, is given by

$$K_{\equiv S_p Na}^{int} = \frac{\{ \equiv S_p Na^o \}}{\{ \equiv S_p^- \} \{ Na^+ \} \exp\left(-\frac{F\psi}{RT}\right)} \quad (3a)$$

where ψ and F are the surface potential (V) and Faraday constant (96500 C/mol), respectively. R and T are the gas constant (8.317 J/mol·K) and the absolute temperature (K). Rearranging this expression yields.

$$K_{\equiv S_p Na}^{int} \exp\left(-\frac{F\psi}{RT}\right) = \frac{\{ \equiv S_p Na^o \}}{\{ \equiv S_p^- \} \{ Na^+ \}} \quad (3b)$$

The exponential term is referred to as a ‘‘coulombic correction’’ factor which indicates the extent of specific adsorption through the surface complexation: the greater the coulombic factor, the greater the amount of surface species produced. If the activity coefficients for the two surface species are assumed equal, then

$$K_{\equiv S_p Na}^{int} \exp\left(-\frac{F\psi}{RT}\right) = \frac{[\equiv S_p Na^o]}{[\equiv S_p^-] \gamma_{Na} [Na^+]} \quad (3c)$$

where $[\]$ represents molar concentration, and γ_{Na} is the solution phase activity coefficient for Na^+ . The equation 3c can also be rearranged to yield the apparent (conditional thermodynamic) equilibrium constant, $K_{\equiv S_p Na}^{app}$ to be defined as:

$$K_{\equiv S_p Na}^{app} = \frac{[\equiv S_p Na^o]}{[\equiv S_p^-] \gamma_{Na} [Na^+]} = K_{\equiv S_p Na}^{int} \exp\left(-\frac{F\psi}{RT}\right) \quad (4)$$

The mass law equation for the apparent equilibrium constant is derived based upon Na^+ ions in the bulk phase as the reacting entity in the surface complexation reaction, unlike the intrinsic equilibrium constant for which Na^+ ions close to the charged surface are considered to be the reactant.

The coulombic correction factor may be derived by separating the thermodynamic free energy of sorption (ΔG^o) into the chemical and electrical parts:

$$\Delta G^o = \Delta G_{int}^o + \Delta G_{coul}^o \quad (5)$$

where ΔG_{int}^o is the chemical (‘‘intrinsic’’) free energy term and ΔG_{coul}^o is the variable electrostatic (‘‘coulombic’’) free energy. Surface complexation models use the electrical potential energy as the electrostatic work, so equation 5 becomes:

$$\Delta G^o = \Delta G_{int}^o + \Delta z F \psi \quad (6)$$

where Δz is the change in the charge of the surface species due to the sorption reaction. The overall and chemical free energy changes for sorption can be represented, using apparent and intrinsic equilibrium constants, as :

$$\Delta G^o = \Delta G_{app}^o = -RT \ln K^{app} \quad (7a)$$

$$\Delta G_{int}^o = -RT \ln K^{int} \quad (7b)$$

To inter-relate two constants, we substitute equation 7a and 7b into equation 6 and rearrange to give

$$K^{app} = K^{int} \exp\left(-\frac{\Delta z F \psi}{RT}\right) \quad (1.8)$$

The coulombic factor is useful to account for surface charge effects on surface complexation reactions. The potential ψ , which determines the magnitude of the coulombic correction may be calculated with Gouy-Chapman theory using the surface charge density.

This study presents a general derivation of the coulombic correction factors employed in current surface complexation models and an assessment of the consistency of these corrections with the molecular theory involved in the models. An evaluation of the extra free energy for an ion in the diffuse layer as defined by Gouy-Chapman theory is presented along with determination of the ion activity and ion activity coefficient in the diffuse layer.

3. CHEMICAL THERMODYNAMICS FOR SURFACE REACTION

3.1 Electrochemical Potential

The free energy change of an aqueous system with change in numbers of moles of the component

is defined as the chemical potential, m_i , of the component which represents its escaping tendency from solution. More specifically, m_i , is defined by:

$$\mu_i = \frac{dG}{dn_i} \quad (9)$$

where G is the free energy of the system and n_i is the number of moles of the component i . If the chemical potential of a component μ_i in a system is high, it has a large escaping tendency, while if it is low, the component has a small escaping tendency. Component i will transport spontaneously from a region of high μ_i to a region of low μ_i : this transport continues until the value of m_i is uniform through the system, that is, until the system is in equilibrium. Thus, the free energy change of the system is zero at equilibrium ($\Delta G = 0$).

The chemical potential can be divided into the "chemical" (μ_i^C) and "electrical" (μ_i^E) contributions to the escaping tendency for a component in a system under an electrical potential.

$$\mu_i = \mu_i^C + \mu_i^E \quad (10)$$

The chemical contribution is produced by the chemical environment in which the species exists as a function of composition at constant temperature and pressure

$$\mu_i^C = \mu_i^o + RT\ln(a_i) = \mu_i^o + RT\ln(m_i) + RT\ln(\gamma_i) \quad (11)$$

where a_i is activity in the given state, i.e., the product of molar concentration (m_i) and the activity coefficient (γ_i); $RT\ln(\gamma_i)$ represents the concentration-dependent part of the free energy of the interaction of species i with its environment; μ_i^o is the standard chemical potential which reflects the free energy status of the component at standard conditions (unit concentration of species i at $T = 25^\circ\text{C}$, $P = 1$ atm, and $\psi = 0$ V).

The electrical contribution to the escaping tendency depends on the electrical condition of the phase which is manifested by the value of electrical potential. This is the extra free energy of the system driven by the electrostatic potential energy (w_i)

$$\mu_i^E = w_i \quad (12)$$

In the presence of an electrical field, the chemical

potential is usually called "electrochemical potential", which is given by

$$\mu_i = \mu_i^o + RT\ln(a_i) + w_i = \mu_i^o + RT\ln(m_i) + RT\ln(\gamma_i) + w_i \quad (13)$$

In common electrochemical cells used for oxidation-reduction reactions at immersed electrodes, the electrostatic potential energy is assumed to be given by $z_i F \psi$ which is uniform throughout the solution. This is only an approximation because various physicochemical phenomena are ignored, such as the electrostatic interaction between ions and the electrode, thermal diffusion, and the unequal transfer rate of ions which results in uneven spatial distribution of ions.

3.2 Chemical Equilibrium for Surface Reactions

In an aqueous suspension containing charged solids, the electrostatic force between the surface charge and the electrolyte ions creates the diffuse layer of countercharge at the interfacial region between the bulk solution and the solid surface. The spatial distribution of ions in this region is governed by the Boltzmann law. The molar concentration of an ion i in the electrical field, m_i can be related to its bulk solution concentration via the Boltzmann equation

$$m_i = m_i^o \exp\left(-\frac{z_i F \psi}{RT}\right) \quad (14)$$

where $z_i F \psi$ is the potential energy of ion i in a near-surface volume element; m_i and m_i^o are the molar concentrations of ion i at potential ψ and the bulk solution, respectively.

The electrical potential energy of an ion i in a volume element in the diffuse layer varies between zero at the bulk solution and $z_i F \psi_o$ at the charged surface. Thus, when the ion i is transferred from the bulk solution at $\psi = 0$ to the diffuse-layer region at ψ , integrated work is done to overcome all the local electrical energies. This work is the extra free energy which the volume element of an ion i in the diffuse layer retains. For example, for an Na^+ ion in the diffuse layer immediately adjacent to a negatively charged surface, the electrochemical potential can be divided into the chemical ($RT\ln\{Na_i^+\}$) and

the electrical contributions (w_{Na}) as follows :

$$\mu_{Na_s} = \mu_{Na}^{\circ} + RT \ln \{Na_s^+\} + w_{Na} \quad (15a)$$

$$= \mu_{Na}^{\circ} + RT \ln(f_{Na}) + RT \ln[Na_s^+] + w_{Na} \quad (15b)$$

where $\{ \}$ and $[\]$ represent activity and molar concentration, respectively; μ° denotes the chemical potential at standard chemical condition (1 molar concentration at $T = 25^{\circ}\text{C}$, $P = 1 \text{ atm}$, and $\psi = 0 \text{ V}$); and f represents the activity coefficient close to the surface. In equations 15a and 15b, w_{Na} represents the total additional free energy added to the system by the presence of the electrical field.

Thermodynamic equilibrium is achieved at zero free energy change ($\Delta G = 0$) and at equal electrochemical potential between phases (in this case, between the bulk solution and the diffuse layer). For the surface reaction for the sorption of Na onto the negatively charged site in Equation 1, the electrochemical potentials of the surface species are given by

$$\mu_{\equiv Sp} = \mu_{\equiv Sp}^{\circ} + RT \ln \{ \equiv Sp^- \} + w_{\equiv Sp} \quad (16a)$$

$$= \mu_{\equiv Sp}^{\circ} + RT \ln[f_{\equiv Sp^-}] + w_{\equiv Sp} \quad (16b)$$

$$\mu_{\equiv Sp Na} = \mu_{\equiv Sp Na}^{\circ} + RT \ln \{ \equiv Sp^- Na^{\circ} \} + w_{\equiv Sp Na} \quad (17a)$$

$$= \mu_{\equiv Sp Na}^{\circ} + RT \ln[f_{\equiv Sp^- Na^{\circ}}] + w_{\equiv Sp Na} \quad (17b)$$

The free energy change is the sum of the product of the chemical potential times the stoichiometric number of moles of reactants and products as follows :

$$\Delta G = \sum \mu_i n_i = \mu_{\equiv Sp Na} - \mu_{\equiv Sp} - \mu_{Na_s} \quad (18a)$$

$$\begin{aligned} &= \mu_{\equiv Sp Na}^{\circ} - \mu_{\equiv Sp}^{\circ} - \mu_{Na_s}^{\circ} + w_{\equiv Sp Na} - w_{\equiv Sp} - w_{Na} \\ &+ RT \ln \frac{f_{\equiv Sp Na} [\equiv Sp^- Na^{\circ}]}{f_{\equiv Sp^-} [\equiv Sp^-] \{Na_s^+\}} \end{aligned} \quad (18b)$$

$$\begin{aligned} &= -RT \ln \left[K_{\equiv Sp Na}^{int} \exp \left(-\frac{w_{\equiv Sp Na} - w_{\equiv Sp} - w_{Na}}{RT} \right) \right] \\ &+ RT \ln \frac{f_{\equiv Sp Na} [\equiv Sp^- Na^{\circ}]}{f_{\equiv Sp^-} [\equiv Sp^-] \{Na_s^+\}} \end{aligned} \quad (18c)$$

where $\exp[-(w_{\equiv Sp Na} - w_{\equiv Sp} - w_{Na})/RT]$ is defined as $K_{\equiv Sp Na}^{int}$, thermodynamic equilibrium constant. The mass law equation corresponding to Na surface reaction can thus be given by

$$K_{\equiv Sp Na}^{int} = \frac{f_{\equiv Sp Na} [\equiv Sp^- Na^{\circ}]}{f_{\equiv Sp^-} [\equiv Sp^-] \{Na_s^+\}}$$

$$\exp \left(\frac{w_{\equiv Sp Na} - w_{\equiv Sp} - w_{Na}}{RT} \right) \quad (19)$$

The equality of chemical potentials between phases at equilibrium (i.e., the bulk phase and the diffuse layer) enables determination of the activity and activity coefficient for Na^+ present close to the surface. The chemical potential of Na^+ in the bulk solution can be written as

$$\mu_{Na} = \mu_{Na}^{\circ} + RT \ln \{Na^+\} \quad (20a)$$

$$= \mu_{Na}^{\circ} + RT \ln(\gamma_{Na}) + RT \ln[Na^+] \quad (20b)$$

Since $\mu_{Na_s} = \mu_{Na}$, equating equations 15a and 20a gives the activity of Na^+ close to the surface relative to the Na^+ activity in the solution phase

$$\{Na_s^+\} = \{Na^+\} \exp \left(-\frac{w_{Na}}{RT} \right) \quad (21)$$

The activity of an ion close to the surface is expressed with the bulk phase activity and the exponential factor of the energy term. The activity coefficient for Na^+ near the charged surface can be obtained in terms of the activity coefficient for Na^+ in the bulk solution by equating 15b and 20b, and incorporating the Boltzmann equation (equation 14):

$$f_{Na} = \gamma_{Na} \exp \left(-\frac{w_{Na} - F\psi}{RT} \right) \quad (22)$$

As this expression indicates, the activity coefficient f_{Na} reflects the activity of Na^+ in the bulk phase (γ_{Na}) plus the electrical interactions between the ion and the charged surface. Thus, f_{Na} represents the modified mutual interactions among ions in the diffuse layer due to the electric field.

By substituting equation 21 for equation 19, the mass law equation for the sorption of Na^+ on $\equiv Sp^-$ becomes :

$$K_{\equiv Sp Na}^{int} = \frac{f_{\equiv Sp Na} [\equiv Sp^- Na^{\circ}]}{f_{\equiv Sp^-} [\equiv Sp^-] \{Na^+\}} \exp \left(\frac{w_{\equiv Sp Na} - w_{\equiv Sp}}{RT} \right) \quad (23)$$

For the surface species on the charged sites, $\equiv Sp^- Na^{\circ}$ and $\equiv Sp^-$, the activity coefficients $f_{\equiv Sp Na}$ and $f_{\equiv Sp}$ may be considered approximately equal because the electrostatic interactions of these species of fixed location will be largely independent of their individual

charges [2]. Thus, the mass law expression for the surface reaction is given by

$$K_{\equiv S_p Na}^{int} = \frac{[\equiv S_p Na^o]}{[\equiv S_p^-] \{Na^+\}} \exp\left(\frac{w_{\equiv S_p Na} - w_{\equiv S_p}}{RT}\right) \quad (24a)$$

$$= \frac{[\equiv S_p Na^o]}{[\equiv S_p^-] \gamma_{Na} \{Na^+\}} \exp\left(\frac{w_{\equiv S_p Na} - w_{\equiv S_p}}{RT}\right) \quad (24b)$$

Substitution of equation 4 into equation 24b yields

$$K_{\equiv S_p Na}^{app} = K_{\equiv S_p Na}^{int} \exp\left(\frac{w_{\equiv S_p Na} - w_{\equiv S_p}}{RT}\right) \quad (25)$$

where $K_{\equiv S_p Na}^{app}$ is the apparent equilibrium constant which includes the thermodynamic constant and the coulombic correction factors.

Chemical thermodynamics demonstrates the need to consider the electrostatic effects in the surface reactions, but provides no information as to how the work done is related to the potential or as to how the potential varies with the distance perpendicular to the surface. This relationship can be obtained by invoking the Gouy-Chapman theory.

4. DETERMINATION OF ELECTROSTATIC WORK

The electrostatic potential that arises from a charged surface acts on volume elements within the electrolyte solution adjacent to the surface. At equilibrium, the balance in forces, i.e., electrostatic force and (osmotic) pressure gradient, will be achieved in the volume elements of the electrolyte solution which lie in equipotential planes parallel to the surface face. The electrical force per unit volume (F_{el}) is given by the multiplication of the solution charge density (ρ) with the field strength (\hat{E}):

$$F_{el} \text{ (N/m}^3\text{)} = \rho \hat{E} \quad (26)$$

Since force is the negative gradient of the potential, the electrical field is also defined as:

$$\hat{E} = -\frac{d\psi}{dx} \quad (27)$$

where ψ is the potential and x is the distance from the charged site.

The electrostatic work per unit volume is the energy required to bring ions from the bulk solution to the volume element at potential ψ in the diffuse layer. The ions in the volume element are not electrically in balance and their net charge is termed the volume charge density. After the substitution of equation 27 for equation 26, the integration of the electrical force over distance yields [3]:

$$W(\text{J/m}^3) = \int_{\infty}^x F_{el} dx = -\int_0^{\psi} \rho d\psi \quad (28)$$

This work defines the extra free energy of the system due to the presence of the surface potential. Thus, the free energy of ions in the volume element due to the electrostatic interaction between ions and the charged sites in the diffuse layer is given as:

$$G^{DL}(\text{J/m}^3) = -W = \int_0^{\psi} \rho d\psi \quad (29)$$

G^{DL} is the negative of the work done. Overbeek [4] and Babcock [5] derived the same equation as equation 28 with consideration of a hypothetical charging process. This equation implies that the free energy depends on the spatial potential drop function and the ion distribution (i.e., charge density) in the electrolyte solution. Below, expressions for w are derived for different molecular models of ion distributions at the solid/water interface.

Let us consider the potential drops for two molecular models of ion distribution near an infinitely large flat charged surface: the Donnan-model and the diffuse layer model, as shown in Figure 1. The respective potential distribution may be a step func-

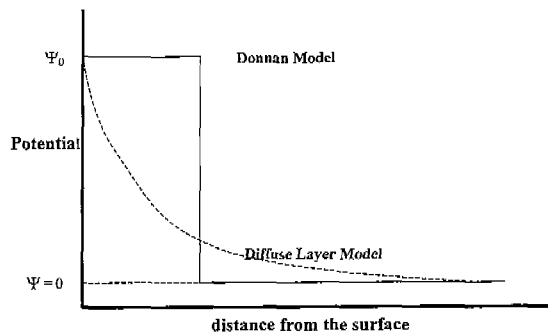


Figure 1. Variation of electrochemical potential with distance according to the Donnan model (—) and the diffuse layer model (- -).

tion or an exponential variation, depending on the ion distribution within the solution which can be expressed by volume charge density. In the Donnan model, the ions are evenly distributed (i.e., uniform charge density) within the Donnan phase which is considered to have an abrupt interface with the bulk phase. In the diffuse layer model, the counterions are considered spread out by thermal diffusion so that the charge density varies with the distance from the surface.

The ion distribution near the charged surface can be expressed by the Boltzmann distribution for Donnan model (D) and diffuse layer model (DL). The molar concentration (m) at the location of potential ψ can be represented by the following equations :

$$m^D = m^o \exp\left(-\frac{z_i F \psi}{RT}\right) \quad (30)$$

$$m^{DL} = m^o \exp\left(\frac{z_i F \psi}{RT}\right) \quad (31)$$

where m^o is the concentration at zero potential (i.e., in the bulk solution).

The volume charge density (ρ) in the solution can be written, using $\rho = \sum z_i F m_i$, by :

$$\rho^D = \sum z_i F m_i^D = \sum z_i F m_i^o \exp\left(-\frac{z_i F \psi}{RT}\right) \quad (32)$$

$$\rho^{DL} = \sum z_i F m_i^{DL} = \sum z_i F m_i^o \exp\left(-\frac{z_i F \psi}{RT}\right) \quad (33)$$

While the charge density is uniform for the Donnan phase, it is asymptotically decreasing over the distance from the surface for the diffuse-layer model.

Expressions for the extra free energy of the volume close to the charged surface, which arises from the electrostatic interaction between ions and charged sites, can now be formulated by substituting equations 32 and 33 for equation 29. The free energy of the volume element at ψ for each model can be given by

$$G^D = \int_0^\psi \rho^D d\psi = \rho^D \psi = \sum z_i F \psi m_i^D \quad (34)$$

$$\begin{aligned} G^{DL} &= \int_0^\psi \rho^{DL} d\psi = \int_0^\psi \sum z_i F m_i^o \exp\left(-\frac{z_i F \psi}{RT}\right) d\psi \\ &= RT \sum m_i^{DL} \left[\exp\left(\frac{z_i F \psi}{RT}\right) - 1 \right] \end{aligned} \quad (35)$$

Note that ρ^D is constant throughout the Donnan phase.

Finally, the electrostatic work, w_i (i.e., μ_i^E) which is given by :

$$w_i = \mu_i^E (\text{J/mol}) = \frac{d}{dm_i} \int_0^\psi \rho d\psi \quad (36)$$

can be obtained for the two models by differentiating the respective equations 34 and 35 with respect to the local concentration of ion i at ψ . These differentiations yield

$$w_i = z_i F \psi \quad \text{for Donnan-phase model} \quad (37)$$

$$w_i = RT [\exp(z_i F \psi / RT) - 1] \quad \text{for diffuse-layer model} \quad (38)$$

The electrostatic work, i.e., the electrical contribution to the electrochemical potential, is equal to the commonly-used electrical potential energy ($z_i F \psi$) only for the Donnan-phase model. For the diffuse layer, the electrostatic work expressions differ from $z_i F \psi$. The work expended to bring one mole of ion i to a spatial position where the potential is ψ should be calculated based upon the molecular model used to describe the potential drop and the volume charge density in the layer of counterions near a charged surface.

5. CURRENT ACTIVITY COEFFICIENT AND COULOMBIC FACTOR IN SURFACE COMPLEXATION MODELS

As mentioned in background section, current surface complexation models adopts $z_i F \psi$ as the electrical work to account for the effect of the electrostatic interaction between ions and the surface. It is the energy needed to transfer the ions through the electrical field near the charged surface. For Na adsorption on a negative surface, the electrostatic work for $\equiv S_p^-$ and $\equiv S_p^- Na^o$ are $-F\psi$ and zero, respectively. These results are substituted into equations 21 and 25 to give the corresponding expressions for the activity and the apparent equilibrium constant :

$$\{Na_s^+\} = \{Na^+\} \exp\left(-\frac{F\psi}{RT}\right) \quad (39)$$

$$K_{s_p Na}^{app} = K_{s_p Na}^{int} \exp\left(-\frac{F\psi}{RT}\right) \quad (40)$$

Using equation 22, the activity coefficient of Na^+ close to the surface site is given by :

$$f_{Na} = \gamma_{Na} \quad (41)$$

In the existing surface complexation models, the generalized equations for ion activity, ion activity coefficient, coulombic correction factor, and relationship between two binding constants which depend on the surface charge are given by :

$$\{M_s^{+z}\} = \{M^{+z}\} \exp\left(-\frac{z_M F\psi}{RT}\right) \quad (42)$$

$$f_M = \gamma_M \quad (43)$$

$$\text{Coulombic factor} = \exp\left(-\frac{\Delta z F\psi}{RT}\right) \quad (44)$$

$$K_{s_p Na}^{app} = K_{s_p Na}^{int} \exp\left(-\frac{\Delta z F\psi}{RT}\right) \quad (45)$$

where M is a cation with charge z_M and Δz is the difference in the charge of the product and reactant surface species in the sorption reaction.

The use of $z_M F\psi$ in the current surface complexation models assumes implicitly no potential gradient close to the charged surface. However, in some surface complexation models, such as the Diffuse Layer and Triple-Layer models, Gouy-Chapman theory is invoked to calculate the surface potential from the calculated surface charge density.

6. CORRECTED ACTIVITY COEFFICIENT AND COULOMBIC CORRECTION FACTOR FOR DIFFUSE LAYER SURFACE COMPLEXATION MODEL

If electrostatic work terms in the free energy expressions for surface complexation models are derived based upon the molecular model used to obtain the charge-potential relationship, the nature of the activity coefficients and the coulombic correction term depend on the molecular model. For the surface reaction in equation 1, the electrostatic work terms for formation of surface species in the diffuse-

layer model are properly formulated using equation 38 :

$$w_{s_p} = RT[\exp(-F\psi/RT) - 1] \quad (46)$$

$$w_{s_p Na} = 0 \quad (47)$$

As a result of the substitution of these equations into equations 21, 24a, and 25, the Na^+ surface activity, the coulombic factor, and the apparent equilibrium constant for reaction 1 can be written by :

$$\{Na_s^+\} = \{Na^+\} \exp\left(-\left[\exp\left(\frac{F\psi}{RT}\right) - 1\right]\right) \quad (48)$$

$$\text{Coulombic factor} = \exp\left(\exp\left(-\frac{F\psi}{RT}\right) - 1\right) \quad (49)$$

$$K_{s_p Na}^{app} = K_{s_p Na}^{int} \exp\left(\exp\left(-\frac{F\psi}{RT}\right) - 1\right) \quad (50)$$

The activity coefficients for Na near the surface can be obtained by substituting equations 46, and 47 for the electrostatic work term in equation 22 :

$$f_{Na} = \gamma_{Na} \exp\left[\frac{F\psi}{RT} + 1 - \exp\left(\frac{F\psi}{RT}\right)\right] \quad (51)$$

Use of the electrostatic work expression derived from Gouy-Chapman theory in the diffuse-layer model yields the following generalized expressions ion activity and its coefficient close to the surface, coulombic correction factor, and the apparent equilibrium constant for the surface complexation reaction :

$$\{M_s^{+z}\} = \{M^{+z}\} \exp\left(-\left[\exp\left(\frac{z_M F\psi}{RT}\right) - 1\right]\right) \quad (52)$$

$$f_M = \gamma_M \exp\left[\frac{z_M F\psi}{RT} + 1 - \exp\left(\frac{z_M F\psi}{RT}\right)\right] \quad (53)$$

Coulombic factor

$$= \exp\left(-\left\{\exp\left(\frac{z_p F\psi}{RT}\right) - \exp\left(\frac{z_r F\psi}{RT}\right)\right\}\right) \quad (54a)$$

$$= \exp(-\{P^{z_p} - P^{z_r}\}) \quad (55b)$$

$$K_{s_p M}^{app} = K_{s_p M}^{int} \exp\left(-\left\{\exp\left(\frac{z_p F\psi}{RT}\right) - \exp\left(\frac{z_r F\psi}{RT}\right)\right\}\right) \quad (56)$$

where z_p and z_r are the charge numbers for the surface species on the product and reactant sides of the

Table 1. Typical surface reactions and their coulombic factors assuming Donnan model and the diffuse layer model for the interface

No	Reactions	Z_p	Z_R	*diffuse layer model factor	*Donnan model factor
1	$\equiv\text{FeO}^- + \text{H}^+ = \equiv\text{FeOH}^0$	0	-1	$\exp[P^{-1} - 1]$	P^{-1}
2	$\equiv\text{FeO}^- + \text{Zn}^{2+} = \equiv\text{FeOZn}^+$	1	-1	$\exp[P^{-1} - P]$	P^{-2}
3	$\equiv\text{FeO}^- + \text{Al}^{3+} = \equiv\text{FeOAl}^{2+}$	2	-1	$\exp[P^{-1} - P^2]$	P^{-3}
4	$\equiv\text{FeOH}^0 + \text{H}^+ = \equiv\text{FeOH}_2^+$	1	0	$\exp[1 - P]$	P^{-1}
5	$\equiv\text{FeOH}^0 + \text{Zn}^{2+} = \equiv\text{FeOZn}^+ + \text{H}^+$	1	0	$\exp[1 - P]$	P^{-1}
6	$\equiv\text{FeOH}^0 + \text{Al}^{3+} = \equiv\text{FeOAl}^{2+} + \text{H}^+$	2	0	$\exp[1 - P^2]$	P^{-2}
7	$\equiv\text{FeOH}_2^+ + \text{Cs}^+ = \equiv\text{FeOHCs}^+ + \text{H}^+$	1	1	1	1
8	$\equiv\text{FeOH}_2^+ + \text{Zn}^{2+} = \equiv\text{FeOZn}^+ + 2\text{H}^+$	1	1	1	1
9	$\equiv\text{FeOH}_2^+ + \text{Al}^{3+} = \equiv\text{FeOAl}^{2+} + 2\text{H}^+$	2	1	$\exp[P - P^2]$	P^{-1}
10	$\equiv\text{S}_p^- + \text{Na}^+ = \equiv\text{S}_p\text{Na}^0$	0	-1	$\exp[P^{-1} - 1]$	P^{-1}
11	$\equiv\text{S}_p^- + \text{Na}^+ + \text{Cl}^- = \equiv\text{S}_p\text{NaCl}^-$	-1	-1	1	1
12	$\equiv\text{S}_p^- + \text{Mg}^{2+} = \equiv\text{S}_p\text{Mg}^+$	1	-1	$\exp[P^{-1} - P]$	P^{-2}
13	$\equiv\text{S}_p^- + \text{Mg}^{2+} + \text{Cl}^- = \equiv\text{S}_p\text{MgCl}^0$	0	-1	$\exp[P^{-1} - 1]$	P^{-1}

* $P = \exp(F\psi/RT)$

surface complexation reactions; P is $\exp(F\psi/RT)$. At very low potential (< 5 mV), the exponential term can be expanded ($e^x = 1 + x$) such that the double exponential terms are simplified to be the same coulombic factor as the current surface complexation model as follows :

Coulombic factor

$$= \exp\left(-\frac{(z_p - z_r)F\psi}{RT}\right) = \exp\left(-\frac{\Delta z F \psi}{RT}\right) \quad (57)$$

Table 1 gives the coulombic factor for typical surface reactions at pH-dependent and permanent charged sites, for use in surface complexation models that invoke Gouy-Chapman or Donnan theory to relate surface charge and potential. Current surface complexation models employ coulombic correction factors consistent only with the Donnan model of the interface, even though charge and potential are related by Gouy-Chapman theory in many current surface complexation models. This inconsistency arises from use of $z_r F \psi$ to represent electrostatic work in all cases.

7. COMPARISON OF CURRENT AND REVISED COULOMBIC FACTORS

Comparison of coulombic factors corresponding

to the Donnan and diffuse layer molecular models is shown in Figure 2 which covers all the reactions listed in Table 1. The coulombic factors for the diffuse layer molecular model in the negative potential

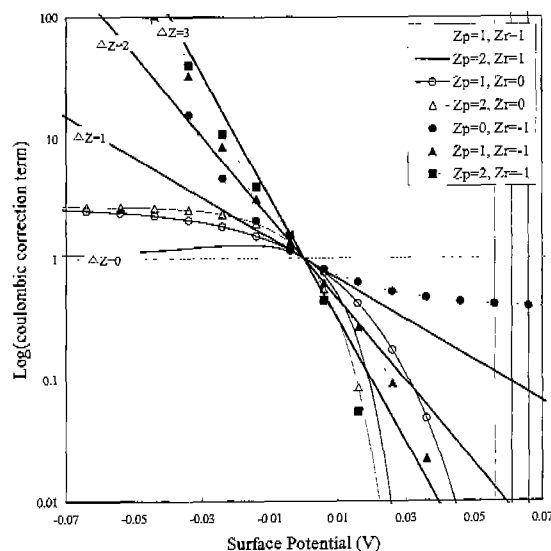


Figure 2. Comparison of the coulombic correction factors corresponding to diffuse layer molecular and Donnan models. The former, $\exp[-(P^{Z_p} - P^{Z_r})]$, is represented as curves and the latter, $P^{-(Z_p - Z_r)}$, is shown as the straight lines for three cases ($Z_p - Z_r = 1, 2,$ and 3). P is $\exp(F\psi/RT)$.

region are strongly dependent on the charge number of the surface species in the reactant side of surface complexation reactions, while the coulombic factors in the positive potential region are related strongly to the charge number of the product-surface species. In the negative potential region, the diffuse layer model factors are always less than the Donnan model factors for counterion adsorption onto negatively charged sites (reactions 1, 10, 13; 2, 12; 3), but they become greater for the cation sorption onto the neutral surface species (reactions 4, 5, 6). For the formation of positively charged surface species (i.e., $z_p = \text{positive value}$) in the positive potential region, the coulombic factors for the diffuse-layer model are always greater than those for the corresponding Donnan model regardless of the charge number of the reacting surface species. Thus, cation adsorption on the pH-dependent charge sites such as alumina or goethite will be predicted to become less with reducing pH with adoption of the corrected coulombic correction factor. The different coulombic factors for reactions with the same Δz shown in Table 1 (e.g., reactions 1, 4, 5, and 9) make intuitive sense because the electrostatic interaction of an ion with a surface species may be affected by the absolute charge of the reacting species.

The magnitude of the coulombic factor corresponding to the diffuse layer model suggests calculated equilibrium values of the surface potential will likely vary between 0.1 and -0.1 V. Since the calculated potential is small for the corrected diffuse layer model, the contribution of diffuse layer sorption will be reduced.

Modeling fits for acid-base titration data on goethite suspensions at the three ionic strengths [6] were worse for the revised (diffuse layer) coulombic correction factors than for the current (Donnan) ones, shown in Figure 3. These fits were obtained with the two-layer (diffuse layer) surface complexation model (Dzombak and Morel, 1990) implemented with the two different coulombic terms. The relevant surface complexation reactions are presented in Table 1 along with the relevant solution reactions. Fitting of surface complexation constants was performed by implementing the model in Maple (University of Waterloo, 1985), using the parameter optimization

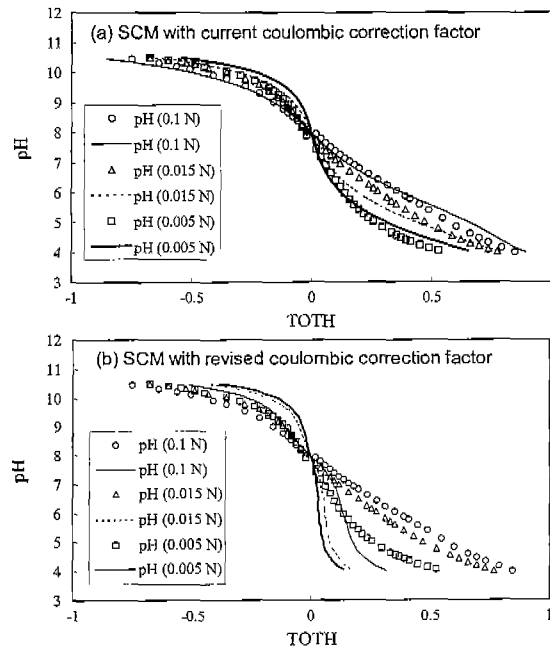


Figure 3. Surface complexation modeling for the titration data on goethite suspensions with the current (a) and revised (b) coulombic correction factors.

algorithm. As evident in Figure 2, the calculated potentials at the solid/water interface in magnitude were lower with the revised factor (60 mV) than with the current factor (173 mV) across the range of data fitted. The lower surface potential calculated with the revised coulombic terms decreased the diffuse-layer sorption and the amount of charged surface complexes (i.e., $\equiv\text{FeOH}^+$, $\equiv\text{FeO}^-$). The dominant surface species was calculated to be the neutral species ($\equiv\text{FeOH}^0$). This made the calculated values for TOTH reduced for the same pH, compared to the current (Donnan model) coulombic correction.

8. SUMMARY

Current surface complexation models describe the reaction of surface functional groups with ions in the solution. Mass law equations are used to describe these reactions at equilibrium. The Gouy-Chapman theory is usually invoked to describe the relationship between surface charge and potential. The surface potential is incorporated in a coulombic correction term that is included in the mass law

expressions to account for the variable electrostatic effects. In current models, however, the coulombic factor derivations are not wholly consistent with the Gouy-Chapman model of the interface. These derivations use $z_i F \psi$ as the electrostatic work to move an ion into the interfacial region, which is consistent with an abrupt variation in the surface potential between the countercharge layer and the bulk solution (i.e., the Donnan model).

A coulombic factor entirely consistent with Gouy-Chapman theory was obtained by considering the work done in transferring the ions under the varying electrical field, based upon the diffuse layer molecular model. Although it is less convenient to apply in equilibrium calculations, it accounts for the charges on the individual surface species that participate in surface reactions, as well as their charge difference. Also, the new coulombic factor generally yields lower surface potentials, calculated by Gouy-Chapman theory, which reduces the calculated diffuse-layer sorption. However, it provided worse fits

for acid-base titration data obtained with application of the two-layer surface complexation model to goethite suspensions.

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