Formulation and Description of Surface Complexation  
Model for Reactions at Solid-Water Interfaces

Sung-Jae Kim • Larry D. Benfield *
Department of Food Science, Fisheries College, Gyeongsang National University,  
Tongyeong, Gyeongnam, 650-160, Korea.  
*Department of Civil Engineering, Auburn University, Auburn, AL 36849, USA.

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Abstract - The development of all surface complexation models are based on electrostatic adsorption reactions which take place at defined coordination sites (in finite numbers) and then can be described quantitatively via mass law equations. A surface complexation model is a useful tool for several processes such as colloid stability and coagulation, particle deposition and filtration, dissolution, and precipitation of solid phases.

In this work, the model development is limited in the diffuse layer (DL) and triple layer (TL) surface complexation models. The equations are written for the reactions on the silanol surface group (SiOH) only and reaction among species (H⁺, OH⁻, Na⁺, Ca²⁺, Cl⁻, and SO₄²⁻) in solution, except for the formation of water, are not included. Electrostatic effects are included in the mass action laws as multiplicative terms similar to the concentration of each species. The entire set of equations can be solved numerically at any pH and electrolyte concentration with known values for the interfacial properties. The concentrations of individual surface species are calculated from the expressions including the solution concentrations [SiOH], the intrinsic equilibrium constants (Kᵢᵢᵢ), and the exponential terms of the electrostatic energy (exp(-σᵢᵢᵢ/kT) and exp(-σᵢᵢᵢ/kT)). The charges (σᵢ, σₑ, and σᵢₑ) and potentials (ψᵢ, ψₑ, and ψᵢₑ) are calculated from charge and potential relationships.

The computer algorithm MINEQL+ was used to compute the DL and TL surface complexation models, which is a computer algorithm for the geochemical equilibrium speciation model for dilute aqueous system.

Key Words: DL and TL surface complexation models, EDL, PZPC, electrostatic interaction, Boltzmann factor, intrinsic equilibrium constant, charge, potential, adsorption

INTRODUCTION

In the literature related to a particle removal process in natural water systems and in water and wastewater treatment systems, the role of differing solution chemistry and the surface properties of solid particles has been admitted only limitedly in determining the rate or extent of chemical reactions (adsorption, dissolution, precipitation) at the particle surface and in determining the resulting surface properties (charge, mineral identity, and ability to form chemical bonds). In practice neither the identity nor the stoichiometry of the particle surface has been generally taken into consideration. Rather, the solid particle-water system has been treated as a physical system. Recent study in surface chemistry provides good intelligence for the rate of many processes in natural water systems and in water and wastewater treatment systems that are controlled by specific chemical reactions and offers a clearer framework for predicting differences resulting from changes in master variables such as pH. For cases in which a specific chemical interaction (i.e., chemical step) is limiting, and the rate of that chemical step depends on the formation of some surface complex, a thermodynamic (equilibrium) description (i.e., surface complexation model) of the system can be used to examine the effect of changes in composition on the rate of many processes in natural water systems and in water and
wastewater treatment systems.

As particle and collector surfaces (or particle and particle surfaces) come close together, the electrical double layer (EDL) and London-van der Waals (LVDW) interaction forces determine if their associations are favorable in which the EDL interaction force can be calculated by using zeta potentials of the particle and collector. The zeta potential can be determined by both experimental methods and computational methods (i.e., surface complexion models), resulting from the nature of the EDL, which is determined by interactions between solid surface and dissolved species. The value of zeta potential is necessary to calculate the EDL terms (i.e., chemical effects) in colloid stability models\(^1\), surface interaction boundary layer models\(^2\) and trajectory models.\(^3\)

The surface complexion model provides a useful basis for examining several processes such as particle deposition in deep bed filtration, particle transport in groundwaters, coagulation, sludge dewatering, and the fate of particle-reactive pollutants in natural waters.

In this work, the particular surface complexion model, which is to examine if the observed effects of simple solution chemistry ([Na\(^+\)], [Ca\(^{2+}\)], and pH) on zeta potential are consistent with predicted effects based on the division of electrostatic and specific chemical interaction effects as described by the model, was formulated. The modeling work was restricted to doing the diffuse layer (DL) and triple layer (TL) surface complexion models.

**BASIC THEORY**

**Surface Charge Development**

In the surface complexion approach, surface charge can also originate by chemical reactions in which solutes (cations or anions except H\(^+\) or OH\(^-\)) become coordinatively bound to specific surface sites. These phenomena are frequently referred to as specific adsorption. Colloid chemists often assign these coordinating ions to the Stern layer: from a coordination chemistry point of view these ions—like H\(^+\) and OH\(^-\)—may be included with the fixed surface charge. Fig. 1 shows the acid-base and surface coordination reactions of a surface charge development for oxides.\(^4\)\(^,\)\(^5\)\(^,\)\(^6\)\(^,\)\(^7\)\n
H\(^+\) and OH\(^-\) are charge generating ions (i.e., potential-determining ions) as shown in Fig. 1 (a): either metal ions that coordinate with surface OH\(^-\) groups or ligands that can exchange with surface OH\(^-\) groups influence the surface potential (Figs. 1 (b), (c)). The specific binding of H\(^+\) and cations increases and the specific binding of OH\(^-\) and anions decreases the net charge of the particle surface.\(^8\)

The surface charge is determined experimentally by comparing the titration curve of an oxide suspension with that of the medium alone. If H\(^+\) or OH\(^-\) is the only specifically adsorbing ion in the system, the net consumption of H\(^+\) or OH\(^-\) by the solid phase can be determined by difference. The surface charge can then be calculated as a function of pH.\(^5\)\(^,\)\(^8\) The surface charge \(\sigma_0\) (C/m\(^2\): coulomb per square meter) is computed as:

\[
\sigma_0 = F(\Gamma_H - \Gamma_{OH})
\]

(1)

where F is the Faraday constant (96,480 C/mol); \(\Gamma_H\) and \(\Gamma_{OH}\) are the adsorption densities (mol/m\(^2\)) of H\(^+\) (and its complexes) and of OH\(^-\) (and its complexes), respectively. If cations and anions are specifically adsorbed on the hydrous
oxide surface, the surface charge is generally:

\[ \sigma_0 = F \left( \Gamma_H - \Gamma_{OH} + \sum \frac{z_i}{F} \Gamma_{M_i}^q + \sum \frac{z_j}{F} \Gamma_{A_j}^q \right) \]  \hspace{1cm} (2)

where \( z \) is magnitude of the charge of the nonhydrolyzed cation or deprotonated anion; \( \Gamma_{M_i}^q \) and \( \Gamma_{A_j}^q \) are the adsorption densities (mol/m²) of cations and of the deprotonated anions, respectively.\(^{10}\)

**Specific Ionic Adsorption**

Any ion whose adsorption or binding at the surface is influenced by forces other than simple electrical potential, may increase, decrease, or reverse the effective surface charge on the solid. The additional forces may be chemical in nature (i.e., involving some degree of covalent bonding with surface atoms) or they may be more physical (e.g., van der Waals forces between the ion and the surface or between clusters of specifically adsorbed ions, as occurs in the adsorption of surfactant ions).\(^{10}\) For chemical forces the adsorption must occur in the inner or compact part of the double layer.\(^{10}\) For physical forces, however, the ions are adsorbed only at the Outer Helmholtz Plane (OHP) because of their hydration sheaths.\(^{11}\) A physically adsorbed ion does not affect the pH of the point of zero proton condition (PZPC) but can reverse the sign of the \( \xi \) potential. A chemisorbed ion, on the other hand, shifts the PZPC and can remain adsorbed even when the underlying surface has the same sign as itself.\(^{11}\) The interaction of \( H^+ \), \( OH^- \), and other cations and anions with the surface groups is described by a chemical reaction and equilibrium constant.

The amphoteric ionization reactions of surface groups that cause charge development on oxide surfaces can be expressed by Fig. 1 (a). Although it is impossible to physically interpret the separation of the free energy of deprotonation into chemical and electrostatic parts with current theories and experiments,\(^{12}\) an ideal expression for the electrical term may be obtained from the Gouy-Chapman double layer theory.\(^{9, 8, 12, 14}\) To do this, the free energy of deprotonation consists of two elements: (1) the proton dissociation as measured by an intrinsic acidity constant \( K_{H}^{\text{in}} \) and (2) the proton transport through the interfacial potential gradient as expressed by the Boltzmann factor \( \exp \left( -e \phi(x)/kT \right) \); this separation of the dissociation reaction is thermodynamically arbitrary because the concentration of \( H^+ \) is not experimentally attainable.\(^{12, 14, 14, 15}\) Under ideal conditions, the proton concentration at the surface is related to the bulk solution concentration by:

\[ [H^+] = [H^+] \exp \left( -e \psi_0 \right) \frac{kT}{kT} \]  \hspace{1cm} (3)

and hence,

\[ K_{H}^{\text{in}} = \frac{[\text{MeOH}] [H^+] \exp(-e \psi_0/kT)}{[\text{MeOH}_2^-]} = K_{H}^{\text{in}} \exp \left( -e \psi_0 \right) \]  \hspace{1cm} (4)

\[ K_{H}^{\text{in}} = \frac{[\text{MeO}^-] [H^+] \exp(-e \psi_0/kT)}{[\text{MeOH}]} = K_{H}^{\text{in}} \exp \left( -e \psi_0 \right) \]  \hspace{1cm} (5)

where \( K_{H}^{\text{in}} \) and \( K_{H}^{\text{in}} \) are the intrinsic equilibrium constants (or the intrinsic acidity constants) which are based on the PZPC (i.e., a hypothetically completely chargeless surrounding) and can be corrected for electrostatic effects by a multiplicative Boltzman factor: \( K_{H}^{\text{in}} \) and \( K_{H}^{\text{in}} \) are the apparent equilibrium constants.\(^{4, 6, 15}\) The Boltzmann factor (exponential term), commonly referred to as an electrostatic or coulombic correction factor, is in fact an activity coefficient for EDL effects on proton exchange.\(^{12, 14, 16}\) The electrostatic effect appears in the mass action laws as a multiplicative term similar to the concentration of each species. This allows the exponential term to be considered as another component in solving the chemical equilibrium problem.\(^{14}\)

There is no direct way to obtain \( \psi_0 \) theoretically or experimentally. It is possible, however, to determine the apparent equilibrium constants experimentally and to extrapolate these constants to the PZPC in order to obtain intrinsic acidity constants. The pH of the PZPC (pH\(_{\text{PZPC}}\)) is given by Stumm and Morgan\(^{6}\) and Hohl et al.\(^{10}\) as

\[ pH_{\text{PZPC}} = \frac{1}{2} \left( pK_{H}^{\text{in}} + pK_{H}^{\text{in}} \right) \]  \hspace{1cm} (6)

Metal cations that form strong complexes with \( OH^- \) ions in solution also bind strongly to hydrous oxides in certain pH ranges. Metal adsorption to oxides is analogous to metal...
hydrolysis in solution in that both adsorption and hydrolysis increase as the pH is increased and both are accompanied by the release of protons.\(^5\) That is, adsorption of metal cations onto oxide surfaces is highly pH dependent.\(^1\)\(^5\)\(^9\) Proton and metal cations compete with each other for the available coordinating sites on the oxide surface. Cation binding can be characterized quantitatively by considering the formation of surface complexes as shown in Fig. 1 (b).

Cations are adsorbed onto oxide surfaces in response to both chemical and electrostatic forces. Effect of electrostatic interactions can be taken into account explicitly by separation of a coulombic term from the intrinsic equilibrium constant:

\[
K^{\text{int}}_{M2} = \frac{[>MeO^-]_2M^{2+}] [H^{+}]^2 \exp(-2e\psi_0/kT)}{[>MeOH]^2[M^{2+}] \exp(-e\psi_0/kT)} = K^{s}_{M2} \exp\left(\frac{ez\psi_0 - 2e\psi_0}{kT}\right)
\]

(7)

\[
K^{\text{int}}_{M1} = \frac{[>MeO^-M^{2+}] [H^{+}] \exp(-e\psi_0/kT)}{[>MeOH][M^{2+}] \exp(-e\psi_0/kT)} = K^{s}_{M1} \exp\left(\frac{ez\psi_0 - e\psi_0}{kT}\right)
\]

(8)

where \(K^{s}_{M1}\) and \(K^{s}_{M2}\) are the intrinsic equilibrium constants for cation adsorption, \(z\) charge of metal ion and \(\psi_0\) the Stern layer potential.\(^1\) Electrostatic interactions seem to have a weak influence on cation adsorption because cations can adsorb against electrostatic repulsion.\(^9\)\(^9\) Then, ionic strength appears to have little effect on the extent of cation adsorption.\(^2\)\(^1\)\(^2\)

Specific adsorption of anions is believed to involve ligand exchange reactions in which hydroxyl surface groups of the oxide are replaced by adsorbate molecules that bind directly to the central metal ions on the surface.\(^2\)\(^2\) That is, most common anions are less strongly hydrated in solution than cations. For this reason, the anions are more strongly adsorbed to the Inner Helmholtz Plane (IHP). Stumm et al.\(^2\)\(^3\) have shown that several anions have comparable tendencies to form metal complexes in solution and at the oxide-water interface.

Ligand exchange reactions of anions at reactive sites on oxide surfaces can be described by surface complexation reactions as shown in Fig. 1 (c). The influence of the interfacial electrostatic field can once again be taken explicitly into account by separation of EDL effects from the intrinsic equilibrium constant:

\[
K^{\text{int}}_{A1} = \frac{[>Me^-A^{2+}] [OH^-] \exp(e\psi_0/kT)}{[>MeOH][A^{2+}] \exp(e\psi_0/kT)} = K^{s}_{A1} \exp\left(\frac{e\psi_0 - ez\psi_0}{kT}\right)
\]

(9)

\[
K^{\text{int}}_{A2} = \frac{[>Me^-A^{2+}] [OH^-] \exp(2e\psi_0/kT)}{[>MeOH][A^{2+}] \exp(e\psi_0/kT)} = K^{s}_{A2} \exp\left(\frac{2e\psi_0 - ez\psi_0}{kT}\right)
\]

(10)

where \(K^{s}_{A1}\) and \(K^{s}_{A2}\) are the intrinsic equilibrium constants for anion adsorption. As is the case with cations, adsorption of anions can also take place against electrostatic repulsion, and ionic strength has only a weak effect on the extent of adsorption.\(^2\)\(^4\)\(^2\)\(^5\)

Anion adsorption is often referred to as the mirror image of cation adsorption because anion binding decreases as pH increases, and the process involves proton uptake.\(^2\) As is the case with cations, the adsorption of anions onto oxide surfaces is highly pH dependent. The anion adsorption is greatest at low pH and decreases gradually as pH increases.\(^1\)

**MODEL DEVELOPMENT**

The development of all surface complexation models are based on electrostatic adsorption reactions which take place at defined coordination sites (in finite numbers) and then can be described quantitatively via mass law equations. Different descriptions about EDL structure at the solid/water interface distinguish various models.\(^5\)\(^2\)\(^3\) In this work, the model development is limited in the so-called diffuse layer (DL) and triple layer (TL) surface complexation models. All of the
surface complexation models include the following equations to be solved numerically: (1) mass law equations for all possible surface reactions; (2) a mole balance equation for total surface sites; (3) an equation for computation of surface charge (charge and potential relationships); and (4) a set of electroneutrality equations representing the constraints imposed by the model chosen for the EDL structure.

In the DL model, there is only one surface plane of charge that includes surface sites and all adsorbed or coordinated species. A Gouy-Chapman diffuse layer is very close to this surface plane. In contrast with this the site binding model\cite{25} or TL model\cite{26} includes another β-plane at which other interacting species are located, in addition to the surface plane of charge that includes surface sites, adsorbed protons, and hydroxyl ions. The diffuse layer in the TL model begins at a plane outside of the β-plane. Charge and potential are related in the two compact inner layers by constant capacitances (C, C_a) assumed for each layer. The TL model is often referred to as the Gouy-Chapman-Stern-Grahame (GCSG) model. Davis et al\cite{26} used Grahame\cite{10} assumption that potential decays linearly between planes of charge in the compact layer. In the GCSG model as applied by Davis et al\cite{26}, the surface charge, σ_a is determined by the surface proton balance. A schematic diagram of the potential distribution in the interfacial region for the DL (a) and TL (b) models is shown in Fig. 2.

In general, the surfaces of the colloidal particle and collector can be considered to have several different types of surface sites simultaneously.\cite{41, 24, 31} James et al.\cite{41} suggested that in addition to monofunctional groups, latex particles may have more than one kind of functional group such as mixed sulfate and carboxylate groups or as zwitterionic carboxylate and amine groups, depending on conditions of preparation. Hunter\cite{9} suggested that some of the surface charge groups reside behind the physical surface of latex particles, possibly associated with some buried water. Herein the collector, which is a glass bead, is assumed to have only one amphoteric surface site capable of metal complexation and ligand exchange. This site is designated by the surface silanol functional group (SiOH) in an uncharged state. The colloidal particle, which is a latex particle, is assumed to have one mono acidic type site (COOH) but to have some amphoteric or zwitterionic surface sites as well.

In this work, the collector surface is negatively charged and can be modeled by considering the surface group as a monoprotic acid wherein the uncharged site dissociates to the negative site (SiO-) with release of a proton. The total surface site densities (mole/m²: No. of sites / (m²N_A) where N_A is Avogadro's number (6.022x10^23)) for the particle and collector are \Gamma_p and \Gamma_c, respectively. The surfaces have a specific surface area of S_p and S_c (m²/g) and mass concentrations of solids of C_p and C_c (g/l). Using the collector as an example, the total concentration of surface sites (X_p) in moles per liter is:

\[
[X_p] = C_c S_c \Gamma_c = \sum [\text{surface species}]_i \tag{11}
\]

This expression provides the constraint for a mass balance of all species that are associated with surface sites. The charge at the surface, or at any proposed plane of discrete charge, can be determined by summing the concentration of charged species that are postulated to occur there. If all of the surface sites were deprotonated, the maximum surface charge density
(C/m²) would be:

$$
\sigma_{0}(\text{mas}) = \left( \frac{F}{C_{c}S_{c}} \right) \chi_{T} = FGc
$$

(12)

From Gouy-Chapman diffuse layer theory, the charge density at the plane at which the diffuse layer begins is related to the potential at that plane and the valence and concentration of ions in bulk solution. For a general mixed electrolyte, the diffuse layer charge density ($\sigma_{d}$) is:

$$
\sigma_{d} = -sgn(\psi_{d})\left( 2e kT \sum_{i} n_{i}^{0} (\exp(-e_{i} \psi_{d}/kT) - 1) \right)^{1/2}
$$

(13)

where $sgn(\psi_{d}) = +1$ if $\psi_{d} > 0$ and $sgn(\psi_{d}) = -1$ if $\psi_{d} < 0$.

Although this expression is derived for planar surfaces, it is applicable for spheres when the radius of sphere particle ($a_{p}$) is large compared to the double layer thickness (i.e., $k_{B}T/a_{p} \gg 1$). The constraint of overall electroneutrality for the interfacial region requires that $\sigma_{n} = -\sigma_{d}$ for the DL model and $\sigma_{v} = -\sigma_{d}$ for the TL model where $\sigma_{n}$ is the charge density at the $\beta$-plane, the location of specific adsorbed species other than $H^{+}$ and $OH^{-}$.

In this work, it is assumed that the potential at the beginning of the diffuse layer is the appropriate potential to utilize when calculating EDL interactions. It also assumed that this potential, $\psi_{0}$, can be approximated by the $\xi$-potential determined from electokinetic experiments. Actually the charge accumulated in the diffuse layer that corresponds to the $\xi$-potential, or the electokinetic charge density ($\sigma_{e}$), is calculated using Eq. (13) modified by replacing $\sigma_{d}$ with $\sigma_{x}$ and $\psi_{d}$ with $\xi$:

$$
\sigma_{e} = -sgn(\xi)\left( 2e kT \sum_{i} n_{i}^{0} (\exp(-e_{i} \xi/kT) - 1) \right)^{1/2}
$$

(14)

Formulations for the DL and TL models are presented in Table 1. In the present work NaCl and CaCl₂ are used for the concentration of electrolyte, and H₂SO₄ and NaOH are used for the adjustment of pH. The equations are written for a specific problem involving the interaction of $H^{+}$, $OH^{-}$, mono and divalent cations ($Na^{+}$, $Ca^{2+}$), and mono and divalent anions ($Cl^{-}$, $SO_{4}^{2-}$) with amphoteric surface sites. However, in the DL model, the adsorption of anions such as $Cl^{-}$ and $SO_{4}^{2-}$ is neglected. The equations are written for the reactions on the silanol surface ($\gamma$SiOH) only, assuming that there are some amphoteric surfaces on the particle surface like the collector surface. Reaction among species in solution, except for the formation of water, are not included.

Electrostatic effects are included in the mass action laws formulated from proposed stoichiometric reactions such as those listed in Table 1. General expressions of mass action laws for surface chemical reactions are presented in the previous chapter (2. Basic Theory). Table 1 also includes the expressions for the calculation of the individual surface species concentrations which are calculated from the solution concentrations [$\gamma$SiOH], the intrinsic equilibrium constants ($K_{eq}$), and the exponential terms of the electrostatic energy ($\exp(-\epsilon_{ij}/kT)$ and $\exp(-\epsilon_{ij}/kT)$).

The formation of surface complexes readjusts the acid-base equilibrium and affects the surface charge. The surface charge density ($\sigma_{s}$) determined from the proton balance represents the net number of protons released or consumed by all surface reactions. Therefore, the surface charge is developed via surface complexation reactions in addition to the role of protons and hydroxyl ions. With the surface species defined, it is possible to write equations for $\sigma_{x}$ and $\sigma_{p}$.

The entire set of equations in Table 1 can be solved numerically at any pH and electrolyte concentration with known values for the interfacial properties that must be determined from experimental data. The model parameters with known values are: (1) the total concentrations of surface site, $\Gamma_{p}$ and $\Gamma_{c}$; (2) the intrinsic equilibrium constants such as $K_{eq}^{Na^{+}}$, $K_{eq}^{Ca^{2+}}$, $K_{eq}^{SiOH}$, $K_{eq}^{SiOH}$, $K_{eq}^{SiOH}$, $K_{eq}^{SiOH}$ and $K_{eq}^{SiOH}$; (3) the integral capacitances for the inner and outer parts of the compact layer, $C_{1}$ and $C_{2}$; (4) the specific surface areas, $S_{p}$ and $S_{c}$ and the mass concentration of solids, $C_{p}$ and $C_{c}$.

Because the accuracy of available techniques for measuring oxide surface areas and site densities is uncertain, surface site concentrations are sometimes considered to be adjustable parameters.

The computer algorithm MINTEQA2 was used to solve these equations. MINTEQA2 is a computer algorithm for the geochemical speciation model for dilute aqueous systems, which is a modification of the program MINTEQ that was developed by a combining the fundamental mathematical structure of MINEQL, a derivative of REDEQN, with the well-developed thermodynamic database of the U.S. Geological Survey's WATEQ3 model.
Table 1. Formulations for the diffuse layer and tripe layer surface complexation models.

<table>
<thead>
<tr>
<th>Surface Chemical Reactions</th>
<th>Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$ $\rightarrow$ $H^+$ + $OH^-$</td>
<td>$K_w$</td>
</tr>
<tr>
<td>$\rightarrow SiOH_2^+$</td>
<td>$\rightarrow SiOH + H^+$</td>
</tr>
<tr>
<td>$\rightarrow SiOH$</td>
<td>$\rightarrow SiO^- + H^+$</td>
</tr>
<tr>
<td>$\rightarrow SiOH + Na^+$</td>
<td>$\rightarrow SiO^-Na^+ + H^+$</td>
</tr>
<tr>
<td>$\rightarrow SiOH + Ca^{2+}$</td>
<td>$\rightarrow SiO^-Ca^{2+} + H^+$</td>
</tr>
<tr>
<td>$2\rightarrow SiOH + Ca^{2+}$</td>
<td>$(\rightarrow SiO^-)_2Ca^{2+} + 2H^+$</td>
</tr>
<tr>
<td>$\rightarrow SiOH + Cl^- + H^+$</td>
<td>$\rightarrow SiOHCl^- + H^+$</td>
</tr>
<tr>
<td>$\rightarrow SiOH + SO_4^{2-} + H^+$</td>
<td>$\rightarrow SiOHSO_4^{2-}$</td>
</tr>
</tbody>
</table>

Expressions for the Calculation of the Individual Surface Species

\[
[\rightarrow SiOH_2^+] = [\rightarrow SiOH]^H_\text{exp}(-e\psi_0/kT)K_{a1}^{int} / [H^+] \]

\[
[\rightarrow SiO^-] = [\rightarrow SiOH]^H_\text{exp}(e\psi_0/kT)K_{a2}^{int} / [H^+] \]

\[
[\rightarrow SiO^-Na^+] = [\rightarrow SiOH][Na^+]^H_\text{exp}(e\psi_0 - e\psi_\beta/kT)K_{Na}^{int} / [H^+] \]

\[
[\rightarrow SiO^-Ca^{2+}] = [\rightarrow SiOH][Ca^{2+}]^H_\text{exp}(e\psi_0 - 2e\psi_\beta/kT)K_{Ca}^{int} / [H^+] \]

\[
[\rightarrow SiO^-]_2Ca^{2+} = [\rightarrow SiOH]^H_2\text{exp}(2e\psi_0 - 2e\psi_\beta/kT)K_{Ca}^{int} / [H^+] \]

\[
[\rightarrow SiOHCl^-] = [\rightarrow SiOH][Cl^-]^H_\text{exp}(e\psi_\beta/kT)K_{Cl}^{int} \]

\[
[\rightarrow SiOH]SO_4^{2-} = [\rightarrow SiOH]^H_\text{exp}(2e\psi_\beta/kT)K_{SO_4}^{int} \]

Charge and Potential Relationships

1) Diffuse Layer Model

\[
\sigma_0 + \sigma_d = 0 \\
\sigma_d = -\sigma_0 = \text{sgn}(\psi_0)(2kekT\tau_0^0(\exp(e\psi_0/kT) - 1))^{1/2} \]

\[
\sigma_0 = (F/C_\text{C}S_C^0)([\rightarrow SiOH_2^+] + [\rightarrow SiO^-Ca^{2+}] + [\rightarrow SiO^-Na^+] - [\rightarrow SiO^-] \}

2) Triple Layer Model

\[
\sigma_0 + \sigma_\beta + \sigma_d = 0 \\
\sigma_d = -\sigma_0 = \text{sgn}(\psi_0)(2kekT\tau_d^0(\exp(e\psi_0/kT) - 1))^{1/2} \]

\[
\sigma_0 = C_1(\psi_\beta - \psi_0) + C_2(\psi_\beta - \psi_d) \]

\[
\sigma_\beta = (F/C_\text{C}S_C^0)([\rightarrow SiOH_2^+] + [\rightarrow SiO^-Ca^{2+}] + [\rightarrow SiOHCl^-] - [\rightarrow SiO^-] - [\rightarrow SiO^-Na^+] - [\rightarrow SiO^-Ca^{2+}] - 2[\rightarrow SiO^-Ca^{2+}] \]

\[
\sigma_\beta = (F/C_\text{C}S_C^0)([\rightarrow SiO^-Na^+] + 2[\rightarrow SiO^-Ca^{2+}] + 2[\rightarrow SiO^-Ca^{2+}] - [\rightarrow SiOHCl^-] \]

\[
- [\rightarrow SiOHCl^-SO_4^{2-}] \]

The intrinsic complexation constants are:

\[
K_{Cl}^{int} = \frac{K_{Cl}^{int}}{K_{a1}^{int}} \text{ where } K_{Cl}^{int} = [\rightarrow SiOHCl^-]/([\rightarrow SiOH_2^+][Cl^-]\text{exp}(e\psi_\beta/kT)) \]

\[
K_{SO_4}^{int} = \frac{K_{SO_4}^{int}}{K_{a1}^{int}} \text{ where } K_{SO_4}^{int} = [\rightarrow SiOHCl^-SO_4^{2-}]/([\rightarrow SiOH_2^+][SO_4^{2-}]\text{exp}(e\psi_\beta/kT)) \]

MINEQL is a general algorithm and database for computing chemical equilibria including solid and gas phases.

The TL model is useful for modeling electrokinetic ($\zeta$-) potentials of surfaces in aqueous solution because it calculates reasonable diffuse layer potential as well as simultaneously predicts the relatively high surface charge that is measured for many oxides and latex particles when the specific ionic adsorption in a separate $\beta$-plane occurs. It is possible that the
DL model can be used for modeling electrokinetic potentials by invoking reactions with the supposed indifferent electrolyte, at the expense of inaccurate prediction of the surface charge. Dzombak and Morel have shown that surface charge for oxide/water interfaces at different ionic strengths can be modeled as accurately by the DL model as by the TL model. The problem to model simultaneously the surface charge and electrokinetic potential of oxide and other surfaces in aqueous solution has been addressed by Hunter and James and Parks in comprehensive manner. However, in order to give reasonable predictions for observed \( \xi \) potentials, the position of the plane of shear must be moved to different positions outside of the beginning of the diffuse layer as the ionic strength changes.

**SUMMARY**

The development of all surface complexation models are based on electrostatic adsorption reactions which take place at defined coordination sites (in finite numbers) and then can be described quantitatively via mass law equations. The surface complexation model is a useful tool for several processes such as colloid stability and coagulation, particle deposition and filtration, dissolution, and precipitation of solid phases.

In this work, the model development is limited in the DL and TL models. In the DL model, there is only one surface plane of charge that includes surface sites and all adsorbed or coordinated species. A Gouy-Chapman diffuse layer is very close to this surface plane. In contrast with this the TL model includes another \( \beta \)-plane at which other interacting species are located, in addition to the surface plane of charge that includes surface sites, adsorbed protons, and hydroxyl ions. The diffuse layer in the TL model begins at a plane outside of the \( \beta \)-plane. In this work it is assumed that the potential at the beginning of the diffuse layer, \( \psi_D \), can be approximated by the \( \xi \) potential determined from electrokinetic experiments, which is the appropriate potential to utilize when calculating EDL interactions.

The TL model is useful for modeling electrokinetic (\( \xi \)) potentials of surfaces in aqueous solution because it calculates reasonable diffuse layer potential as well as simultaneously predicts the relatively high surface charge that is measured for many oxides and latex particles when the specific ionic adsorption in a separate \( \beta \)-plane occurs. The DL model can be used for modeling electrokinetic potentials by invoking reactions with the supposed indifferent electrolyte, at the expense of inaccurate prediction of the surface charge.

In this work, the collector surface is negatively charged and can be modeled by considering the surface group as a monoprotic acid wherein the uncharged site dissociates to the negative site (\( \text{SiO}^{-} \)) with release of a proton. The equations are written for the reactions on the silanol surface group (\( \text{SiOH} \)) only and reaction among species in solution, except for the formation of water, are not included.

The entire set of equations in Table 1 can be solved numerically at any pH and electrolyte concentration with known values for the interfacial properties that must be determined from experimental data. The concentrations of individual surface species are calculated from the expressions including the solution concentrations \( [\text{SiOH}] \), the intrinsic equilibrium constants \( (K_{eq}) \), and the exponential terms of the electrostatic energy \( (\exp(-e\phi/kT) \) and \( \exp(-ez\phi/kT) \). The charges \( (\sigma_a, \sigma_i, \text{ and } \sigma_g) \) and potentials \( (\phi_a, \phi_i \text{ and } \phi_g) \) are calculated from charge and potential relationships.

The computer algorithm MINTEQA2 was used to solve these equations. MINTEQA2 is a computer algorithm for the geochemical equilibrium speciation model for dilute aqueous system, which was developed by a combining the fundamental mathematical structure of MINEQL.

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**NOMENCLATURE**

\[ a_p \quad \text{radius of suspended particle} \]
\[ C_1, C_2 \quad \text{capacitance of inner, outer layer in triple layer model} \]
\[ C_{T_p}, C_{T_c} \quad \text{mass concentration of particle, collector, g/l} \]
\[ e \quad \text{unit charge of electron, } 1.602 \times 10^{-19} \text{ C} \]
\[ F \quad \text{Faraday constant, } 96,490 \text{ C/mol} \]
\[ k \quad \text{Boltzmann constant, } 1.38 \times 10^{-23} \text{ J/K} \]
\[ K_{11}, K_{22}, K_{33} \quad \text{intrinsic acidity constants} \]
\[ K_{A1}, K_{A2}, K_{A3} \quad \text{intrinsic equilibrium constants for anion} \]
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**REFERENCES**


