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Adsorption Models Incorporated into Chemical Equilibrium Models

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Adsorption is the net accumulation of a chemical species at the interface between a solid phase and an aqueous solution phase, leading to a loss from the solution phase (Sposito, 1989). Adsorption reactions can be described by various models. Empirical models provide descriptions of adsorption data without theoretical basis. Examples are the distribution coefficient, the Freundlich adsorption isotherm, and the Langmuir adsorption isotherm. Chemical models provide a molecular description of adsorption using an equilibrium approach. Surface complexation models are chemical models designed to calculate values of thermodynamic properties mathematically. Examples are the constant capacitance model (Stumm et al., 1980) the diffuse layer model, and the triple layer model (Davis et al., 1978). MICROQL (Westall, 1979) and FITEQL (Westall, 1982) are computer programs that have been used to optimize parameters for the surface complexation models. Equilibrium speciation models that contain the surface complexation models are MINTEQ (Felmy et al., 1984; Allison et al., 1990), SOILCHEM (Sposito & Coves, 1988) and HYDRAQL (Papelis et al., 1988). Transport models containing surface complexation models include TRANQL (Cederberg et al., 1985), HYDROGEOCHEM (Yeh & Tripathi, 1990), and the model of Jennings et al. (1982).

The purpose of this article is to review the common adsorption models and their incorporation into chemical equilibrium models. Model characteristics such as surface species, chemical reactions, equilibrium constant expressions, and surface activity coefficients will be described. Adjustable parameters and numerical methods for obtaining their values will be discussed. Limitations in the application of models to soil systems will be indicated.

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ADSORPTION MODELS

Empirical Models

A generalized empirical adsorption isotherm equation can be written as

$$x = \frac{bKc^{\beta}}{1 + Kc^{\beta}} \qquad [1]$$

where x is the amount adsorbed per unit mass; c is the equilibrium solution concentration; and ***b, K,*** and β are empirical parameters (Goldberg & Sposito, 1984a).

The distribution coefficient, K_d, is a linear equilibrium adsorption isotherm

$$x = K_d c \qquad [2]$$

Adsorption data usually conform to the linear assumption of the distribution coefficient expression over a very restricted solution concentration range. The distribution coefficient is a special case of Eq. [1] where $b = \beta = 1$ and $K_d c << 1$.

The Langmuir adsorption isotherm equation was developed to describe the adsorption of gases onto clean solids and implies uniform adsorption sites and absence of lateral interactions

$$x = \frac{bKc}{1+Kc} \qquad [3]$$

In many situations the Langmuir isotherm is able to describe adsorption only for low solution concentrations. The Langmuir isotherm is a special case of Eq. [1] where $\beta = 1$ (Goldberg & Sposito, 1984a). The Langmuir equation can be obtained theoretically based on rates of evaporation and condensation.

The Freundlich adsorption isotherm equation implies heterogeneity of adsorption sites

$$x = Kc^{\beta} \qquad [4]$$

The Freundlich isotherm is valid only for adsorption occurring at low solution concentration (Sposito, 1984). The Freundlich isotherm is a special case of Eq. [1] where $b = 1$, $0 < \beta < 1$, and $Kc^{\beta} < < 1$ (Goldberg & Sposito, 1984a).

Although the empirical models are often excellent at describing adsorption, they are simply numerical relationships used to curve-fit data (Harter & Smith, 1981). The parameters ***b, K,*** and β, obtained using the empirical models are valid only for the conditions under which the experiment was conducted. Use of these models to predict adsorption under changing conditions of solution concentration, ionic strength, and pH is not possible.

Chemical Models

As their name implies, surface complexation models treat ion adsorption as complexation reactions analogous to complex formation in solution. Surface complexes can exist in two types of structural configurations. Inner-sphere surface complexes contain no water molecules between the adsorbing ion and the surface functional group. These complexes are strong complexes involving either ionic or covalent bonding (Sposito, 1984). Outer-sphere surface complexes contain at least one water molecule between the adsorbing ion and the surface functional group. These complexes involve electrostatic bonding and are less stable than inner-sphere surface complexes (Sposito, 1984).

Surface complexation models consider the charge of both the adsorbate ion and the adsorbent surface. This can be considered their most significant advancement over the empirical models. The models differ in their structural representation of the solid-solution interface, that is, the location and hydration status of the adsorbed ions. The constant capacitance model, the diffuse layer model, and the triple layer model will be presented in detail. These surface complexation models have been incorporated into several chemical speciation models, and large data sets of equilibrium constants are available from the literature.

Constant Capacitance Model

The constant capacitance model of the oxide-solution interface was developed by Schindler, Stumm, and their coworkers (Schindler & Gamsjiger, 1972; Hohl & Stumm, 1976; Schindler et al., 1976; Stumm et al., 1976, 1980). The assumptions in the constant capacitance model are: (i) all surface complexes are inner-sphere complexes; (ii) the constant ionic medium reference state determines the activity of the aqueous species and therefore no surface complexes are formed with ions from the background electrolyte; (iii) one plane of charge represents the surface; (iv) the relationship between surface charge density, σ_o and surface potential. ψ_o, (where o represents the surface plane), is

$$\sigma_o = \frac{CSa}{F}\psi_o \qquad [5]$$

where C is the capacitance density (F m^{-2}), S is the surface area (m^2 g^{-1}), a is the suspension density (g L^{-1}), *F* is the Faraday constant (C mol_c^{-1}), σ has units of mol_c L^{-1}, and ψ_o has units of *V*. A diagram of the structure of the surface-solution interface for the constant capacitance model is provided in Fig. S-l.

The equations for the surface complexation reactions are (Hohl et al., 1980)

$$XOH + H+ \rightleftarrows XOH_2^+ \qquad [6]$$

$$XOH \leftrightarrows XO^- + H+ \qquad [7]$$

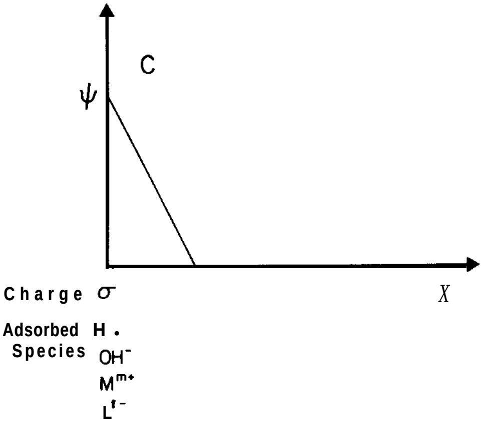

Fig. 5-1. Structure of the surface-solution interface for the constant capacitance model (after Westall, 1986).

$$XOH + M^{m+} \rightleftarrows XOM^{(m-1)} + H+ \qquad [8]$$

$$2XOH + M^{m+} \rightleftarrows (XO)_2M^{(m-2)} + 2H^+ \qquad [9]$$

$$XOH + L^{\ell-} \rightleftarrows XL^{(\ell-1)^-} + OH^- \qquad [10]$$

$$2XOH + L^{\ell-} \rightleftarrows X_2L^{(\ell-2)^-} + 2OH^- \qquad [11]$$

XOH represents the surface functional group, M is a metal ion of charge m^+, and L is a ligand of charge l-.

The intrinsic conditions equilibrium constants describing the surface complexation reactions are (Hohl et al., 1980)

$$K_+(\text{int}) = \frac{[XOH_2^+]}{[XOH][H^+]}\exp[F\psi_0/RT] \qquad [12]$$

$$K_-(\text{int}) = \frac{[XO^-][H^+]}{[XOH]}\exp[-F\psi_0/RT] \qquad [13]$$

$$K_M^1(\text{int}) = \frac{[XOM^{(m-1)}][H^+]}{[XOH][M^{m+}]}\exp[(m-1)F\psi_0/RT] \qquad [14]$$

$$K_M^2(\text{int}) = \frac{[(XO)_2M^{(m-2)}][H^+]^2}{[XOH]^2[M^{m+}]}\exp[(m-2)F\psi_0/RT] \qquad [15]$$

$$K_L^1(\mathrm{int}) = \frac{[XL^{(\ell-1)-}][OH^-]}{[XOH][L^{\ell-}]}\exp[-(\ell-1)F\psi_0/RT] \qquad [16]$$

$$K_L^2(\mathrm{int}) = \frac{[X_2L^{(\ell-2)-}][OH^-]^2}{[XOH]^2[L^{\ell-}]}\exp\left[-(\ell-2)F\psi_0/RT\right] \qquad [17]$$

where R is the molar gas constant (J $mol^{-1}K^{-1}$), int represents intrinsic, T is the absolute temperature (K), and square brackets represent concentrations (mol L^{-1}).

The mass balance expression for the surface functional group, XOH, is

$$[XOH], = [XOH] + [XOH_2^+] + [XO^-] + [XOM^{(m-1)}]$$

$$+2[(XO)_2M^{(m-2)}] + [XL^{(l-1)-}] + 2[X_2L^{(l-2)-}] \qquad [18]$$

The charge balance expression is

$$\sigma_o = [XOH_2^+] - [XO^-] + (m-1)[XOM^{(m-1)}] + (m-2)[(XO)_2M^{(m-2)}]$$

$$-(l-1)[XL^{(l-1)-}] - (l-2)[X_2L^{(l-2)-}] \qquad [19]$$

The constant capacitance model resembles the Helmholtz double layer in that the adsorbing ions are located immediately adjacent to the surface.

Diffuse Layer Model

The diffuse layer model of the oxide-solution interface was proposed by Stumm and coworkers (Stumm et al., 1970; Huang & Stumm, 1973) and developed as the generalized two-layer model by Dzombak and Morel (1990). The assumptions in the diffuse layer model are: (i) all surface complexes are inner-sphere complexes; (ii) no surface complexes are formed with ions in the background electrolyte; (iii) two planes of charge represent the surface; (iv) the relationships between surface charges and surface potentials are (Sposito, 1984; Papelis et al., 1988)

$$\psi_o = \psi_d \qquad [20]$$

$$\sigma_d = -\frac{Sa}{F}\left(8\varepsilon_o DRTI\right)^{1/2}\sinh\left(F\psi_d/\ 2RT\right) \qquad [21]$$

or

$$\sigma_d = -\frac{Sa}{F}\mathrm{sgn}\,\psi_d\left\{2\varepsilon_o DRT\sum_i c_i\left[\exp\left(-z_iF\psi_d/\ RT\right)-1\right]\right\}^{1/2} \qquad [22]$$

where ε_o is the premittivity of vacuum, ***D*** is the dielectric constant of water, **I** is the ionic strength, $\mathbf{sgn}\psi_d = 1$ if $\psi_d > 0$ and $\mathbf{sgn}\psi_d = -1$ if $\psi_d < 0$ (where *d* represents the diffuse plane), and c_i and z_i are the concentration and charge of solution Species ***i***. Equation [21] is equivalent to the Gouy-Chapman equation and applies to symmetrical electrolytes while Eq. [22] represents the general case. A diagram of the structure of the surface-solution interface for the diffuse layer model is provided in Fig. 5-2.

The equations for the surface complexation reactions are Eq. [6] and [7] for protonation-dissociation and Eq. [8] for metal adsorption. In the generalized two layer model no bidentate surface complexes are defined. The equations for the ligand surface complexation reactions are (Dzombak & Morel, 1990)

$$X\mathrm{OH} + \mathrm{L}^{\ell-} + \mathrm{H}^+ \rightleftarrows X\mathrm{L}^{(\ell-1)^-} + \mathrm{H_2O} \qquad [23]$$

$$X\mathrm{OH} + \mathrm{L}^{\ell-} + 2\mathrm{H}^+ \rightleftarrows X\mathrm{HL}^{(\ell-2)^-} + \mathrm{H_2O} \qquad [24]$$

The intrinsic conditional equilibrium constants for the surface complexation reactions are Eq. [12] and [13] for protonation-dissociation and Eq. [14] for metal adsorption where $\psi_o = \psi_d$. The intrinsic conditional equilibrium constants describing the ligand surface complexation reactions are (Dzombak & Morel, 1990)

$$K_{\mathrm{L}}^{1}(\mathrm{int}) = \frac{\left[X\mathrm{L}^{(\ell-1)^-}\right]}{[X\mathrm{OH}][\mathrm{L}^{\ell-}][\mathrm{H}^+]}\exp\left[-(\ell-1)F\psi_{\mathrm{d}}/RT\right] \qquad [25]$$

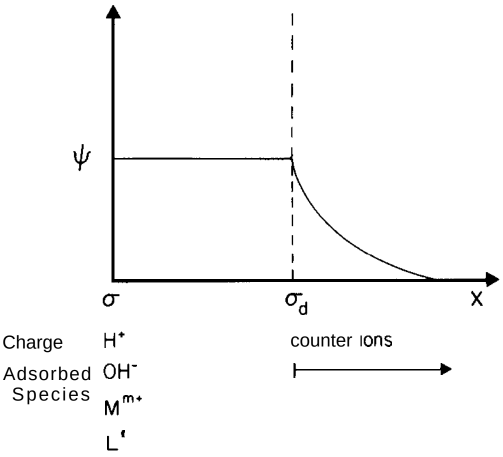

Fig. 5-2. Structure of the surface-solution interface for the diffuse layer model (after Dzombak & Morel, 1990).

$$K_L^2(\mathrm{int}) = \frac{\left[XHL^{(\ell-2)^-}\right]}{[XOH][L^{\ell-}][H^+]^2}\exp\left[-(\ell-2)F\psi_d \quad /RT\right] \qquad [26]$$

The mass balance expression for the surface functional group, XOH, is

$$[XOH]_T = [XOH] + \left[XOH_2^+\right] + \left[XO^-\right] + \left[XOM^{(m-1)}\right] + \left[XL^{(\ell-1)^-}\right] + \left[XHL^{(\ell-2)^-}\right] \qquad [27]$$

The charge balance expression is

$$\sigma_o = \left[XOH_2^+\right] - \left[XO^-\right] + (m-1)\left[XOM^{(m-1)}\right] - (\ell-1)\left[XL^{(\ell-1)^-}\right] - (\ell-2)\left[XHL^{(\ell-2)^-}\right] \qquad [28]$$

Triple Layer Model

The triple layer model of the oxide-solution interface was developed by Davis and coworkers (Davis et al., 1978; Davis & Leckie, 1978, 1980) as an extension of the site binding model (Yates et al., 1974) and modified to include inner-sphere surface complexation (Blesa et al., 1984a; Hayes & Leckie, 1986). The assumptions of the triple layer model are: (i) protons and hydroxyl ions form inner-sphere surface complexes, (ii) ion adsorption reactions form either outer-sphere or inner-sphere surface complexes, (iii) outer-sphere surface complexes are formed with ions from the background electrolyte, (iv) three planes of charge represent the surface, (v) the relationships between surface charges and surface potentials are Eq. [21] or [22] and

$$\sigma_o = \frac{C_1 Sa}{F}\left(\psi_o - \psi_\beta\right) \qquad [29]$$

$$\sigma_d = \frac{C_2 Sa}{F}\left(\psi_d - \psi_\beta\right) \qquad [30]$$

where C_1 and C_2 are capacitance densities. A diagram of the structure of the surface-solution interface for the triple layer model is provided in Fig. 5-3.

The equations for the inner-sphere surface complexation reactions in the triple layer model are Eq. [6] through [11] as written for the constant capacitance model. The equations for the outer-sphere surface complexation reactions are (Davis et al., 1978; Davis & Leckie, 1978, 1980)

$$XOH + M^{m+} \rightleftarrows XO^- - M^{m+} + H^+ \qquad [31]$$

$$XOH + M^{m+} + H_2O \rightleftarrows XO^- - MOH^{(m-1)} + 2H^+ \qquad [32]$$

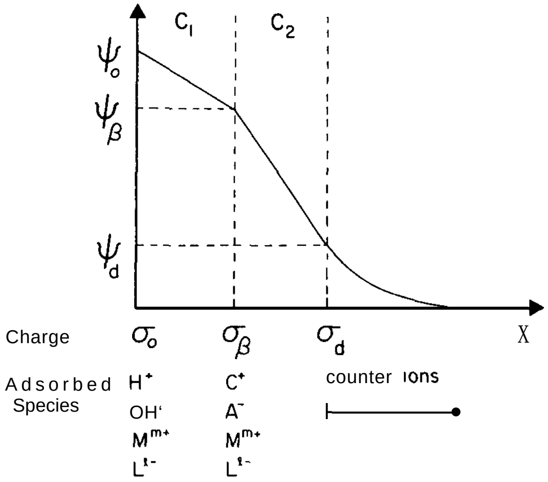

Fig. 5-3. Structure of the surface-solution interface for the triple layer model (after Westall, 1980).

$$\mathrm{XOH + H+ + L^{\ell-} \rightleftarrows \mathit{X}OH_2^+ - L^{\ell-}} \qquad [33]$$

$$\mathrm{XOH + 2H^+ + L^{\ell-} \rightleftarrows \mathit{X}OH_2^+ - LH^{(\ell-1)^-}} \qquad [34]$$

$$\mathrm{XOH{+}C{+} \rightleftarrows \mathit{X}O^- - C^+ {+}H{+}} \qquad [35]$$

$$\mathrm{XOH{+}H{+}\ {+}A{-} \rightleftarrows \mathit{X}OH_2^+ - A^-} \qquad [36]$$

where C+ is the cation and *A*- is the anion of the background electrolyte. Outer-sphere complexes are indicated by splitting the surface complexes with dashes.

The intrinsic conditional equilibrium constants for inner-sphere surface complexation are Eq. [12] through [17] as written for the constant capacitance model. The intrinsic conditional equilibrium constants for outer-sphere surface complexation are (Davis et al., 1978; Davis & Leckie, 1978, 1980)

$$K_{\mathrm{M}}^{1}\,(\mathrm{int}) = \frac{\left[X\mathrm{O}^- - \mathrm{M}^{m+}\right]\left[\mathrm{H}+\right]}{\left[X\mathrm{OH}\right]\left[\mathrm{M}^{m+}\right]}\exp\left[F\left(m\psi_\beta - \psi_o\right)/RT\right] \qquad [37]$$

$$K_{\mathrm{M}}^{2}\,(\mathrm{int}) = \frac{\left[X\mathrm{O}^- - \mathrm{MOH}^{(m-}\right]\left[\mathrm{H}^+\right]^2}{\left[X\mathrm{OH}\right]\left[\mathrm{M}^{m+}\right]}\exp\left\{F\left[(m-1)\psi_\beta - \psi_o\right]/RT\right\} \qquad [38]$$

$$K_{\mathrm{L}}^{1}(\mathrm{int}) = \frac{\left[X\mathrm{OH}_2^+ - \mathrm{L}^{\ell-}\right]}{[X\mathrm{OH}]\left[\mathrm{H}^+\right]\left[\mathrm{L}^{\ell-}\right]} \exp\left[F\left(\psi_o - \ell\psi_\beta\right)/RT\right] \qquad [39]$$

$$K_{\mathrm{L}}^{2}(\mathrm{int}) = \frac{\left[X\mathrm{OH}_2^+ - \mathrm{LH}^{(\ell-1)^-}\right]}{[X\mathrm{OH}]\left[\mathrm{H}^+\right]^2\left[\mathrm{L}^{\ell-}\right]} \exp\left\{F\left[\psi_O - (l-1)\psi_\beta\right]/RT\right\} \qquad [40]$$

$$K_{\mathrm{C}} + (\mathrm{int}) = \frac{\left[X\mathrm{O}^- - C^+\right]\left[\mathrm{H}^+\right]}{[X\mathrm{OH}]\left[C^+\right]} \exp\left[F\left(\psi_\beta - \psi_o\right)/RT\right] \qquad [41]$$

$$K_{\mathrm{A}} - (\mathrm{int}) = \frac{[\mathrm{XOH;\ \ -A-}]}{[X\mathrm{OH}]\left[\mathrm{H}^+\right]\left[\mathrm{A}^-\right]} \exp\left[F\left(\psi_o - \psi_\beta\right)/RT\right] \qquad [42]$$

The mass balance expression for the surface functional group, XOH, is

$$\begin{aligned} [X\mathrm{OH}]_{\mathrm{T}} &= [X\mathrm{OH}] + \left[X\mathrm{OH}_2^+\right] + \left[X\mathrm{O}^-\right] + \left[X\mathrm{OM}^{(m-1)}\right] \\ &+2\left[(X\mathrm{O})_2\,\mathrm{M}^{(m-2)}\right] + \left[X\mathrm{L}^{(\ell-1)-}\right] + 2\left[X_2\mathrm{L}^{(\ell-2)-}\right] + \left[X\mathrm{O}^- - \mathrm{M}^{m+}\right] \\ &+[\mathrm{XO-}\ \ - M\mathrm{OH}^{(m-1)}\Big] + \left[X\mathrm{OH}_2^+ - \mathrm{L}^{\ell-}\right] + \left[X\mathrm{OH}_2^+ - \mathrm{LH}^{(\ell-1)-}\right] \\ &+[\mathrm{XO-}\ \ - \mathrm{C}^+\Big] + \Big[X\mathrm{OH}_2^+\ \ \text{-}A\text{-}] \end{aligned} \qquad [43]$$

The charge balance expressions are

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \qquad [44]$$

$$\begin{aligned} \sigma_o &= \left[X\mathrm{OH}_2^+\right] + \left[X\mathrm{OH}_2^+ - \mathrm{L}^{\ell-}\right] + \left[X\mathrm{OH}_2^+ - \mathrm{LH}^{(\ell-1)-}\right] \\ &+(m-1)\left[X\mathrm{OM}^{(m-1)}\right] + (m-2)\left[(X\mathrm{O})_2\,\mathrm{M}^{(m-2)}\right] \\ &+\Big[X\mathrm{OH}_2^+\ \ \mathrm{-A-]\text{-}[XO-]\text{-}[XO-}\ \ - \mathrm{M}^{m+}\Big] - \left[X\mathrm{O}^- - \mathrm{MOH}^{(m-1)}\right] \\ &-(\ell-1)\left[X\mathrm{L}^{(\ell-1)-}\right] - (\ell-2)\left[X_2\mathrm{L}^{(\ell-2)-}\right] - \Big[X\mathrm{O}^-\ \ \mathrm{-c+}] \end{aligned} \qquad [45]$$

$$\begin{aligned} \sigma_\beta &= m\left[X\mathrm{O}^- - \mathrm{M}^{m+}\right] + (m-1)\left[X\mathrm{O}^- - \mathrm{MOH}^{(m-1)}\right] \\ &+\left[X\mathrm{O}^- + C^+\right] - \ell\left[X\mathrm{OH}_2^+ - \mathrm{L}^{\ell-}\right] \\ &-(\ell-1)\left[X\mathrm{OH}_2^+ - \mathrm{LH}^{(\ell-1)^-}\right] - \Big[X\mathrm{OH}_2^+\ \ \text{-}A\text{-}] \end{aligned} \qquad [46]$$

In the charge balance equations the coefficients are the charges on the portions of the surface complexes located in the particular surface plane.

OBTAINING VALUES OF ADJUSTABLE PARAMETERS

Surface Site Density

The total number of reactive surface functional groups, $[X\mathrm{OH}]_\mathrm{T}$ is an important adjustable parameter in surface complexation models. It is related to the surface site density, N_s, by the following equation (Westall, 1979)

$$[\mathrm{XOH}], = \frac{Sa10^{18}}{N_\mathrm{A}} N_\mathrm{S} \qquad [47]$$

where N_A is Avogadro's number and N_s has units of sites per square nanometer.

Values of surface site density can be determined using a wide variety of experimental methods, calculated from crystal dimensions (Sposito, 1984) or optimized to fit experimental adsorption data (Hayes et al., 1988). Experimental methods include tritium exchange (Davis & Leckie, 1978, 1980), potentiometric titration (Balistrieri & Murray, 1981; Hohl & Stumm, 1976; Kummert & Stumm, 1980), fluoride adsorption (Sigg, 1979) and maximum adsorption (Goldberg & Sposito, 1984a; Goldberg, 1985, 1986). James and Parks (1982) describe various methods of measuring of surface site density and provide values obtained with diverse methods for many oxide minerals. Determinations of surface site density vary by an order of magnitude depending on the method used. The lowest values are obtained from crystallographic calculations while the highest values are determined using tritium exchange. Recently, sensitivity analyses for acid-base titration data showed the goodness of fit of the surface complexation models to be relatively insensitive to surface site density values in the range of 1 to 100 sites per square meter (Hayes et al., 1991). However, the actual values of the protonation-dissociation constants decreased with increasing surface site density. The ability of the surface complexation models to describe anion adsorption using inner-sphere and outer-sphere surface complexes is sensitively dependent on the value of the surface site density (Goldberg, 1991).

Uncertainty in the value of the surface site density is one of the major limitations in the use of surface complexation models. Further research is needed to determine the most appropriate determination of surface site density. Because of the sensitivity to this parameter, agreement among researchers on a preferred methodology is necessary for the standardization of surface complexation modeling.

Capacitance Densities

Capacitance densities, C_i, relate the surface charges, σ_i, and the surface potentials, ψ_i, of the i^{th} plane. For the constant capacitance model, values of capacitance density can be obtained from the slope of plots of the conditional protonation-dissociation constants vs. surface charge as described in detail in

Goldberg (1992). A weakness of the constant capacitance model is that values of capacitance density obtained from linear extrapolations below the zero point of charge are usually not equal to the values obtained from linear extrapolations above the zero point of charge. Capacitance densities extrapolated in this fashion exhibit great variability even for experiments using the same batch of a reference mineral (Goldberg, 1992). Because of this variability, single values of capacitance density, considered optimum to fit experimental data are often used in applications of the constant capacitance model. These values are C = 1.8 F m^{-2} for goethite (Sigg, 1979) and C = 1.06 F m^{-2} for aluminum oxide (Westall & Hohl, 1980). The constant capacitance model is very insensitive to values of capacitance density.

In the diffuse layer model the relationship between surface charge and surface potential is defined by Eq. [21] or [22] andno capacitance density parameter is needed. At high ionic strength and for surfaces of low potential the diffuse layer model reduces to the constant capacitance model because Eq. [5] and Eq. [21] or [22] become approximately equivalent (Allison et al., 1990).

For the triple layer model, values of the capacitance density, C,, can be obtained from the slope of plots used in the linear extrapolation (Davis et al., 1978) and the double extrapolation techniques (James et al., 1978). In the Sprycha electrokinetic extrapolation (Sprycha, 1984, 1989a,b) the capacitance density, C,, is obtained from the slope of charge vs. potential curves (Eq. [29]), calculated using potential differences; the capacitance density, C_2, is obtained after determining the potential distribution within the electric double layer using electrokinetic data and Eq. [30]. The three extrapolation procedures are described in detail in Goldberg (1992). A weakness of the triple layer model is that, as for the constant capacitance model, the values of capacitance density obtained from extrapolations below the zero point of charge are not equivalent to the capacitance density values obtained from extrapolations above the zero point of charge (Smit & Holten, 1980; Blesa et al., 1984b). Capacitance density values are not completely constant, as assumed by the triple layer model, but vary as a function of pH and ionic strength (Sprycha, 1984, 1989b). With the exception of the above studies, the capacitance densities in the triple layer model have universally been taken as adjustable parameters. The capacitance density, C,, is adjusted to optimize the fit to experimental data and the capacitance density, C_2, is fixed at a value of 0.2 F m^{-2}.

Surface Complexation Constants

Values of the intrinsic conditional equilibrium constants for the surface complexation models can be obtained using extrapolation procedures or with the help of computer programs. For the constant capacitance model values of the intrinsic conditional protonation and dissociation constants have been obtained from alkimetric and acidimetric titration curves carried out in the absence of specifically adsorbing ions (Stumm et al., 1980). By plotting the titration data as the logarithms of the conditional protonation-dissociation constants vs. surface charge, the logarithms of the intrinsic conditional protonation-dissociation constants are obtained from the intercept where surface charge is zero. Values of intrinsic conditional protonation and dissociation constants obtained by various authors using the linear extrapolation technique are compiled in Goldberg (1992). Values of the intrinsic conditional protonation-dissociation constants also can be obtained by optimization of titration data using a computer program such as FITEQL (Westall, 1982). FITEQL will be discussed in detail in a subsequent section of the manuscript. In order to graphically evaluate intrinsic conditional surface complexation constants for metal adsorption, the simplifying assumption is made that $\psi_o = 0$ (Schindler et al., 1976). With this assumption the conditional intrinsic surface complexation constants are equal to the conditional surface complexation constants. Intrinsic conditional surface complexation constants for ligand adsorption have been obtained using the computer program MICROQL (Westall, 1979) or by computer optimization using FITEQL. MICROQL will be discussed in a later section of the manuscript. Values for intrinsic conditional surface complexation constants for metal adsorption obtained using graphical methods and for ligand adsorption obtained using computer optimization are compiled in Goldberg (1992).

So far, the application for the generalized two layer version of the diffuse layer model has been restricted to reactions occurring on the surface of hydrous ferric oxide (Dzombak & Morel, 1990). FITEQL was applied to individual titration data sets at each ionic strength to obtain best estimates of the intrinsic conditional surface complexation constants. Individual optimum values were weighted to obtain the best estimate with the following equation

$$\overline{\log K(\text{int})} = \sum \frac{\left(1/\sigma_{\log K(\text{int})}\right)_i}{\sum \left(1/\sigma_{\log K(\text{int})}\right)_i} \left[\log K(\text{int})\right]_i \qquad [48]$$

where $(\sigma_{\log K(\text{int})})_i$ is the standard deviation calculated by FITEQL for logK(int) of the i^{th} data set. Values of individual logK(int) and best estimates of logK(int) obtained by FITEQL computer optimization of various titration and adsorption data sets for hydrous ferric oxide are compiled in Dzombak and Morel (1990). Advantages of computer optimization are that the parameters are considered bias free and that parameter standard deviations and quality of fit criteria are available. Intrinsic conditional surface complexation constants for the generalized two layer version of the diffuse layer model are unique in that they are self-consistent. That is, all metal and ligand intrinsic conditional surface complexation constants were optimized using the best estimates of the intrinsic conditional protonation-dissociation constants obtained for hydrous ferric oxide, $\log \overline{K_+(\text{int})} = 7.29$ and $\log\overline{K_-(\text{int})} = -8.93$. No other self-consistent set of surface complexation constants are presently available for other surfaces or other surface complexation models.

For the triple layer model, intrinsic conditional protonation-dissociation constants and intrinsic conditional surface complexation constants for the background electrolyte can be obtained from linear extrapolation (Davis et al., 1978), double extrapolation, or Sprycha electrokinetic extrapolation (Sprycha, 1984, 1989a,b). These constants also can be obtained using the computer program FITEQL. Intrinsic conditional surface complexation constants for metal and ligand adsorption have been obtained using the computer program MICROQL or by computer optimization using FITEQL. Values for the intrinsic conditional surface complexation constants are compiled in Goldberg (1992).

NUMERICAL SOLUTION OF THE EQUILIBRIUM PROBLEM

The mathematical solution of the chemical equilibrium problem involves definition of a set of species and a set of components. Species are all chemical entities considered in the chemical equilibrium problem. Components are defined such that every species can be formed as a result of a reaction involving only components and no component can be formed solely from reaction of other components (Westall, 1980). Mass law equations describe the formation of each species from the components (Westall, 1980)

$$\log C_i = \log K_i + \sum_j a_{ij} \log X_j \qquad [49]$$

where C_i is the concentration of Species i, K_i is the formation constant for species i, a_{ij} is the stoichiometric coefficient of Component j in Species i, and X_i is the free concentration of Component j. For each component there is associated a mass balance equation (Westall, 1980)

$$Y_j = \sum a_{ij} C_i - T_j \qquad [50]$$

where Y_j is the residual or error in the mass balance equation and T_j is the total concentration of Component j. An iterative Newton-Raphson technique is used to find improved values of X so that the value of the error Y becomes smaller

$$Z \bullet \Delta X = Y \qquad [51]$$

where Z is the Jacobian whose elements are given by (Westall, 1980)

$$Z_{jk} = \frac{\partial Y_j}{\partial X_K} = \sum_i \left(a_{ij} a_{ik} C_i / X_K \right) \qquad [52]$$

The iteration procedure is carried out until the error in the mass balance equation is small (Westall, 1980)

$$\in > \frac{|Y_j|}{\sum |a_{ij} C_i| + |T_j|} \qquad [53]$$

where $\in$ is the convergence criterion.

Electrostatic Potential Terms

The constant capacitance model, the diffuse layer model, and the triple layer model all contain at least one coulombic correction factor to account for the effect of surface charge on surface complexation. These coulombic correction factors take the form of electrostatic potential terms, $e^{-F\psi_i}$/RT where ψ_i is the surface potential in the i^{th} surface plane in the intrinsic conditional surface complexation constant expressions. Sposito (1983) has shown that surface complexation models of the oxide-solution interface can be considered as special cases of the van der Waals model in statistical mechanics. In the van der Waals model, charged surface complexes create a long-ranged mean electric force field from screened coulomb forces by mutual interaction and short-ranged interactions are neglected. The mean field effect is responsible for the presence of electrostatic potential terms in the intrinsic conditional surface complexation constant expressions. According to the van der Waals model, the surface activity coefficient differs from a value of unity because total potential energy changes when neutral surface hydroxyl groups are replaced by charged surface complexes (Sposito, 1983). Invocation of diffuse double layer theory is not necessary to lend chemical significance to the exponential terms (Sposito, 1983). Unfortunately, diffuse double layer effects have been invoked almost universally in surface complexation model applications to explain the presence of the exponential terms (Allison et al., 1990). The electrostatic potential terms should simply be considered as solid-phase activity coefficients that correct for the charges on the surface complexes.

Electrostatic potential terms are included in the set of components as "dummy components." The Jacobian element is modified to (Westall, 1980)

$$Z_{\psi\psi} = \frac{\partial Y_\psi}{\partial X_\psi} = \sum_i \left(a_{i\psi} a_{i\psi} C_i C_\psi \right) - \frac{\partial T_\sigma}{\partial X_\psi} \qquad [54]$$

A species-component matrix shows the formation of the species from the components. Generalized species-component matrices are provided for the constant capacitance model (Table 5-1), the diffuse layer model (Table 5-2), and the triple layer model (Table 5-3).

FITEQL Program

FITEQL (Westall, 1982) is an iterative nonlinear least squares optimization program designed to fit values of equilibrium constants or total component con-

Table 5-1 Stoichiometry of the equilibrium problem for the constant capacitance model.

	Components				
Species	XOH	$e^{-F\psi_\sigma/RT}$	M^{m+}	L^{l-}	H^+
H^+	0	0	0	0	1
OH^-	0	0	0	0	-1
XOH_2^+	1	1	0	0	
XOH	1	0	0	0	0
XO^-	1	-1	0	0	-1
M^{m+}	0	0	1	0	0
$XOM^{(m-1)}$	1	m-1	1	0	-1
$(XO)_2M^{(m-2)}$	2	m-2	1	0	-2
L^{l-}	0	0	0	1	0
$XL^{(1-l)-}$	1	1-l	0	1	1
$X_2L^{(1-2)-}$	2	2-l	0	1	2

Table 5-2. Stoichiometry of the equilibrium problem for the diffuse layer model.

	Components				
Species	XOH	$e^{-F\psi_d/RT}$	M^{m+}	L^{1-}	H^+
H^+	0	0	0	0	1
OH^-	0	0	0	0	-1
XOH_2^+	1	1	0	0	1
XOH	1	0	0	0	0
XO^-	1	-1	0	0	-1
M^{m+}	0	0	1	0	0
$XOM^{(m-1)}$	1	m-l	1	0	-1
L^{1-}	0	0	0	1	0
$XL^{(1-l)-}$	1	1-l	0	1	1
$XHL^{(1-2)-}$	1	2-l	0	1	2

Table 5-3. Stoichiometry of the equilibrium problem for the triple layer model.

	Components							
Species	XOH	$e^{-F\psi_o/RT}$	$e^{-F\psi_\beta/RT}$	M^{m+}	L^{1-}	C^+	A^-	H^+
H^+	0	0	0	0	0	0	0	1
OH^-	0	0	0	0	0	0	0	-1
XOH_2^+	1	1	0	0	0	0	0	1
XOH	1	0	0	0	0	0	0	0
XO^-	1	-1	0	0	0	0	0	-1
M^{m+}	0	0	0	1	0	0	0	0
$XOM^{(m-1)}$	1	m-l	0	1	0	0	0	-1
$(XO)_2M^{(m-2)}$	2	m-2	0	1	0	0	0	-2
$XO^-–M^{m+}$	1	-1	m	1	0	0	0	-1
$XO^-–MOH^{(m-1)}$	1	-1	m-l	1	0	0	0	-2
L^{1-}	0	0	0	0	1	0	0	0
$XL^{(1-l)-}$	1	1-l	0	0	1	0	0	1
$X_2L^{(1-2)-}$	2	2-l	0	0	1	0	0	2
$XOH_2^+–L^{1-}$	1	1	-1	0	1	0	0	1
$XOH_2^+–LH^{(1-l)-}$	1	1	1-l	0	1	0	0	2
C^+	0	0	0	0	0	1	0	0
$XO^-–C^+$	1	-1	1	0	0	1	0	-1
A^-	0	0	0	0	0	0	1	0
$XOH_2^+–A^-$	1	1	-1	0	0	0	1	1

centrations to experimental data. FITEQL version 2.0 (Westall, 1982) contains the following surface complexation models: constant capacitance, diffuse layer, Stem, and triple layer. The program includes ionic strength calculations with the Davies equation. Basic steps in the use of FITEQL for the optimization of surface complexation constants are (Dzombak & Morel, 1990): (i) input the chemical equilibrium problem; (ii) input the total component concentrations and known K_i values and guesses for the unknown K_i values; (iii) input the experimental total and free concentrations; (iv) compute equilibrium concentrations; (v) compute the residuals for all components where both total and free concentration are known; (vi) test for convergence, that is, minimization of the squares of the residuals; (vii) compute improved estimates for the unknown K_i values and continue until convergence is achieved. An indicator of goodness of fit is the overall variance, V, in Y (Westall, 1982)

$$V_Y = \frac{\mathrm{SOS}}{\mathrm{DF}} \qquad [55]$$

where SOS is the weighted sum of squares of the residuals and ***DF*** is the degrees of freedom.

MICROQL **Program**

MICROQL (Westall, 1979) is a chemical equilibrium program written in BASIC that includes the following surface complexation models: constant capacitance, diffuse layer, Stern, and triple layer. Similar to the FITEQL model, thermodynamic equilibrium constants and the species-component matrix are entered by the user. Unlike FITEQL, MICROQL cannot be used to optimize unknown surface complexation constants mathematically. However, the MICROQL program has been used to find surface complexation constant values that produce a visually acceptable fit to data by trial and error.

INCORPORATION OF SURFACE COMPLEXATION MODELS INTO CHEMICAL SPECIATION MODELS

SOILCHEM

The chemical speciation model SOILCHEM (Sposito & Coves, 1988) a successor to the programs GEOCHEM (Sposito & Mattigod, 1980) and REDEQL2 (McDuff & Morel, 1973), contains the constant capacitance model. The model identifies all components as uncomplexed metals or ligands. Thus surface complexation reactions are written as occurring via reaction with the "metal," $X\mathrm{OH}_2^+$, or the "ligand," $X\mathrm{O}^-$. When the constant capacitance model is considered both components $X\mathrm{OH}_2^+$ and $X\mathrm{O}^-$ must be entered. Their total concentration sums to the number of average reactive surface sites on the soil particle surface. SOILCHEM contains intrinsic conditional surface complexation constant values for the adsorption of the metals Cu^{2+}, Pb^{2+}, Cd^{2+}, and Ba^{2+} and the ligands F^-, PO_4^{3-}, $\mathrm{SiO}_2(\mathrm{OH})_2^{2-}$, $\mathrm{B(OH)}_4^-$, AsO_4^{3-}, SeO_3^{2-}, acetate, salicylate, and catechol.

SOILCHEM also includes a cation exchange model to describe adsorption via outer-sphere surface complexes or diffuse ion swarm formation. Cation exchange is treated as a multicomponent precipitation-dissolution reaction and applies to monovalent and bivalent cations only (Sposito & Coves, 1988). The soil exchanger is represented by the "ligands" $XCON^-$ for the constant charge exchange sites and $XVAR^-$ for the variable charge exchange sites. The exchange reactions have the form (Sposito & Coves, 1988)

$$\mathrm{M}^{m+} + mX\mathrm{CON}^- \rightleftarrows \mathrm{M}X\mathrm{CON}_m \qquad [56]$$

$$\mathrm{M}^{m+} + mX\mathrm{VAR}^- \rightleftarrows \mathrm{MXVAR}, \qquad [57]$$

The activities of $\mathrm{M}X\mathrm{CON}_m$ and $\mathrm{M}X\mathrm{VAR}_m$ are assumed to equal unity and the activities of $X\mathrm{CON}^-$ and $X\mathrm{VAR}^-$ are set equal to their concentrations.

SOILCHEM contains cation exchange constant values for Ca^{2+}, Mg^{2+}, Sr^{2+}, Cu^{2+}, Ba^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, K^{+}, Na^{+}, and H^{+}.

SOILCHEM uses the Davies equation to calculate the activity coefficients for charged solution species. Activity coefficient expressions for uncharged solution species allow accurate speciation up to ionic strength of 2 mol L^{-1} (Sposito & Traina, 1987). The sources of the intrinsic conditional surface complexation constants and cation exchange constants are not provided in SOILCHEM.

MINTEQ

The chemical speciation program MINTEQA2 (Allison et al., 1990) contains seven adsorption models: the distribution coefficient, the Langmuir isotherm, the Freundlich isotherm, ion exchange, the constant capacitance model, the diffuse layer model, and the triple layer model. Two types of sites can be defined for each surface. In MINTEQA2 the distribution coefficient and the Langmuir and Freundlich isotherms are modified so that they are written in terms of solution activity of the adsorbing species. For the distribution coefficient and the Freundlich isotherm, the assumption is made that surface saturation cannot be attained. The Langmuir isotherm, however, accounts for a finite concentration of reactive surface sites.

The ion exchange model in MINTEQA2 is defined by the following equation (Allison et al., 1990)

$$XOH \bullet M_1 + M_2 \rightleftarrows XOH \bullet M_2 + M_1 \qquad [58]$$

The user specifies the exchangeable ion, M_1, that initially occupies the exchange sites, XOH, and is replaced by the adsorbing ion, M_2.

MINTEQA2 does not contain a thermodynamic data base for adsorption models. The user must provide the set of surface reactions and the accompanying equilibrium constants. Version 3.0 includes a data base for describing adsorption of the trace metals Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Be^{2+}, Ca^{2+}, and Ba^{2+}, and the ligands SO_4^{2-}, PO_4^{3-}, H_3AsO_3, H_3AsO_4, and H_3BO_3 onto two types of iron oxide sites with the diffuse layer model (Allison et al., 1990). The sources of the intrinsic conditional surface complexation constants are not provided in MINTEQA2. Activity coefficients in MINTEQA2 can be calculated using either the modified Debye-Htickel equation or the Davies equation. If the necessary Debye-Htickel parameters are unavailable the program defaults to the Davies equation for that ion.

HYDRAQL

The chemical speciation program HYDRAQL (Papelis et al., 1988) is a descendant of MINEQL (Westall et al., 1976) and contains five surface complexation models: the constant capacitance model, the diffuse layer model, the Stern model, the triple layer model, and a four layer model. The four layer model allows the smaller cations to approach the surface more closely than the bigger anions necessitating the addition of a fourth charge-potential relationship and a third capacitance density parameter. Two adsorbent surfaces can be considered by the HYDRAQL program. The thermodynamic data base for

HYDRAQL does not contain any intrinsic conditional surface complexation constants. For all ions and all surface complexation models these parameters must be input by the user. HYDRAQL calculates activity coefficients using the Davies equation for ionic strengths up to 0.5 mol L^{-1}. For ionic strengths greater than 0.5 mol L^{-1}, the program warns the user to individually modify all intrinsic conditional surface complexation constants.

INCORPORATION OF SURFACE COMPLEXATION MODELS INTO TRANSPORT MODELS

Jennings and Coworkers (1982) Model

Jennings et al. (1982) developed a model to predict the one-dimensional transport of chemical species experiencing both solution complexation and competitive adsorption. They included the constant capacitance model to describe adsorption. Generalized examples of transport of hypothetical metals undergoing competitive adsorption at constant pH are presented.

TRANQL

The computer program TRANQL (Cederberg et al., 1985) combines the computer program MICROQL (Westall, 1979) containing the constant capacitance model with the transport model ISOQUAD (G.F. Pinder, 1976, unpublished data). TRANQL has been used to simulate the one-dimensional transport of Cd in a solution containing chloride and bromide at constant pH. Cadmium forms solution complexes with chloride and bromide as well as surface complexes.

HYDROGEOCHEM

The computer program HYDROGEOCHEM (Yeh & Tripathi, 1990,1991) is a two-dimensional transport model that contains the triple layer model to describe adsorption. It simulates the transport of multiple reactive solutes. An example simulates the one-dimensional transport of U and Np considering soluble complex formation, mineral precipitation and dissolution, and adsorption on iron oxide, goethite sites (Yeh & Tripathi, 1991). Electrostatic interactions are ignored for computational simplification.

LIMITATIONS IN APPLICATION OF SURFACE COMPLEXATION MODELS TO SOIL SYSTEMS

All surface complexation models contain the assumption that ion adsorption takes place at one or at most two sets of homogeneous reactive surface functional groups. Clearly, soils are complex, multisite mixtures having a variety of functional groups. However, experimental evidence suggests that even oxide mineral surfaces contain several sets of reactive surface functional groups (Rochester & Topham, 1979a,b; Benjamin & Leckie, 1980, 1981). Thus the intrinsic conditional surface complexation constants determined with the surface complexation models for soils and even for pure minerals represent average composite values for all sets of reactive surface functional groups (Goldberg, 1992).

Application of the surface complexation models to describe reactions on soil surfaces has been limited. The constant capacitance model has been used to describe phosphate (Goldberg & Sposito, 1984b), borate (Goldberg & Glaubig, 1986) arsenate (Goldberg & Glaubig, 1988), and selenite (Sposito et al., 1988) adsorption on soils. Using the intrinsic conditional equilibrium constants obtained for one soil or set of soils, Sposito et al. (1988) and Goldberg and Glaubig (1986) were able to qualitatively predict adsorption of selenite and borate, respectively, on another set of soils. The diffuse layer model has not yet been applied to soil materials. The triple layer model has been applied to titration data and background electrolyte adsorption data on soils (Charlet & Sposito, 1987). The triple layer model also has been used to describe Ca, Mg, sulfate (Charlet & Sposito, 1987) and chromate (Zachara et al., 1989) adsorption on soils. The study of Charlet and Sposito (1987, 1989) is the only one where intrinsic conditional protonation-dissociation constants and background electrolyte surface complexation constants were obtained for the soil sample, making all surface complexation constants self-consistent. In other studies, these constants were obtained from a literature compilation of various reference minerals (Goldberg & Sposito, 1984b; Goldberg & Glaubig, 1986, 1988; Sposito et al., 1988) or from the study of one reference mineral (Zachara et al., 1988). To allow incorporation of intrinsic conditional surface complexation constants into chemical equilibrium models, standardization of parameter values would be helpful. Sources of these constants should be provided in the computer programs.

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