Chapter 10

Equations and Models Describing Adsorption Processes in Soils

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Adsorption is defined as the net accumulation of a chemical species at the interface between a solid phase and an aqueous solution phase (Sposito, 1989). In adsorption this accumulation is restricted to a two-dimensional molecular structure on the surface. The chemical species that accumulates at the interface is called the adsorbate, while the surface where the accumulation takes place is called the adsorbent. Adsorption processes in soils can be described by a variety of models. Empirical adsorption models provide descriptions of experimental data without theoretical basis. Chemical adsorption models, on the other hand, provide a molecular description of the adsorption process using an equilibrium approach.

The purpose of this chapter is to review various equations and models used to describe ion adsorption in soils. First, the common empirical models used in soil chemistry will be described and their limitations evaluated. Second, the common chemical models used to describe adsorption on soil minerals will be presented and their advantages over the empirical approaches discussed. Last, limitations and approximations in the use of these chemical models in soil systems will be explained.

EMPIRICAL MODELS

Adsorption processes in soils have historically been described using empirical adsorption isotherm equations. Typically, such equations are excellent at describing experimental data despite their lack of theoretical basis. Popularity of the isotherm equations results in part from their simplicity and from the ease of estimation of their adjustable parameters.

Distribution Coefficient

A linear function is the simplest and most widely used adsorption isotherm equation. Such an adsorption isotherm equation is conventionally expressed in terms of the distribution coefficient, K_d:

$$x = K_d c \qquad [1]$$

where x is the amount of ion adsorbed per unit mass and c is the equilibrium solution ion concentration. Distribution coefficients have found wide use in describing contaminant adsorption in flowing systems (Reardon, 1981) and in transport models (Travis and Etnier, 1981). Because of the linear assumption, the distribution coefficient usually describes ion adsorption data only across a very restricted solution ion concentration range. Figure 10–1 shows the ability of the distribution coefficient to describe linear adsorption of the pesticide parathion from hexane onto a partially hydrated Israeli soil (Yaron and Saltzman, 1972). In this example adsorption is linear across the solution concentration range investigated.

Langmuir Isotherm Equation

The Langmuir adsorption isotherm equation was initially developed to describe the adsorption of gases onto clean solids. This equation can be derived theoretically based on evaporation and condensation rates. The Langmuir adsorption isotherm equation is:

$$x = \frac{x_m K c}{1 + Kc} \qquad [2]$$

where x_m is the maximum adsorption per unit mass and K is an affinity parameter related to the bonding energy of the surface. Use of the Langmuir isotherm implies a finite number of uniform adsorption sites and absence of lateral interactions. Despite the fact that these assumptions are violated in soils, the Langmuir equation has often been used to describe ion adsorption on soil materials. In many studies the Langmuir isotherm equation only described adsorption for low solution ion concentrations. Such an example is presented in Fig. 10–2a for phosphate adsorption on two Australian soils (Mead, 1981).
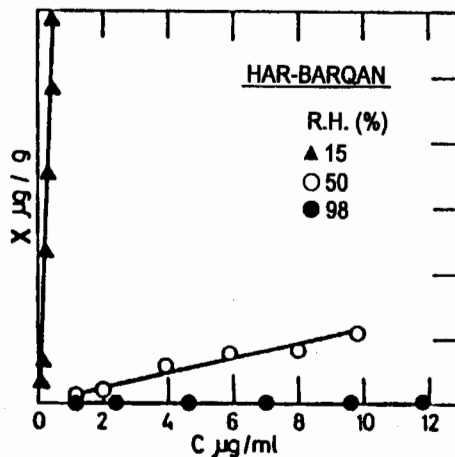

Fig. 10–1. Linear adsorption of parathion from hexane onto a partially hydrated Israeli soil at various relative humidities (from Yaron and Saltzman, 1972).

Multi-Surface Langmuir Adsorption Isotherm Equation

The Langmuir adsorption isotherm equation also has been formulated for the simultaneous adsorption of a gas by more than one surface. The multi-surface Langmuir isotherm is:

$$x = \sum_{i=1}^{n} \frac{x_{m_i} K_i c}{1 + K_i c}$$

[3]

where n is the number of sets of surface sites. Because of the increase in the number of adjustable parameters, fit to ion adsorption data with the multi-surface Langmuir isotherm equation is usually excellent. This improvement in fit can be observed in Fig. 10–2a for phosphate adsorption on two Australian soils (Mead, 1981).

Freundlich Adsorption Isotherm Equation

The Freundlich adsorption isotherm equation is the oldest of the nonlinear isotherms and its use implies heterogeneity of adsorption sites. The Freundlich isotherm equation is:

$$x = K c^{\beta}$$

[4]

where β is a heterogeneity parameter, th e smaller β the greater the expected heterogeneity (Kinniburgh, 1985). This expression reduces to a linear adsorption isotherm when $\beta = 1$. Although the Freundlich equation is strictly valid only for
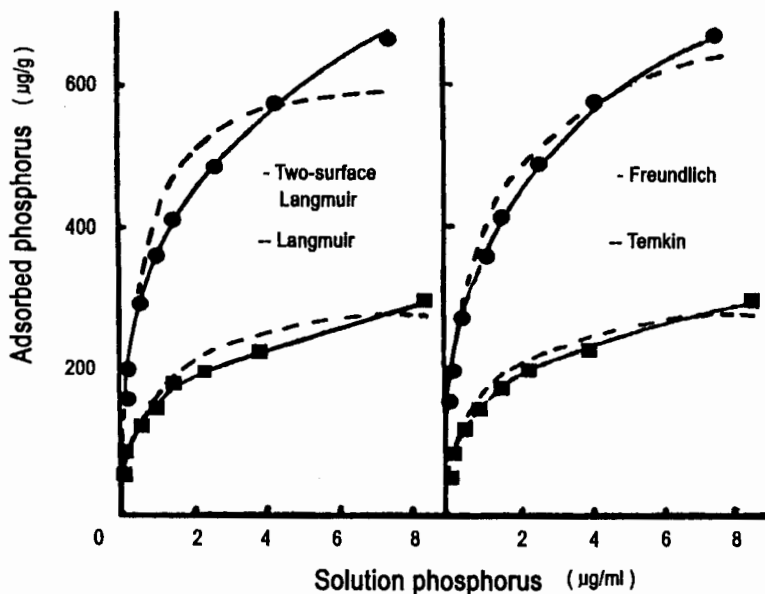

Fig. 10–2. Fit of various adsorption isotherm equations to phosphate adsorption by two Australian soils: (a) Euchrozem and (b) Black Earth (from Mead, 1981).

ion adsorption at low solution ion concentration (Sposito, 1984), it has often been used to describe ion adsorption by soils across the entire ion concentration range investigated. The ability of the Freundlich adsorption isotherm to describe data is indicated in Fig. 10–2b and 10–3 for phosphate adsorption by soils (Mead, 1981). The Freundlich adsorption isotherm does not obey Henry's law at low ion concentration nor does it reach an adsorption maximum at high ion concentration (Kinniburgh, 1985).

Temkin Adsorption Isotherm Equation

For the Temkin adsorption isotherm equation, the energy of adsorption is a linear function of the surface coverage (Travis and Etnier, 1981). The Temkin isotherm equation is:

$$x = a + b \log c \quad [5]$$

where a and b are parameters. The Temkin isotherm is valid only for an intermediate range of ion concentrations (Kinniburgh, 1985). Figure 10–2b indicates that the ability of the Temkin adsorption isotherm to describe phosphate adsorption is reduced at higher solution concentration (Mead, 1981).

Toth Adsorption Isotherm Equation

The Toth adsorption isotherm equation obeys Henry's law at low ion concentration and reaches an adsorption maximum at high ion concentration (Kinniburgh, 1985). The Toth isotherm equation is:

$$x = \frac{x_m Kc}{[1 + (Kc)^\beta]^{1/\beta}} \quad [6]$$

This expression reduces to the Langmuir adsorption isotherm when $\beta = 1$ (Kinniburgh, 1985). Figure 10–3 shows the fit of the Toth equation to phosphate adsorption on a Scottish soil (Kinniburgh, 1986).
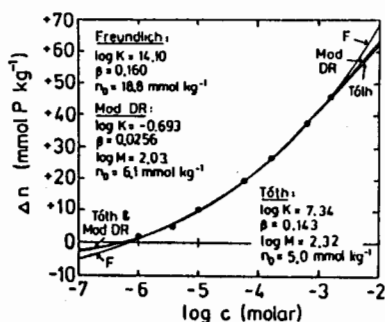

Fig. 10–3. Fit of various adsorption isotherm equations to phosphate adsorption on a Scottish soil (from Kinniburgh, 1986).

Dubinin-Radushkevich Adsorption Isotherm Equation

The Dubinin-Radushkevich adsorption isotherm equation is:

$$\log x = -\beta[\log(Kc)]^2 + \log x_m \qquad [7]$$

This isotherm is suitable only for an intermediate range of ion concentrations because it exhibits unrealistic asymptotic behavior (Kinniburgh, 1985). Such a fit is indicated in Fig. 10–3 for phosphate adsorption (Kinniburgh, 1986).

Limitations of the Empirical Approach

Operationally the Langmuir adsorption isotherm equation can describe experimental data from a precipitation reaction, although theoretically this is impossible (Veith and Sposito, 1977). Two theorems have been developed for the Langmuir adsorption isotherm equation (Sposito, 1982). The mechanism theorem states that the adherence of experimental data to the Langmuir adsorption isotherm equation provides no information about the chemical reaction mechanism. The interpolation theorem states that any reaction process for which the distribution coefficient, K_d, is a finite, decreasing function of the amount adsorbed, x, and extrapolates to zero at a finite value of x, can be represented mathematically using a two-surface Langmuir adsorption isotherm equation.

Although all of the above adsorption isotherm equations are often excellent at describing ion adsorption they must be considered simply as numerical relationships used to fit data. Independent experimental evidence of an adsorption process must be present before any chemical meaning can be assigned to isotherm equation parameters. Since the use of the adsorption isotherm equations constitutes essentially a curve-fitting procedure, isotherm parameters are valid only for the chemical conditions under which the experiment was conducted. Use of these equations for prediction of ion adsorption behavior under changing conditions of solution pH, ionic strength, and solution ion concentration is impossible.

Linear Transformations

The Langmuir and the Freundlich adsorption isotherm equations can be transformed to linear form thereby allowing the parameters to be estimated graphically or with linear regression. Various linear transformations of the Langmuir adsorption isotherm equation result in:

1. the reciprocal Langmuir plot:

$$\frac{c}{x} = \frac{1}{x_m K} + \frac{c}{x_m} \qquad [8]$$

2. the distribution coefficient or Scatchard plot:

$$\frac{x}{c} = x_m K - xK \qquad [9]$$

3. the Eadie-Hofstee plot:

$$x = x_m - \frac{x}{Kc}$$ [10]

4. the double reciprocal or Lineweaver-Burk plot:

$$\frac{1}{x} = \frac{1}{x_m} + \frac{1}{x_m Kc}$$ [11]

Each of these linear transformations produces changes in the original error distribution by giving greater weighting to low adsorption values than to high adsorption values (Kinniburgh, 1986). The reciprocal Langmuir plot is the linearization that has been used most commonly by soil scientists. An example of the reciprocal Langmuir plot is indicated in Fig. 10–4 for sulfate adsorption by four Oregon soils (Chao et al., 1962). The reciprocal Langmuir plot is less sensitive in detecting deviations from linearity than the Eadie-Hofstee plot (Dowd and Riggs, 1965). An additional disadvantage of Eadie-Hofstee and Scatchard plots is that they use the amount adsorbed, x, usually assumed to contain all of the measurement error, as the independent variable assumed to be error free in conventional regression analysis (Kinniburgh, 1986). The best linear transformation is not necessarily the one that gives the highest correlation coefficient but rather it is the one having an error distribution most closely matching the true error distribution (Kinniburgh, 1986).

The linear form of the Freundlich adsorption isotherm equation is:

$$\log x = \log K + \beta \log c$$ [12]

The frequent good fit of data to the Freundlich adsorption isotherm equation is at least partially due to the insensitivity of the linear form. Log-log plots are well known for their insensitivity. Figure 10–5 shows fit of the linear Freundlich plot to sulfate adsorption data (Chao et al., 1962). An additional disadvantage of the linear form
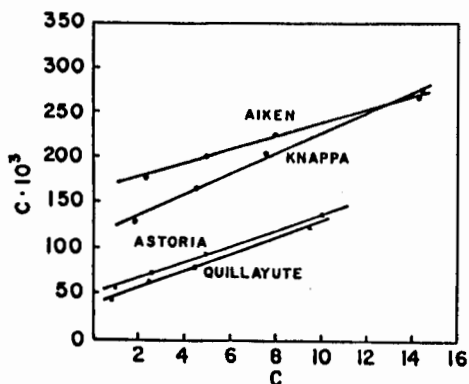

Fig. 10–4. Fit of the reciprocal Langmuir linearization to sulfate adsorption on four Oregon soils (from Chao et al., 1962).

is that all data points are not given equal weightings in the analysis of log-transformed values (Barrow, 1978).

Nonlinear Least Squares Methods

For equations such as the Temkin, Toth, and Dubinin-Radushkevich isotherms, containing three parameters, it is not possible to estimate parameters with linear regression or any reliable graphical method. Nonlinear regression is required to fit these isotherms. Nonlinear regression usually involves the minimization of residual sums of squares. This operation is no longer computationally difficult because of the wide availability of computer algorithms (Kinniburgh, 1986). Direct fitting of adsorption data using nonlinear least squares methods avoids the problems of changing error distribution and biased parameters associated with linear transformations. Such fitting is indicated in Fig. 10–3 for phosphate adsorption. Use of linear regression of any linear form with proper weighting, however, can provide parameter estimates close to those obtained using nonlinear least squares methods (Kinniburgh, 1986).

Nonlinear least squares methods involve finding the set of parameters that minimizes the weighted residual sum of squares, WRSS:

$$\text{WRSS} = \sum_{i=1}^{m} w_i(n_i - \hat{n}_i)^2 \qquad [13]$$

where $\hat{n}_i$ is the fitted value for observation i, w_i is the weighting factor, and m is the number of observations (Kinniburgh, 1986). The computer program ISOTHERM (Kinniburgh, 1985) contains nonlinear least squares routines for fitting numerous adsorption isotherm equations including those listed above. The principal criterion for comparing the goodness-of-fit of different isotherms to the same data set is the coefficient of determination, R^2 (Kinniburgh, 1985):
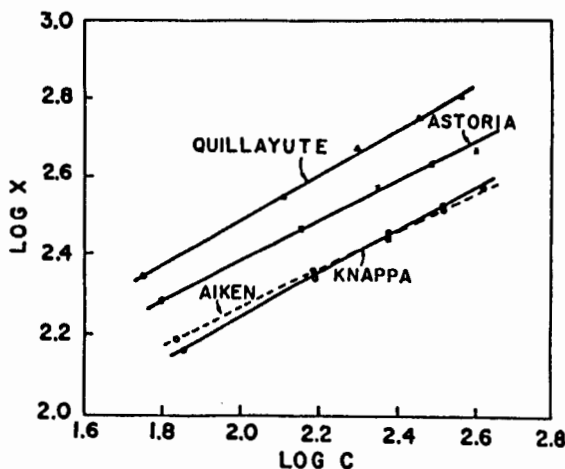

Fig. 10–5. Fit of the linear Freundlich isotherm to sulfate adsorption on four Oregon soils (from Chao et al., 1962).

$$R^2 = \frac{\text{RSS}}{\text{TSS}} \qquad [14]$$

where RSS is the residual sum of squares:

$$\text{RSS} = \sum_{i=1}^{m} (n_i - \hat{n}_i)^2 \qquad [15]$$

and TSS is the corrected total sum of squares:

$$\text{TSS} = \sum_{i=1}^{m} (n_i - \bar{n})^2 \qquad [16]$$

where $\bar{n}$ is the mean value of n_i. Nonlinear fitting of adsorption data can produce values of the coefficient of determination greatly improved over linear transformations (Goldberg and Forster, 1991).

CHEMICAL MODELS

Various chemical surface complexation models have been developed to describe ion adsorption and potentiometric titration data at the oxide-mineral solution interface. Surface complexation models provide molecular descriptions of ion adsorption using an equilibrium approach that defines surface species, chemical reactions, mass balances, and charge balance. Thermodynamic properties such as solid phase activity coefficients and equilibrium constant expressions are calculated mathematically. The major advancement of the chemical surface complexation models is consideration of charge on both the adsorbate ion and the adsorbent surface. Application of these models to reference oxide minerals has been extensive but their use in describing ion adsorption in soils has been limited. Three chemical surface complexation models have been applied to soil systems and will be discussed.

Balance of Surface Charge

The balance of surface charge on a soil particle in aqueous solution is defined by the following expression (Sposito, 1984):

$$\sigma_s + \sigma_H + \sigma_{is} + \sigma_{os} + \sigma_d = 0 \qquad [17]$$

where σ_s is the permanent charge due to isomorphous substitution in soil minerals, σ_H is the net proton charge due to formation of inner-sphere surface complexes between protons and hydroxyl ions and surface functional groups, σ_{is} is the charge due to formation of inner-sphere complexes between ions, other than protons and hydroxyls, and surface functional groups, σ_{os} is the charge due to formation of outer-sphere complexes with surface functional groups or with ions in inner-sphere complexes, and σ_d is the dissociated charge equal to minus the surface charge neutralized by background electrolyte ions in solution.

An inner-sphere surface complex contains no water between the adsorbate ion and the surface functional group. An outer-sphere complex, however, contains

at least one water molecule between the adsorbate ion and the surface functional group. Inner-sphere surface complexation of ions is called specific adsorption, or ligand exchange in the case of surface complexation of anions. Outer-sphere surface complexation is called nonspecific adsorption. The surface functional group is defined as XOH, where X represents a metal ion in the oxide mineral that is bound to a reactive surface hydroxyl group. In the application of surface complexation models to clay and soil systems, the surface functional group can also represent an aluminol or silanol group at the edge of a clay mineral particle.

Constant Capacitance Model

The constant capacitance model of the oxide–solution interface was developed by two research groups in Switzerland (Schindler and Gamsjäger, 1972; Hohl and Stumm, 1976; Schindler et al., 1976; Stumm et al., 1976, 1980). This model contains the following assumptions:

1. All surface complexes are inner-sphere complexes.
2. No surface complexes are formed with ions from the background electrolyte.
3. The Constant Ionic Medium Reference State determines the activity coefficients of the aqueous species.
4. Surface complexes exist in a chargeless environment in the Standard State.
5. The relationship between surface charge, σ, and surface potential, ψ, is linear and given by:
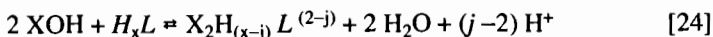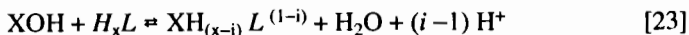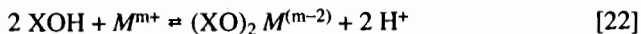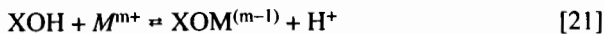
$$\sigma = \frac{CSa\,\psi}{F} \qquad [18]$$

where C is the capacitance (F m^{-2}), S is the surface area (m^2 g^{-1}), a is the suspension density (g L^{-1}), σ has units of mol$_c$ L^{-1}, F is the Faraday constant (C mol$_c^{-1}$), and ψ has units of V.

The protonation and dissociation reactions of the surface functional group are:

$$XOH + H^+ \rightleftharpoons XOH_2^+ \qquad [19]$$

$$XOH \rightleftharpoons XO^- + H^+ \qquad [20]$$

The surface complexation reactions for ion adsorption are:

$$XOH + M^{m+} \rightleftharpoons XOM^{(m-1)} + H^+ \qquad [21]$$

$$2\,XOH + M^{m+} \rightleftharpoons (XO)_2\,M^{(m-2)} + 2\,H^+ \qquad [22]$$

$$XOH + H_xL \rightleftharpoons XH_{(x-i)}\,L^{(1-i)} + H_2O + (i-1)\,H^+ \qquad [23]$$

$$2\,XOH + H_xL \rightleftharpoons X_2H_{(x-j)}\,L^{(2-j)} + 2\,H_2O + (j-2)\,H^+ \qquad [24]$$

where M represents a metal ion, $m+$ is the charge on the metal ion, L represents a ligand, x is the number of protons present in the undissociated form of the ligand, $1 \leq i \leq n$, and $2 \leq j \leq n$ where n is the number of ligand surface complexes and is equal to the number of dissociations undergone by the ligand.

The equilibrium constant expressions describing the above reactions are:

$$K_+(\text{int}) = \frac{[XOH_2^+]}{[XOH][H^+]} \exp[F\psi/RT] \tag{25}$$

$$K_-(\text{int}) = \frac{[XO^-][H^+]}{[XOH]} \exp[-F\psi/RT] \tag{26}$$

$$K_M^1(\text{int}) = \frac{[XOM^{(m-1)}][H^+]}{[XOH][M^{m+}]} \exp[(m-1)F\psi/RT] \tag{27}$$

$$K_M^2(\text{int}) = \frac{[(XO)_2M^{(m-2)}][H^+]^2}{[XOH]^2[M^{m+}]} \exp[(m-2)F\psi/RT] \tag{28}$$

$$K_L^i(\text{int}) = \frac{[XH_{(x-i)}L^{(1-i)}][H^+]^{(i-1)}}{[XOH][H_xL]} \exp[(1-i)F\psi/RT] \tag{29}$$

$$K_L^j(\text{int}) = \frac{[X_2H_{(x-j)}L^{(2-j)}][H^+]^{(j-2)}}{[XOH]^2[H_xL]} \exp[(2-j)F\psi/RT] \tag{30}$$

where R is the molar gas constant (J mol^{-1} K^{-1}), T is the absolute temperature ($^\circ$K), and square brackets represent concentrations (mol L^{-1}). The electrostatic potential terms $\exp(-F\psi_i/RT)$ are coulombic correction factors accounting for the effect of surface charge on surface complexation and can be considered as solid phase activity coefficients.

The mass balance for the surface functional group is:

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

$$+ \sum_{i=1}^{n} [XH_{(x-i)}L^{(1-i)}] + \sum_{j=2}^{n} 2[X_2H_{(x-j)}L^{(2-j)}] \tag{31}$$

and the charge balance is:

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

$$+ \sum_{i=1}^{n} (1-i)[XH_{(x-i)}L^{(1-i)}] + \sum_{j=2}^{n} (2-j)[X_2H_{(x-j)}L^{(2-j)}] \tag{32}$$

This set of equations can be solved by hand or with a computer program using the mathematical approach outlined in Westall (1980).

Triple Layer Model

The triple layer model of adsorption was developed at Stanford University (Davis et al., 1978; Davis and Leckie, 1978, 1980; Hayes and Leckie, 1986). The model contains the following assumptions:

1. Protons and hydroxyl ions form inner-sphere surface complexes.
2. Ion adsorption reactions produce either outer-sphere or inner-sphere surface complexes.
3. Ions from the background electrolyte form outer-sphere complexes.
4. The Infinite Dilution Reference State determines the activity coefficients of the aqueous species.
5. Three planes of charge represent the oxide surface.
6. The relationships between surface charges, σ_o and σ_d, and surface potentials, ψ_o, ψ_β, and ψ_d, are:
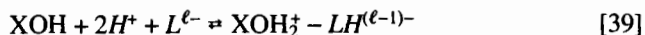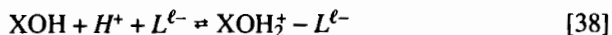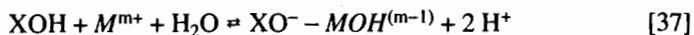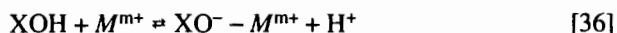
$$\sigma_d = -\frac{Sa}{F}(8\varepsilon_o DRTI)^{1/2}sinh(F\psi_d/2RT) \qquad [33]$$

$$\sigma_o = \frac{C_1 Sa}{F}(\psi_o - \psi_\beta) \qquad [34]$$

$$\sigma_d = \frac{C_2 Sa}{F}(\psi_d - \psi_\beta) \qquad [35]$$

where ε_o is the permittivity of vacuum, D is the dielectric constant of water, I is the ionic strength, and C_1 and C_2 are capacitance densities.

The equations for inner-sphere surface complexation are Eq. [19] through [24] as in the constant capacitance model, where ψ is replaced by ψ_o. The equations for outer-sphere surface complexation are (Davis et al., 1978; Davis and Leckie, 1978, 1980):

$$XOH + M^{m+} \rightleftharpoons XO^- - M^{m+} + H^+ \qquad [36]$$

$$XOH + M^{m+} + H_2O \rightleftharpoons XO^- - MOH^{(m-1)} + 2H^+ \qquad [37]$$

$$XOH + H^+ + L^{\ell-} \rightleftharpoons XOH_2^+ - L^{\ell-} \qquad [38]$$

$$XOH + 2H^+ + L^{\ell-} \rightleftharpoons XOH_2^+ - LH^{(\ell-1)-} \qquad [39]$$

$$XOH + C^+ \rightleftharpoons XO^- - C^+ + H^+ \qquad [40]$$

$$XOH + H^+ + A^- \rightleftharpoons XOH_2^+ - A^- \qquad [41]$$
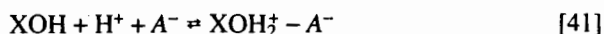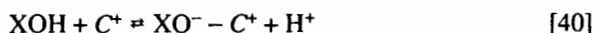
where C^+ is the cation and A^- is the anion of the background electrolyte and outer-sphere complexes are indicated by splitting the surface complexes with dashes. In the triple layer model one of the inner-sphere metal surface complexes is represented as bidentate, Eq. [22], while one of the outer-sphere metal surface complexes is rep-

resented as a hydroxy-metal surface species, Eq. [37]. Outer-sphere hydroxy-metal complexation reactions were more consistent with experimental data (Davis and Leckie, 1978). For anion surface complexation, a protonated outer-sphere surface complex, Eq. [39], rather than a bidentate inner-sphere surface complex, Eq. [24], represented experimental data more consistently (Davis and Leckie, 1980).

The triple layer model equilibrium constants for inner-sphere surface complexation are Eq. [25] through [30] as in the constant capacitance model, where ψ is replaced by ψ_o. The equilibrium constant expressions for outer-sphere surface complexation are (Davis et al., 1978; Davis and Leckie, 1978, 1980):

$$K_M^1(\text{int}) = \frac{[XO^- - M^{m+}][H^+]}{[XOH][M^{m+}]} \exp[F(m\psi_\beta - \psi_o)/RT] \qquad [42]$$

$$K^2{}_M(\text{int}) = \frac{[XO^- - MOH^{(m-1)}][H^+]^2}{[XOH][M^{m+}]} \exp[F((m-1)\psi_\beta - \psi_o)/RT] \qquad [43]$$

$$K_L^1(\text{int}) = \frac{[XOH_2^+ - L^{\ell-}]}{[XOH][H^+][L^{\ell-}]} \exp[F(\psi_o - \ell\psi_\beta)/RT] \qquad [44]$$

$$K_L^2(\text{int}) = \frac{[XOH_2^+ - LH^{(\ell-1)-}]}{[XOH][H^+]^2[L^{\ell-}]} \exp[F(\psi_o - (\ell-1)\psi_\beta)/RT] \qquad [45]$$

$$K_{C+}(\text{int}) = \frac{[XO^- - C^+][H^+]}{[XOH][C^+]} \exp[F(\psi_\beta - \psi_o)/RT] \qquad [46]$$

$$K_{A^-}(\text{int}) = \frac{[XOH_2^+ - A^-]}{[XOH][H^+][A^-]} \exp[F(\psi_o - \psi_\beta)/RT] \qquad [47]$$

The mass balance for the surface functional group is:

$$[XOH]_T = [XOH] + [XOH_2^+] + [XO^-] + [XOM^{(m-1)}] + 2[(XO)_2 M^{(m-2)}]$$

$$+ [XL^{(\ell-1)-}] + 2[X_2L^{(\ell-2)-}] + [XO^- - M^{m+}] + [XO^- - MOH^{(m-1)}]$$

$$+ [XOH_2^+ - L^{\ell-}] + [XOH_2^+ - LH^{(\ell-1)-}] + [XO^- - C^+] + XOH_2^+ - A^-] \qquad [48]$$

and the charge balances are:

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \qquad [49]$$

$$\sigma_o = [XOH_2^+] + [XOH_2^+ - L^{\ell-}] + [XOH_2^+ - LH^{(\ell-1)-}] + (m-1)[XOM^{(m-1)}]$$

$$+ (m-2)[(XO)_2M^{(m-2)}] + [XOH_2^+ - A^-] - [XO^-] - [XO^- - M^{m+}]$$

$$- [XO^- - MOH^{(m-1)}] - (\ell-1)[XL^{(\ell-1)-}] - (\ell-2)[X_2L^{(\ell-2)-}] - [XO^- - C^+] \quad [50]$$

$$\sigma_\beta = m[XO^- - M^{m+}] + (m-1)[XO^- - MOH^{(m-1)}] + [XO^- - C^+]$$

$$-\ell[XOH_2^+ - L^{\ell-}] - (\ell-1)[XOH_2^+ - LH^{(\ell-1)-}] - [XOH_2^+ - A^-] \qquad [51]$$

The above set of equations can be solved with a computer program using the mathematical approach described in Westall (1980).

Stern Variable-Surface Charge Variable-Surface-Potential Model

The Stern VSC-VSP model of adsorption was developed in Australia (Bowden et al., 1977, 1980; Barrow et al., 1980, 1981; Barrow, 1987). This model contains the following assumptions:

1. Protons, hydroxyl ions, and "strongly adsorbed" oxyanions and metals form inner-sphere surface complexes.
2. Protons and hydroxyl ions reside in the o-plane close to the surface.
3. "Strongly adsorbed" ions reside in an a-plane a short distance away from the surface o-plane.
4. Major cations and anions form outer-sphere surface complexes and reside in the β-plane a short distance away from the a-plane.
5. The surface functional group is defined as $OH-X-OH_2$ allowing only one protonation or dissociation to occur for every two surface hydroxyl groups
6. The relationships between surfaces charges, σ_o, σ_a, σ_β, and σ_d, and surface potentials, ψ_o, ψ_a, ψ_β, and ψ_d, are Eq. [33] and:

$$\psi_o - \psi_a = \sigma_o/C_{oa} \qquad [52]$$

$$\psi_a - \psi_\beta = (\sigma_o + \sigma_a)/C_{a\beta} \qquad [53]$$

$$\psi_\beta - \psi_d = -\sigma_d/C_{\beta d} \qquad [54]$$

where σ_o, σ_a, σ_β, and σ_d have units of mol_c m^{-2} and C_{oa}, $C_{a\beta}$, and $C_{\beta d}$ have units of mol_c V^{-1} m^{-2}. The diffuse layer charge, σ_d, Eq. [33] has units of mol_c L^{-1} and must be divided by the surface area and the suspension density.

The Stern VSC-VSP model emphasizes parameter optimization. Therefore it does not define specific surface species and surface reactions and does not provide equilibrium constant expressions and mass balance. The charge balance expressions are:

$$\sigma_o + \sigma_a + \sigma_\beta + \sigma_d = 0 \qquad [55]$$

$$\sigma_o = \frac{N_S\{K_H[H^+]exp(-F\psi_o/RT) - K_{OH}[OH^-]exp(F\psi_o/RT)\}}{1 + K_H[H^+]exp(-F\psi_o/RT) + K_{OH}[OH^-]exp(F\psi_o/RT)} \qquad [56]$$

$$\sigma_a = \frac{N_T\sum_i Z_i K_i a_i exp(-Z_i F\psi_a/RT)}{1 + \sum_i K_i a_i exp(-Z_i F\psi_a/RT)} \qquad [57]$$

$$\sigma_\beta = \frac{N_S\{K_{cat}[C^+]exp(-F\psi_\beta/RT) - K_{an}[A^-]exp(F\psi_\beta/RT)\}}{1 + K_{cat}[C^+]exp(-F\psi_\beta/RT) + K_{an}[A^-]exp(F\psi_\beta/RT)} \qquad [58]$$

where N_S is the maximum surface charge density (mol_c m^{-2}), N_T is the maximum adsorption of specifically adsorbed ions (mol_c m^{-2}), K_i, a_i, and Z_i are the binding

constant, the activity, and the charge of the ith specifically adsorbed ion, respectively.

To solve this set of equations, values of N_S, N_T, K_i, and C_i, are chosen to optimize model fit to the data. Subsequently, the charge densities, σ_i, and the electrostatic potentials, ψ_i, are calculated with a computer program (Barrow, 1979).

The Stern VSC-VSP model has been extended to describe ion adsorption processes by soil materials (Barrow, 1983) including the rate of the adsorption reaction (Barrow, 1986a). This extended Stern VSC-VSP model contains the following assumptions:

1. Individual sites react with adsorbing ions as with sites on variable charge oxides.
2. A range of sites exists whose summed adsorption behavior can be modeled using a distribution of parameters of the Stern VSC-VSP model.
3. The initial adsorption reaction induces a diffusion gradient into the particle interior that begins a solid-state diffusion process.

The equations in the extended Stern VSC-VSP model describe (Barrow, 1986a):

A. Heterogeneity of the surface:

$$P_j = 1/(\sigma/\sqrt{2\pi}) \exp[-0.5(\psi_{a0j} - \bar{\psi}_{a0}/\sigma)^2] \qquad [59]$$

where P_j is the probability that a particle has initial potential ψ_{a0j}, $\bar{\psi}_{a0}$ is the mean value of ψ_{a0j}, and σ is the standard deviation of ψ_{a0j}.

B. Adsorption on each component of the surface:

1. at equilibrium:

$$\theta_j = \frac{K_i \alpha \gamma c \exp(-Z_i F \psi_{aj}/RT)}{1 + K_i \alpha \gamma c \exp(-Z_i F \psi_{aj}/RT)} \qquad [60]$$

where θ_j is the proportion of the jth component occupied by the ith adsorbed ion, ψ_{aj} is the potential of the jth component, α is the fraction of adsorbate present as the ith ion, γ is the activity coefficient, and c is the total concentration of adsorbate.

2. rate of adsorption:

$$\theta_{jt} = \frac{K_1^* c(1 - \theta_j) - k_2^* \theta_j}{k_1^* c + k_2^*} \{1 - \exp[-t(k_1^* c + k_2^*)]\} \qquad [61]$$

θ_{jt} is the increment in θ_j over time interval t, and

$$k_1^* = k_1 \alpha \gamma \exp(\overleftarrow{\alpha} F \psi_{aj}/RT) \qquad [62]$$

$$k_2^* = k_2 \alpha \gamma \exp(\overrightarrow{\alpha} F \psi_{aj}/RT) \qquad [63]$$

where k_1 and k_2 are rate coefficients and $\overleftarrow{\alpha}$ and $\overrightarrow{\alpha}$ are transfer coefficients.

C. Diffusive penetration:

$$M_j = 2/\sqrt{\pi}\{C_{0j}\sqrt{(Dft)} + \sum_0^k(C_{kj} - C_{kj-1})\sqrt{[\tilde{D}f_k(t - t_k)]}\}$$ [64]

where M_j is the amount of material transferred to the interior of the jth component on an area basis, C_{0j} is the surface concentration of the adsorbed ion at time t, C_{kj} is the value of C_{0j} at time t_k, $\tilde{D}$ is the coefficient related to the diffusion coefficient via the thickness of the adsorbed layer, and f is the thermodynamic factor.

D. Feedback effects on potential:

1. for a single period of measurement:

$$\psi_{aj} = \psi_{a0j} - m_1\theta_j$$ [65]

where ψ_{aj} is the potential of the jth component after reaction and m_1 is a parameter.

2. for measurement through time:

$$\psi_{aj} = \psi_{a0j} - m_1\theta_j - m_2M_j/N_{mj}$$ [66]

where N_{mj} is the maximum adsorption on component j and m_2 is a parameter.

E. Effects of temperature:

$$D = A\exp(-E/RT)$$ [67]

where E is an activation energy and A is a parameter.

$$K_i = \exp(B/RT)$$ [68]

where B represents potentials in specified standard states plus an interaction term (Bowden et al., 1977).

    To describe phosphate adsorption in soil the continuous distribution of Eq. [59] was divided into 30 discrete elements (Barrow, 1983). These 30 sets of equations were solved iteratively with a computer program using the criterion of goodness-of-fit to experimental sorption data (Barrow, 1983). Despite its foundation in chemical principles, the Stern VSC-VSP model should be regarded as a curve-fitting procedure because of its very large number of adjustable parameters.

Advantages of Chemical Models

    The major advantage of the chemical surface complexation models is that they consider surface charge arising from the protonation-dissociation reactions and from the ion surface complexation reactions. These models are descriptions of adsorption processes whose molecular features can be given thermodynamic significance

(Sposito, 1983); however, goodness-of-fit to experimental adsorption data cannot be used as evidence for the presence of any of the surface complexes postulated in the surface complexation models.

As the complexity of a model increases, the number of adjustable parameters also increases, and this improves the model's curve-fitting ability. Chemical significance of a model application suffers when model parameters whose value are available experimentally are adjusted mathematically. This is the case for the maximum surface charge density and the maximum ion adsorption density parameters in the Stern VSC-VSP model. The Stern VSC-VSP model also is compromised chemically because mass balance is not carried out for the surface functional group. Until such time as independent experimental evidence allows the determination of the exact structure of adsorbed surface complexes, models having chemical simplicity and a small number of adjustable parameters are preferable.

Applications of Chemical Models to Soil Systems

Constant Capacitance Model

Applications of the constant capacitance model to soil systems have been restricted to the description of anion adsorption. This model has been used to describe phosphate (Goldberg and Sposito, 1984), borate (Goldberg and Glaubig, 1986; Goldberg, 1999; Goldberg et al., 2000), selenite (Sposito et al., 1988; Goldberg and Glaubig, 1988a), arsenate (Goldberg and Glaubig, 1988b), sulfate (Kooner et al., 1995), and molybdate (Goldberg et al., 1998, 2002) adsorption on soils. For all studies except that of Kooner et al. (1995) values of the protonation and dissociation constants were averages obtained from a literature compilation of $\log K_+(\text{int})$ and $\log K_-(\text{int})$ values for aluminum and iron oxide minerals. Kooner et al. (1995) obtained $\log K_+(\text{int})$ and $\log K_-(\text{int})$ values by optimizing potentiometric titration data with the computer program FITEQL (Westall, 1982). FITEQL is an iterative nonlinear least squares optimization program designed to fit equilibrium constants to experimental data and contains surface complexation models including the constant capacitance model and the triple layer model. Capacitance density values for these soil studies ranged from 1.06 F m^{-2} (Goldberg and Sposito, 1984) to 2.7 F m^{-2} (Sposito et al., 1988).

Monodentate anion surface species, Eq. [23], were defined in all of the above studies. Sposito et al. (1988) assumed that in addition to monodentate selenite species formed on one set of surface sites bidentate selenite species formed on another set of surface sites. Fit of the constant capacitance model to selenite adsorption on a California soil is depicted in Fig. 10–6. Anion surface complexation constants for all studies were optimized with the FITEQL computer program. To describe borate (Goldberg and Glaubig, 1986) and selenite (Goldberg and Glaubig, 1988a) adsorption, values of $\log K_+(\text{int})$ and $\log K_-(\text{int})$ were optimized together with the anion surface complexation constants. The optimized value of $\log K_-(\text{int})$ for some of the soils was insignificantly small producing a chemically unrealistic situation that reduced the particular application of the model to a curve-fitting procedure. A reanalysis using both trigonal and tetrahedral surface species was well able to describe boron adsorption without this chemically unrealistic behavior (Goldberg, 1999).
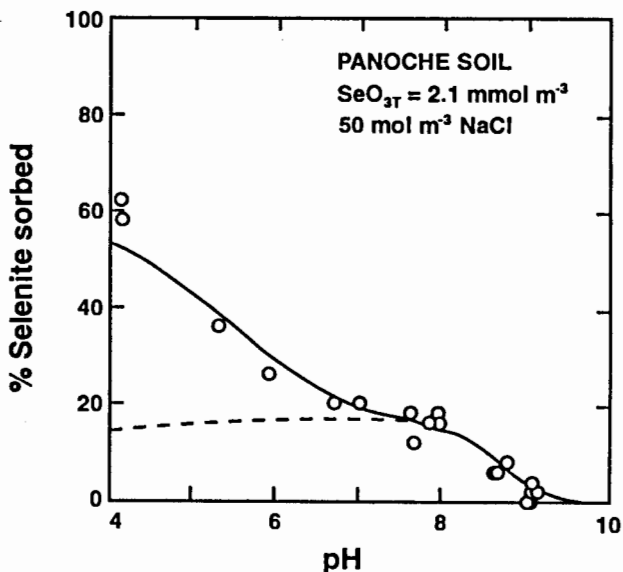
Fig. 10–6. Fit of the constant capacitance model to selenite adsorption on a California soil. The solid line indicates the model fit (from Sposito et al., 1988).

The predictive capability of the constant capacitance model to describe ion adsorption has been tested for phosphate (Goldberg and Sposito, 1984), borate (Goldberg and Glaubig, 1986; Goldberg et al., 2000), selenite (Sposito et al., 1988), and molybdate (Goldberg et al., 2002). Qualitative prediction of selenite adsorption on four California soils was possible using the selenite surface complexation constants obtained for one other California soil as indicated in Fig. 10–7 (Sposito et al., 1988). Using an average set of anion surface complexation constants obtained from numerous soils, the model qualitatively predicted phosphate (Goldberg and Sposito, 1984) and borate (Goldberg and Glaubig, 1986) adsorption on individual soils. A new approach for predicting boron adsorption used a general regression model to predict model parameters from the easily measured soil chemical properties surface area, organic and inorganic carbon and aluminum oxide content (Goldberg et al., 2000). This approach has provided a completely independent model evaluation and was well able to predict boron adsorption on numerous soils of diverse soil orders having a wide range of chemical properties. This predictive capability is presented in Fig. 10–8. A similar modeling approach was used to predict molybdate adsorption. The general regression equations predict model parameters from the chemical properties: cation exchange capacity, organic and inorganic carbon content, and iron oxide content (Goldberg et al., 2002) The predictive capability of this approach is shown in Fig. 10–9 for both monodentate and bidentate molybdenum surface configurations.

Triple Layer Model

The triple layer model has been applied to the adsorption of calcium, magnesium, sulfate (Charlet, 1986; Charlet and Sposito, 1987, 1989; Charlet et al., 1993),
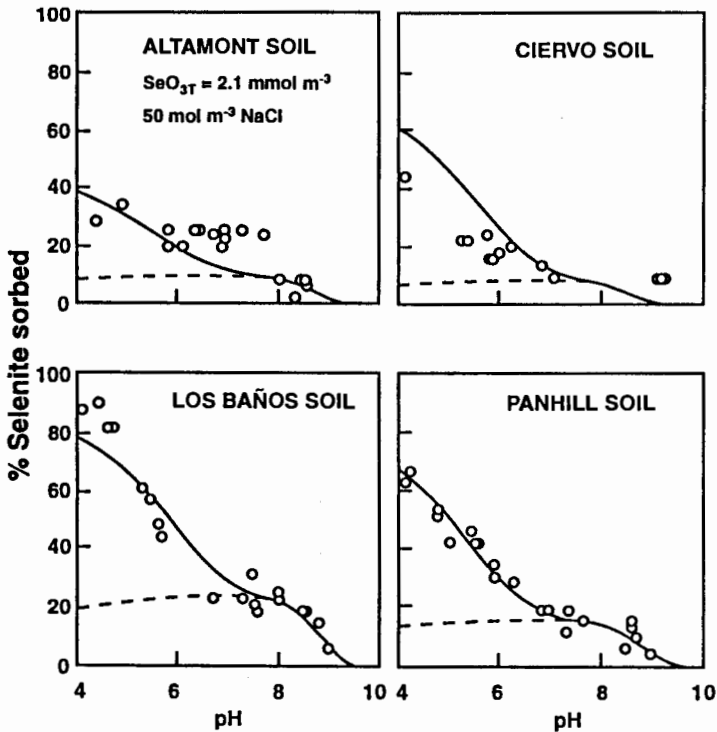
Fig. 10–7. Constant capacitance model predictions of selenite adsorption by California soils. Solid lines indicate the model fits (from Sposito et al., 1988).

chromate (Zachara et al., 1989), and molybdate (Goldberg et al., 1998, 2002) on soils. Potentiometric titrations and measurements of background electrolyte adsorption on a Brazilian oxisol were used to extrapolate values of the protonation and dissociation constants and the surface complexation constants for the background electrolyte (Charlet, 1986; Charlet and Sposito, 1987).

The triple layer model was well able to fit calcium, magnesium, and sulfate adsorption on a Brazilian oxisol using monodentate inner-sphere surface complexes and experimentally determined values of $\log K_+(int)$, $\log K_-(int)$, $\log K_{C+}(int)$, and $\log K_{A-}(int)$ (Charlet, 1986; Charlet and Sposito, 1989). The ability of the triple layer model to describe calcium and magnesium adsorption on a Brazilian oxisol is indicated in Fig. 10–10 and 10–11, respectively. On the other hand, Charlet et al. (1993) described sulfate adsorption on an acidic forest soil as a monodentate outer-sphere surface complex by using literature values of $\log K_+(int)$, $\log K_-(int)$, $\log K_{C+}(int)$, and $\log K_{A-}(int)$ previously determined for goethite (Hsi and Langmuir, 1985) with the justification that the clay components of the soil consisted of phyllosilicates and iron oxide minerals. In a similar approach, Zachara et al. (1989) used literature values of $\log K_+(int)$, $\log K_-(int)$, $\log K_{C+}(int)$, and $\log K_{A-}$ (int) previously determined for an aluminum-substituted goethite (Ainsworth et al., 1989) to describe chromate adsorption as a monodentate outer-sphere surface com-
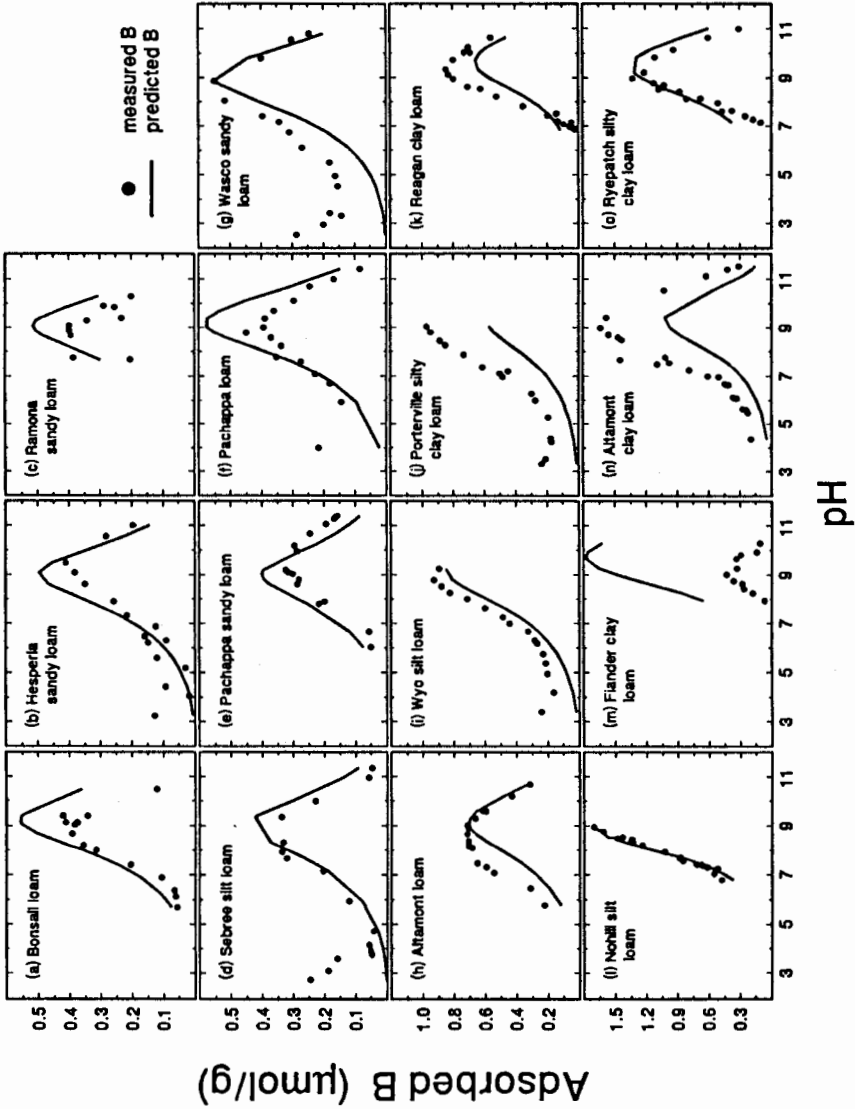
Fig. 10–8. Constant capacitance model predictions of boron adsorption by soils of various soil chemical properties and diverse soil orders. Solid lines indicate model fits (from Goldberg et al., 2000).
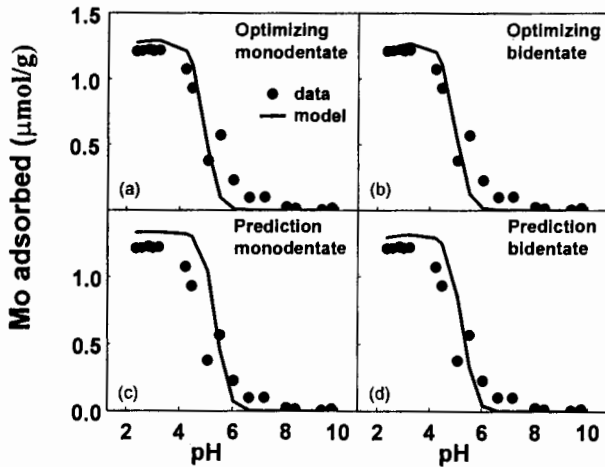
Fig. 10–9. Constant capacitance model predictions of molybdenum adsorption by an acid soil. Solid lines indicate model fits (from Goldberg et al., 2002).

plex by two soils assuming that chromate adsorbed only on the iron sites. The ability of this modeling approach to describe chromate adsorption is depicted in Fig. 10–12. On the other hand, Goldberg et al. (1998) used literature values of $\log K_+(\text{int})$, $\log K_-(\text{int})$, $\log K_{C+}(\text{int})$, and $\log K_{A-}(\text{int})$ obtained for $\gamma\text{-Al}_2O_3$ (Sprycha, 1989a,b) to describe molybdate adsorption on two arid-zone soils using both inner-sphere and outer-sphere adsorption mechanisms. The assumptions were made that the aluminol group is the molybdate reactive functional group in these soils and that surface complexation reactions of aluminols can be described with constants for the reactive surface hydroxyls of $\gamma\text{-Al}_2O_3$. The ability of this modeling approach to describe molybdate adsorption on a California soil is depicted in Fig. 10–13.
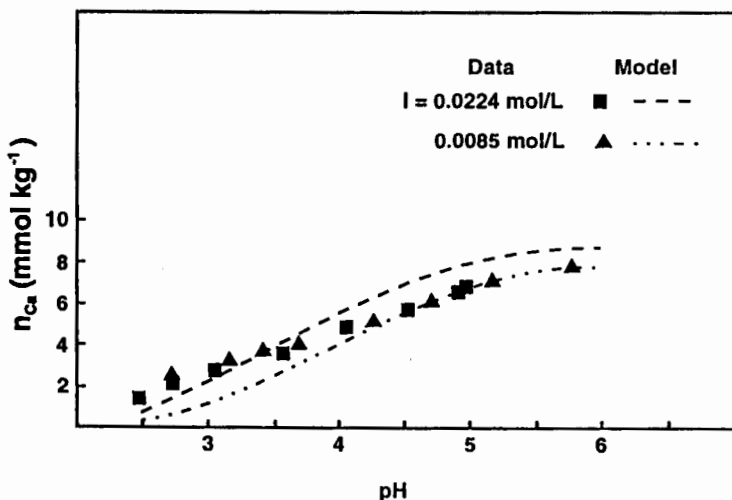

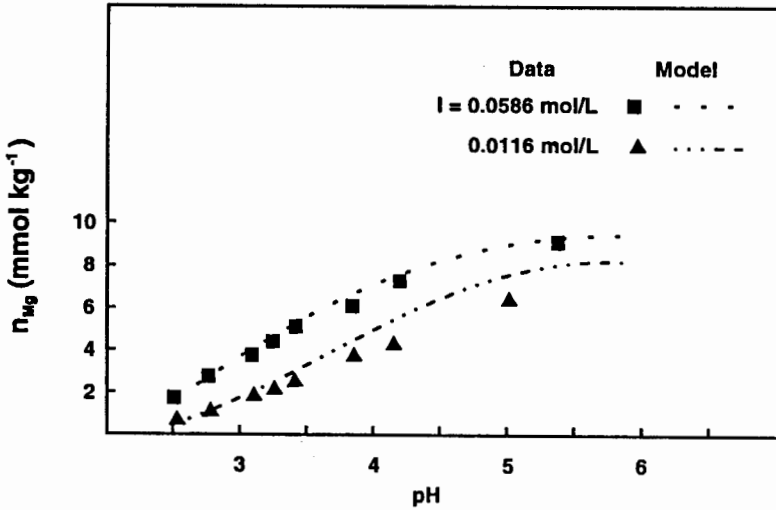Fig. 10–10. Fit of the triple layer model to calcium adsorption on a Brazilian oxisol (from Charlet, 1986).

Fig. 10–11. Fit of the triple layer model to magnesium adsorption on a Brazilian oxisol (from Charlet, 1986).

Stern Variable-Surface Charge Variable-Surface Potential Model

The extended Stern VSC-VSP model of adsorption has been used to describe the effect of time and temperature on fluoride, molybdate (Barrow, 1986a), cadmium, cobalt, nickel, zinc (Barrow, 1986b, 1998), selenite, and selenate (Barrow and Whelan, 1989b) adsorption, the effect of pH on phosphate (Barrow, 1984,
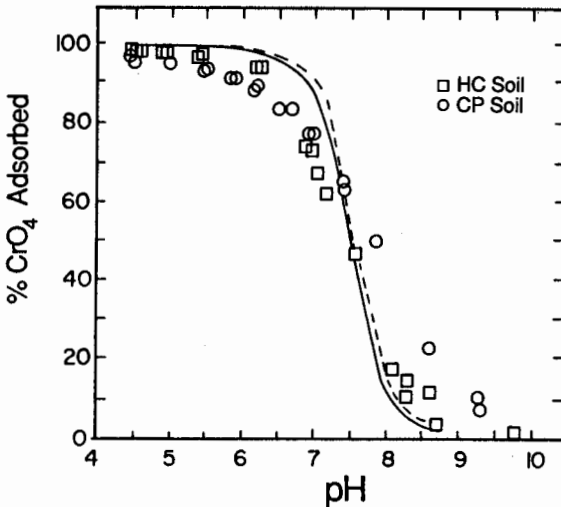

Fig. 10–12. Fit of the triple layer model to chromate adsorption on a North Carolina (CP) and a Tennessee (HC) soil. The solid line indicates the fit to the HC data. The dashed line indicates the fit to the CP data (from Zachara et al., 1989).
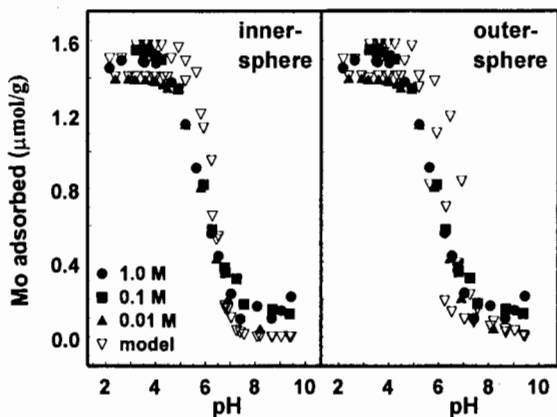
Fig. 10–13. Fit of the triple layer model to molybdate adsorption on a California soil as a function of solution pH and ionic strength. Model results are represented by open triangles (from Goldberg et al., 1998).
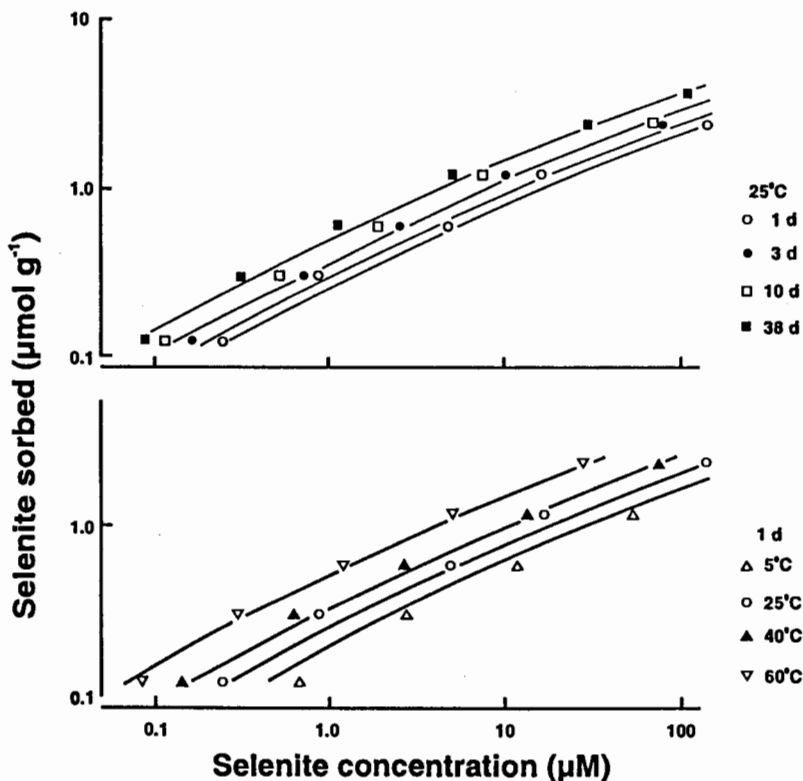

Fig. 10–14. Fit of the Stern VSC-VSP model to selenite adsorption on an Australian soil as a function of time and temperature (from Barrow and Whelan, 1989b).

1986d), zinc (Barrow, 1986c, d), fluoride (Barrow and Ellis, 1986), selenite, sele-nate (Barrow and Whelan, 1989a), and borate (Barrow, 1989) adsorption, and the effect of ionic strength on selenite, selenate (Barrow and Whelan, 1989a), and bo-rate (Barrow, 1989) adsorption on Australian soils. The Stern VSC-VSP model was able to provide a good fit to the experimental data for all of the above cases because of its very large number of adjustable parameters as indicated in Fig. 10–14 through 10–17. In the description of the effect of pH on phosphate (Barrow, 1984) and zinc (Barrow, 1986c) adsorption on soils, binding constants obtained previously for the iron oxide goethite were used.

Approximations in the Use of Chemical Models in Soil Systems

The chemical surface complexation models described above contain the as-sumption that ion adsorption takes place on one or at most on two sets of reactive surface sites. This is clearly a gross simplification since soils are complex multi-site mixtures having a variety of reactive surface functional groups. Thus the equi-librium constants determined for soils represent average composite values for all sets of reactive functional groups present in soils.
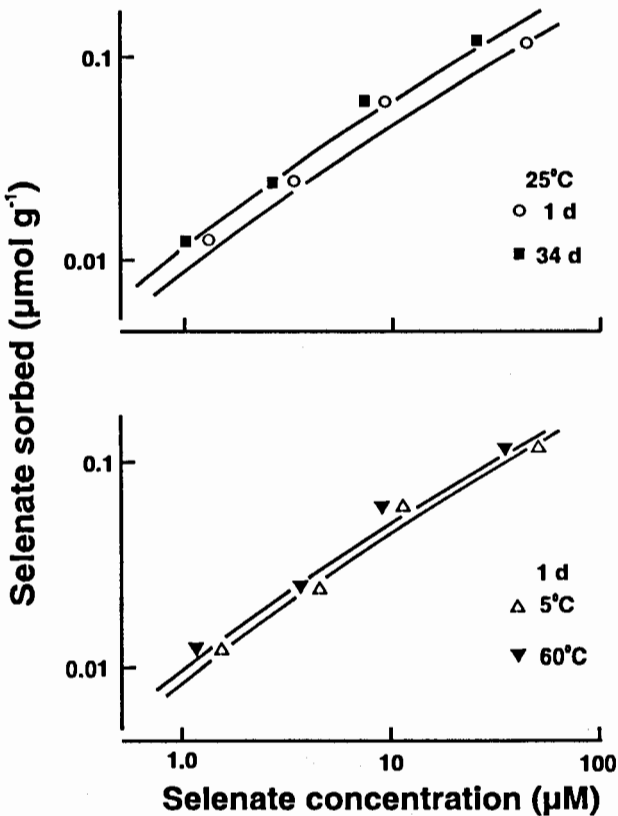

Fig. 10–15. Fit of the Stern VSC-VSP model to selenate adsorption on an Australian soil as a function of time and temperature (from Barrow and Whelan, 1989b).
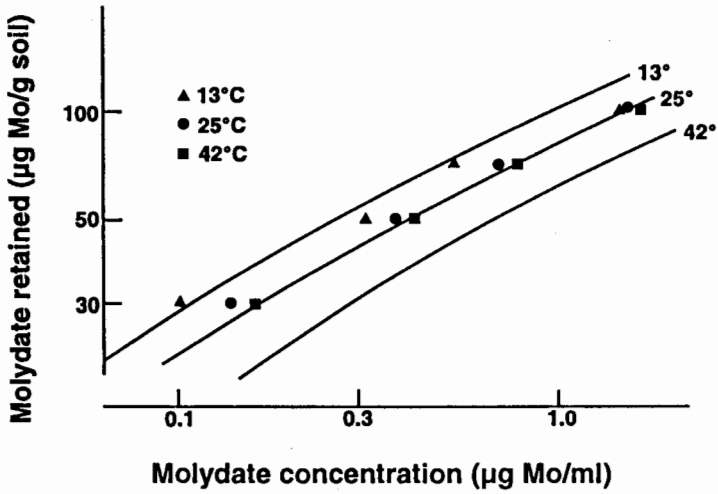
Fig. 10–16. Fit of the Stern VSC-VSP model to molybdate adsorption on an Australian soil as a function of temperature (from Barrow, 1986a).
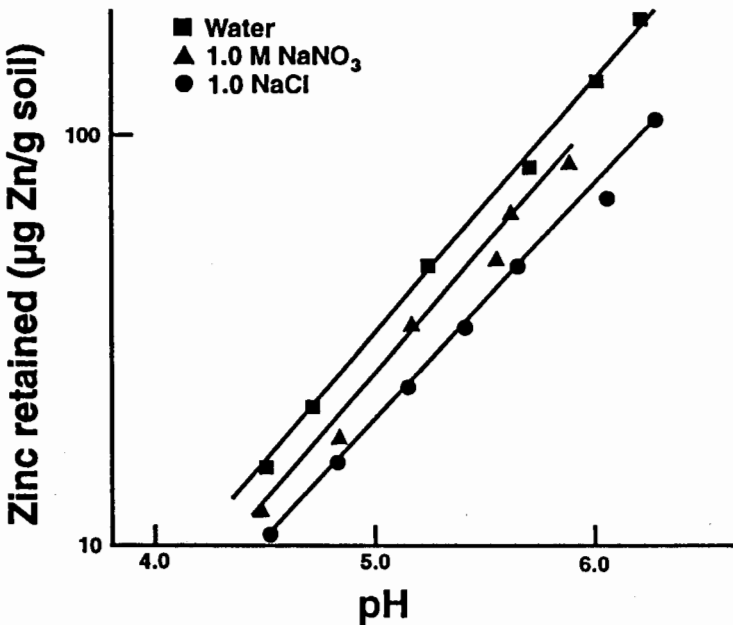

Fig. 10–17. Fit of the Stern VSC-VSP model to zinc adsorption on an Australian soil as a function of background electrolyte (from Barrow and Ellis, 1986).

The total number of reactive surface functional groups, $[SOH]_T$ is an important parameter in the chemical surface complexation models and is related to the surface site density, N_S, by the following expression:

$$[SOH]_T = \frac{Sa10^{18}N_S}{N_A} \qquad [69]$$

where N_A is Avogadro's number and N_S has units of sites nm^{-2}. In the application of chemical surface complexation models to soils, surface site density values have been obtained from maximum ion adsorption (Goldberg and Sposito, 1984) or optimized to fit the experimental adsorption data (Barrow, 1983). To allow standardization of surface complexation modeling approaches and the development of self-consistent thermodynamic databases, Davis and Kent (1990) recommended use of a surface site density value of 2.31 sites nm^{-2} for all natural adsorbents including soil materials. This site density values was used in the prediction of borate (Goldberg et al., 2000) and molybdate (Goldberg et al., 2002) adsorption.

In the application of the surface complexation models to soils dominant in clay minerals, the assumption is made that ion adsorption occurs on the aluminol and silanol groups of clay edges. The effect of the permanent charge sites on this adsorption process is not considered. This simplification may be inappropriate, particularly for anions, since repulsive electrostatic forces emanating from particle faces may spill over and affect the ion adsorption process on clay edges (Secor and Radke, 1985).

APPENDIX

Example: Boron Adsorption on a California Soil

In this section, the application of various equations and modeling approaches to one set of adsorption data will be provided to demonstrate their utility and limitations. Boron adsorption was determined as an isotherm (amount adsorbed as a function of equilibrium solution ion concentration) and as an envelope (amount adsorbed as a function of solution pH per fixed total ion concentration) on the Hanford soil from California.

The ISOTHERM program (Kinniburgh, 1986) was used to fit the Langmuir, Freundlich, two-surface Langmuir, Temkin, Toth, and Dubinin-Radushkevich equations to the B adsorption isotherm data. Figure 10–A1 shows the ability of the isotherm equations to fit the data. With the exception of the Temkin equation, fit of the models to the data is excellent with each having a highly statistically significant coefficient of determination, $R^2 = 0.98^{**}$. Although the fit of the Temkin equation ($R^2 = 0.84^{**}$, $a = 1.12$, $b = 2.97$) was also statistically significant, it is clearly inferior. Parameter values for the other isotherms are as follows: Freundlich: $K = 0.628$, $\beta = 0.761$, Langmuir: $K = 0.0302$, $x_m = 16.1$, two-surface Langmuir: $K_1 = 0.00524$, $x_{m1} = 53.5$, $K_2 = 0.413$, $x_{m2} = 1.18$, Toth: $K = 0.00000164$, $\beta = 0.124$, $x_m = 630625$, Dubinin-Radushkevich: $K = 3070000$, $\beta = -0.0518$, $x_m = 0.00441$. For the Toth and the Dubinin-Radushkevich equations, the fit results in highly unrealistic values of K and maximum adsorption, x_m. These values must therefore be regarded solely as empirical fitting parameters and not true measures of maximum adsorption.

The constant capacitance model was applied to boron adsorption isotherm and envelope data simultaneously. The ability to consider both of these variables is one of the ad-
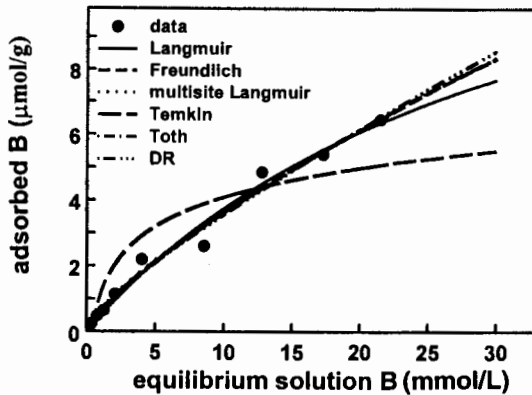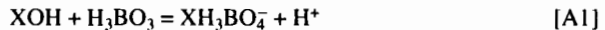
Boron adsorption on Hanford soil

Fig. 10–A1.Fit of various adsorption isotherm equations to boron adsorption on a California soil.

vantages of surface complexation models over the empirical isotherm equations. In addition to Eq. [19] and [20], the surface complexation reaction for boron adsorption is defined as:

$$XOH + H_3BO_3 = XH_3BO_4^- + H^+ \qquad [A1]$$

and the equilibrium constant expression for this reaction is:

$$K_{B-} = \frac{[XH_3BO_4^-][H^+]}{[XOH][H_3BO_3]} \; \exp(-F\psi/RT) \qquad [A2]$$

The mass balance equation for the surface functional group is:

$$[XOH_T] = [XOH] + [XOH_2^+] + [XO^-] \, [XH_3BO_4^-] \qquad [A3]$$

and the charge balance equation is:

$$\sigma = [XOH_2^+] - [XO^-] - [XH_3BO_4^-] \qquad [A4]$$

The solid line in Fig. 10–A2 indicates the ability of the constant capacitance model to fit boron adsorption simultaneously as a function of solution boron concentration and solution pH. While the fit is not quite as good as it is when each type of adsorption curve is fit individually (not shown), the ability of the model to predict adsorption as a function of both of these variables is impressive. Parameter values are $\log K_{B-} = -7.14$, $\log K_+ = 7.06$, and $\log K_- = -10.77$. The dashed line in Fig. 10–A2 shows the boron adsorption predicted by the constant capacitance model when the generalized regression equations of Goldberg et al. (2002) are used to predict $\log K_{B-}$, $\log K_+$, and $\log K_-$. Using these equations the predicted values are $\log K_{B-} = -7.48$, $\log K_+ = 7.71$, and $\log K_- = -11.14$. The predicted boron adsorption is obtained independent of any experimental measurement. The model prediction for the adsorption envelope is similar in quality to the model fit. For the adsorption isotherm, the predicted adsorption is only about 10% different from the fitted adsorption, indicating the utility of this approach.
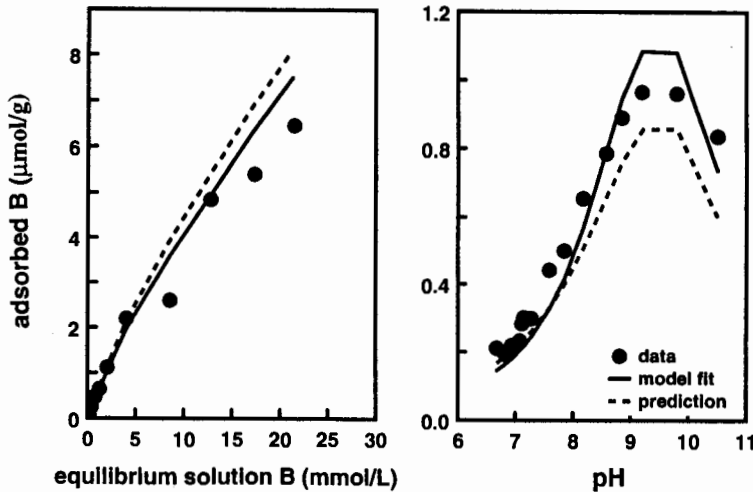
Boron adsorption on Hanford soil

Fig. 10–A2.Constant capacitance model predictions of boron adsorption on a California soil as a function of solution B concentration and solution pH.

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