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Adsorption

In the context of this book, adsorption is attachment of a solute to the surface of a solid or, more generally, the accumulation of solutes in the vicinity of a solid-solution interface. We can subdivide adsorption mechanisms into *physical adsorption*, where the attraction to the surface is due to relatively weak van der Waals forces; *electrostatic adsorption*, where ions in solution are attracted by a surface of the opposite electrical charge; and *chemical adsorption*, where there is chemical bonding between the solute molecule and one or more atoms on the surface of the solid. Cation exchange, discussed in the previous chapter, is an example of electrostatic adsorption. Adsorption is probably the most important chemical process affecting the movement of contaminants in groundwater (Chapter 16) and is an important influence on mineral dissolution rates (Chapter 11). Typically, the concentrations of heavy metals in natural waters are far below the values that would be predicted for saturation with respect to a solid phase. The most common reason for the low concentrations is adsorption onto a solid phase such as an iron or manganese oxide or hydroxide (collectively referred to as oxyhydroxides). If we are to predict the movement of heavy metals in soils and groundwater, we need to be able to model adsorption processes quantitatively. The mathematical approach that is used to describe adsorption ranges from relatively simple empirical equations to sophisticated mechanistic models of interactions at the solid-solution interface. The discussion here is presented in terms of adsorption of inorganic ions. However, many of the same principles and equations apply to the adsorption of organic solutes (Chapter 6).

EMPIRICAL EQUATIONS

There are many situations where a relatively simple equation is adequate to describe adsorption. For example, in the previous chapter we saw that, for an ion present in trace concentrations in a solution of constant composition, the equations describing cation exchange could be reduced to a simple distribution coefficient (Eq. 4-4). Use of a simple equation is advantageous when adsorption is added to an already complex hydrologic

model, and in many instances the amount of data available is insufficient to justify a more sophisticated approach. The equation (or its graphical representation) relating the concentration of a species adsorbed on a solid to its concentration in solution is often referred to as an *isotherm*, stemming originally from the fact that the measurements were made at constant temperature.

Linear Distribution Coefficient

The simplest adsorption isotherm is the linear distribution coefficient or linear K_d (Fig. 5-1)

$$m_{i(\text{ads})} = K_d m_{i(\text{soln})}$$

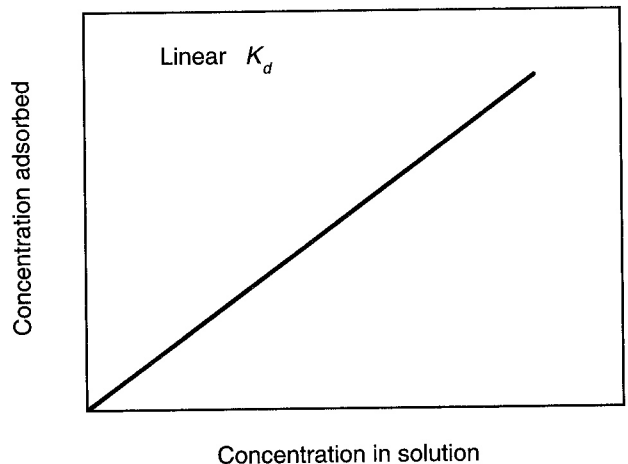
where $m_{i(\text{ads})}$ is the concentration of the species of interest adsorbed on the solid phase (commonly moles/kg of solid) and $m_{i(\text{soln})}$ is the concentration of the species in solution (commonly moles/l). The distribution coefficient thus has the units l/kg. Various other systems of units are also used. A closely related quantity is the “activity K_d ,” which is defined by

$$m_{i(\text{ads})} = K_d a_{i(\text{soln})}$$

where $a_{i(\text{soln})}$ represents the activity rather than the concentration of the species in solution. The activity K_d is commonly used in conjunction with computer codes such as MINTEQA2, in which speciation and activity coefficients have already been calculated.

The linear K_d is widely used in hydrologic models that incorporate some chemical transport (see Chapter 16). The fact that it is linear and involves no variables other than the concentration of the species of interest make it computationally simple. Many more complex adsorption models may reduce to a linear K_d under certain restrictive assumptions, as is the case with cation exchange discussed above. The numerical value of a distribution coefficient is a function of the properties of the solid substrate and the composition of the solution. It must generally be measured experimentally for each system of interest and cannot be easily transferred from one system to another.

FIGURE 5-1 Linear distribution coefficient.



Freundlich Isotherm

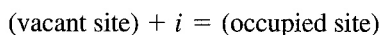
The Freundlich isotherm takes the form

$$m_{i(\text{ads})} = K_f m_{i(\text{soln})}^n$$

where n is a constant, usually less than 1. The exponent causes the isotherm to curve, becoming less steep at higher concentrations (Fig. 5-2). It can be regarded as strictly empirical or it can be justified theoretically in several ways. It would result from the adsorbed species forming a non-ideal solid solution on the solid surface, or it could result from heterogeneity in the sites to which the solute binds on the surface. If the surface contained sites with different binding energies for the solute, the first solute molecules to be adsorbed would be adsorbed at the sites with the strongest binding energy, which corresponds to the steep portion of isotherm. As the sites became filled, adsorption would take place at sites with lower binding energies, decreasing the slope of the isotherm.

Langmuir Isotherm

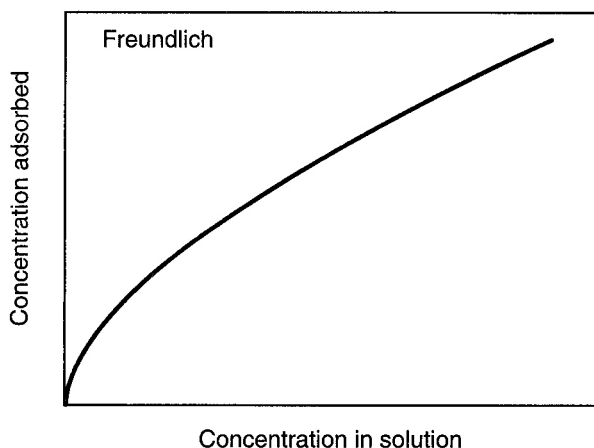
The Langmuir isotherm was originally derived to describe the adsorption of a gas monolayer on a solid surface. An analogous form can be derived for aqueous systems (Stumm, 1992). Consider a surface in which the total concentration of sites for adsorption is $m_{i(\text{ads, max})}$, the concentration of sites to which solute i is adsorbed is $m_{i(\text{ads})}$ and the concentration of sites not occupied by i is $m_{\text{vacant sites}}$. These concentrations can all be expressed in moles per liter of solution. The adsorption reaction can be written



The corresponding equilibrium constant for this reaction can be written

$$K_{\text{Lang}} = \frac{m_{i(\text{ads})}}{m_{i(\text{soln})} m_{\text{vacant sites}}}$$

FIGURE 5-2 Example of a Freundlich isotherm (exponent = 0.6).



Substituting $m_{i(\text{ads, max})} = m_{i(\text{ads})} + m_{\text{vacant sites}}$ and rearranging gives

$$m_{i(\text{ads})} = m_{i(\text{ads, max})} \frac{K_{\text{Lang}} m_{i(\text{soln})}}{1 + K_{\text{Lang}} m_{i(\text{soln})}}$$

The form of this equation is shown in Fig. 5-3. At high concentrations the Langmuir isotherm flattens, owing to saturation of the available surface sites. However high $m_{i(\text{soln})}$ becomes, $m_{i(\text{ads})}$ can never exceed $m_{i(\text{ads, max})}$. The Langmuir isotherm can also be transformed to a linear form:

$$\frac{1}{m_{i(\text{ads})}} = \frac{1}{m_{i(\text{ads, max})}} + \frac{1}{K_{\text{Lang}} m_{i(\text{ads, max})}} \frac{1}{m_{i(\text{soln})}}$$

A plot of $1/m_{i(\text{ads})}$ against $1/m_{i(\text{soln})}$ will give a straight line of slope $1/K_{\text{Lang}} m_{i(\text{ads, max})}$ and an intercept of $1/m_{i(\text{ads, max})}$.

At low concentrations, the term $K_{\text{Lang}} m_{i(\text{soln})}$ becomes small compared to 1 and the Langmuir isotherm reduces to the linear K_d , where

$$K_d = m_{i(\text{ads, max})} K_{\text{Lang}}$$

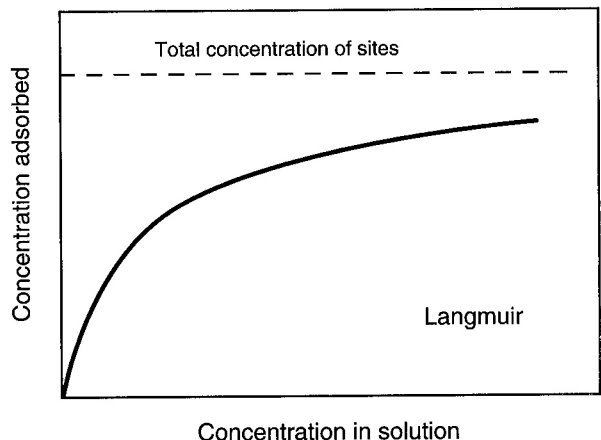
This is an example of how a more complex isotherm can be represented by a linear K_d under certain restricted circumstances.

Cation exchange reactions involving clay minerals are analogous to the Langmuir isotherm because the concentration of cations adsorbed can never be greater than the cation exchange capacity of the solid.

SURFACE COMPLEXATION

Mechanistic models for adsorption of inorganic species are generally based on the idea of *surface complexation*. The detailed models are conceptually and mathematically quite complex, and only an overview is provided here. For more detailed information, see Stumm (1992),

FIGURE 5-3 Example of a Langmuir isotherm. The dashed line represents the maximum concentration that can be adsorbed.



Davis and Kent (1990), or Dzombak and Morel (1990). Surface complexation is incorporated into the computer code MINTEQA2 and is currently regarded as the most accurate way of modeling adsorption of inorganic species at mineral surfaces. The objective of such modeling is usually to predict the concentration of an environmentally important cation or anion in groundwater or surface water following some perturbation such as waste disposal, mining activities, or a chemical spill.

Conceptually, the surface of an oxide or a silicate can be regarded as a plane of hydroxyl groups. A hypothetical oxide mineral is shown in Fig. 5-4a. Cations in the interior of the structure are coordinated on all sides by oxygen ions. Cations at the surface, however, are not fully coordinated. They adsorb a water molecule from solution to complete their coordination shell (Fig. 5-4b). The protons attached to the adsorbed water molecules then tend to redistribute themselves, as shown in Fig. 5-4c (Stumm, 1992). In the discussion that follows, OH groups at the surface of an oxide are shown as $\equiv\text{S}-\text{OH}$.

The hydroxyl groups at the surface of an oxide behave in a similar way to $-\text{OH}$ groups attached to dissolved species. They can dissociate

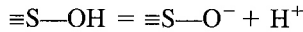
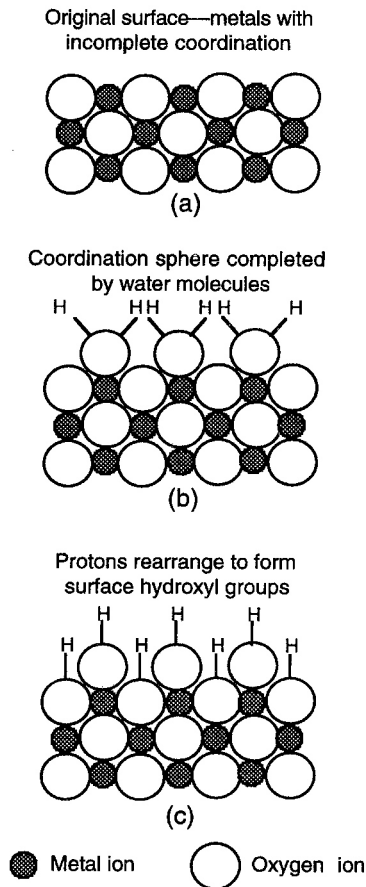
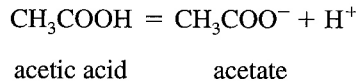


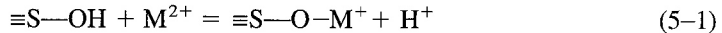
FIGURE 5-4 Schematic representation of the cross section of a metal oxide: (a) Metal ions at the surface have vacancies in their coordination sphere; (b) Vacant positions occupied by H_2O molecules; (c) Protons rearrange to form surface hydroxyl groups (after Schindler, 1981; Stumm, 1992).



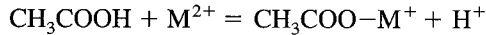
which is completely analogous to the dissociation of an organic acid



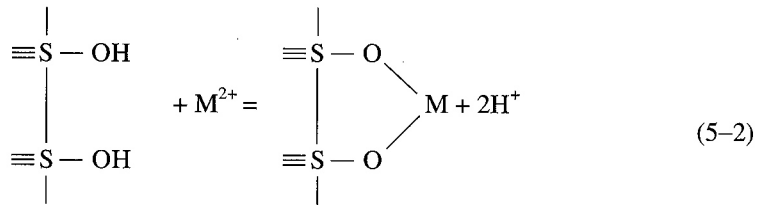
They can also form complexes with a metal (represented here as a divalent cation M^{2+}), which is again analogous to complex formation in solution. The surface may act as a monodentate ligand



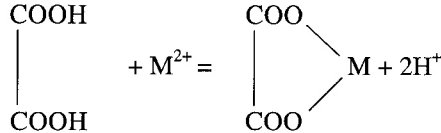
as in the analogous reaction



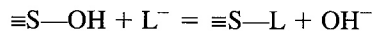
or as a bidentate ligand



analogous to complexation by oxalate in solution



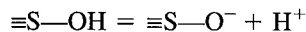
Adsorption of anions at the surface of an oxide can also take place by a process analogous to ligand exchange



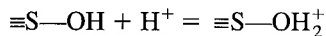
where L^- represents a simple anionic ligand such as F^- . Some possible schematic configurations of surface complexes are shown in Fig. 5-5.

Acid-Base Equilibria

As mentioned above, surface hydroxyl groups can dissociate



and they can also be protonated



Dissociation tends to give the surface a negative electrical charge, whereas protonation tends to give it a positive charge. This process gives oxides a variable surface charge, unlike the fixed charge that results from substitution of Al^{3+} for Si^{4+} and Mg^{2+} for Al^{3+} in clay minerals. From the law of mass action, low pH will favor protonation; high pH will favor deprotonation. For each oxide there exists a pH at which the positive charge on the surface due to protonated

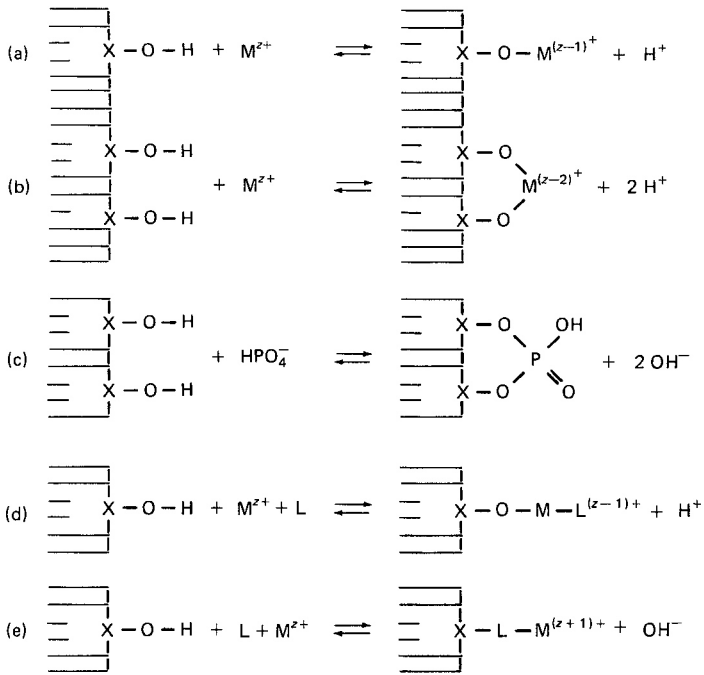
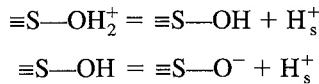


FIGURE 5-5 Some possible surface coordination reactions. X represents a metal cation forming the oxide surface (after Schindler, 1981).

groups equals the negative charge on the surface due to deprotonated groups. At that pH the net charge on the surface will be zero. That pH is called the *zero point of charge* (ZPC). If the only process affecting surface charge is loss or gain of protons (as distinct from adsorption–desorption of other ions such as metals) the ZPC is also referred to as the *zero point of net proton charge* (ZPNPC) or *isoelectric point* (IEP). Some isoelectric points are shown in Table 5-1.

For convenience, protonation–deprotonation equilibria can be written as the dissociation of acids:



The subscript *s* indicates the hydrogen ions are in the immediate vicinity of the surface. The corresponding equilibrium constants are

$$K_{a1}^{\text{intr}} = \frac{[\equiv\text{S}-\text{OH}][\text{H}^+]_s}{[\equiv\text{S}-\text{OH}_2^+]} \quad (5-3)$$

$$K_{a2}^{\text{intr}} = \frac{[\equiv\text{S}-\text{O}^-][\text{H}^+]_s}{[\equiv\text{S}-\text{OH}]} \quad (5-4)$$

where [] formally represent activities, with the []_{*s*} indicating an activity in solution close to the surface. The differences between activities and concentrations of surface species are often

TABLE 5-1 Isoelectric Points (pH) of Some Naturally Occurring Substances

[from James and MacNaughton, 1977; Leckie and James, 1974; Parks, 1965]

SiO ₂ (quartz)	2.0
SiO ₂ (gel)	1.0–2.5
Al ₂ O ₃ (corundum)	9.1
Al(OH) ₃ (gibbsite)	~9
TiO ₂ (anatase)	7.2
Fe ₃ O ₄ (magnetite)	6.5
Fe ₂ O ₃ (hematite)	5–9 (commonly 6–7)
FeO(OH) (goethite)	6–7
Fe ₂ O ₃ · nH ₂ O	6–9
δ-MnO ₂	2
Kaolinite	~3.5
Montmorillonite	<2.5

ignored in surface complexation modeling (Stumm, 1992). The units of the surface species (moles per kg of solid, moles per liter of solution, moles per square meter of surface) do not really have to be specified at this point because any conversion factor among units will cancel in Eqs. (5-3) and (5-4). The most generally useful units are moles per kg of solution. This is related to more fundamental quantities by

$$[\text{total surface sites}]_{\text{moles/l soln}} = \frac{N_s S_A C_s}{N_A} \quad (5-5)$$

where N_s is the number of sites per m², S_A is the specific surface area of the solid (m²/g), C_s is the concentration of the solid (g solid/l of solution), and N_A is Avogadro's number (6.02×10^{23}). N_s can be measured (or estimated) in several ways, for example by deuterium exchange or from the known structure of the solid, but is most commonly derived from surface titration experiments (see below). S_A is commonly measured by the BET method (Brunauer, Emmett, and Teller, 1938), in which the amount of a gas (most commonly nitrogen) required to form a monolayer on the surface of the solid is measured.

The activity $[H^+]_s$ in Eqs. (5-3) and (5-4) represent the activity of hydrogen ions in solution *at the surface of the solid*. This will generally not be the same as the activity of hydrogen ions in bulk solution because, if the surface is charged, the concentration of ions close to the surface will be affected by the charge on the surface (see Fig. 4-9). If the surface is positively charged, the activity of H⁺ near it will be less than in bulk solution, and if the surface charge is negative, the activity of H⁺ near it will be greater than in bulk solution. The electrostatic or *coulombic* effect can be quantified by

$$[H^+]_{\text{location } x} = [H^+]_{\text{bulk soln}} \exp\left(\frac{-zF\Psi_{(x)}}{RT}\right) \quad (5-6)$$

where z is the charge on the ion (1 in the case of H⁺), F is Faraday's constant (96,485 Coulombs per mole of electrons), $\Psi_{(x)}$ is the electrical potential at location x , R is the gas constant and T the temperature on the Kelvin scale (Stumm, 1992). The expression $\exp\left(\frac{-zF\Psi_{(x)}}{RT}\right)$ is referred to as the *electrostatic* or *coulombic* term in the equation.

Eqs. (5-3) and (5-4) can thus be rewritten as

$$K_{a1}^{\text{intr}} = \frac{[\equiv\text{S}-\text{OH}][\text{H}^+]_{\text{bulk}}}{[\equiv\text{S}-\text{OH}_2^+]} \exp\left(\frac{-zF\Psi_{(\text{surface})}}{RT}\right) \quad (5-7)$$

and

$$K_{a2}^{\text{intr}} = \frac{[\text{S}-\text{O}^-][\text{H}^+]_{\text{bulk}}}{[\text{S}-\text{OH}]} \exp\left(\frac{-zF\Psi_{(\text{surface})}}{RT}\right) \quad (5-8)$$

where $[\text{H}^+]_{\text{bulk}}$ represents the hydrogen ion activity in the bulk solution. K_{a1}^{intr} and K_{a2}^{intr} are *intrinsic constants*. The intrinsic constant is the value of the equilibrium constant written in terms of concentrations at the surface rather than in bulk solution. It is a function of the nature of the solid surface and adsorbing ion only and is not a function of the charge on the surface. K_{a2}^{intr} reflects only the chemical energy involved in an adsorption reaction, whereas K_{a1} , written in terms of activities in bulk solution,

$$K_{a1} = \frac{[\equiv\text{S}-\text{OH}][\text{H}^+]_{\text{bulk}}}{[\equiv\text{S}-\text{OH}_2^+]}$$

includes both chemical and electrostatic effects.

Substitution of $[\equiv\text{S}-\text{OH}_2^+] = [\equiv\text{S}-\text{O}^-]$ and $\Psi = 0$ (the definition of the ZPNPC; when the charge is zero the potential is zero) into Eqs. (5-7) and (5-8) gives

$$\text{pH}_{\text{ZPNPC}} = 0.5(\text{p}K_{a1}^{\text{intr}} + \text{p}K_{a2}^{\text{intr}})$$

Surface Titrations. The quantities $[\equiv\text{S}-\text{OH}_2^+]$ and $[\equiv\text{S}-\text{O}^-]$ and hence the intrinsic acidity constants, can be measured by what are called *surface titrations*. In a surface titration, a stirred suspension of the solid in a solution containing (usually) a supporting electrolyte (a solution of a salt whose ions do not interact strongly with the surface, commonly NaNO_3 or NaClO_4) is titrated by addition of a strong acid (commonly HNO_3 or HCl) or strong base (commonly NaOH). Of the added H^+ or OH^- ions, some are adsorbed by the surface and some accumulate in solution. If the amount of acid added is C_A and the amount of base C_B (in units of moles per liter of the solution being titrated), then

$$C_A - C_B + m_{\text{OH}^-} - m_{\text{H}^+} = [\equiv\text{S}-\text{OH}_2^+] - [\equiv\text{S}-\text{O}^-]$$

where m_{OH^-} and m_{H^+} are concentrations present in solution, and $[\equiv\text{S}-\text{OH}_2^+]$ and $[\equiv\text{S}-\text{O}^-]$ are also in units of moles per liter of solution. Titration curves for $\gamma\text{-Al}_2\text{O}_3$ are shown in Fig. 5-6. The curves show the pH of the solution as a function of the amount of acid or base added. The curves corresponding to different supporting electrolyte concentrations intersect at a single pH and diverge away from that pH in either direction. The reason for the divergence is the electrostatic term in Eqs. (5-7) and (5-8). The distribution of charge and hence Ψ close to the surface is a function of the ionic strength of the solution. At the ZPC of the surface, however, the charge is zero, Ψ is zero, and the titration curves intersect. This represents one way of identifying the ZPC of the surface. If it is assumed that at a pH less than the ZPC the concentration of $[\equiv\text{S}-\text{O}^-]$ is small compared to that of $[\equiv\text{S}-\text{OH}_2^+]$, then titration of the surface with acid yields

$$C_A - m_{\text{H}^+} = [\equiv\text{S}-\text{OH}_2^+] \quad (\text{below ZPC})$$

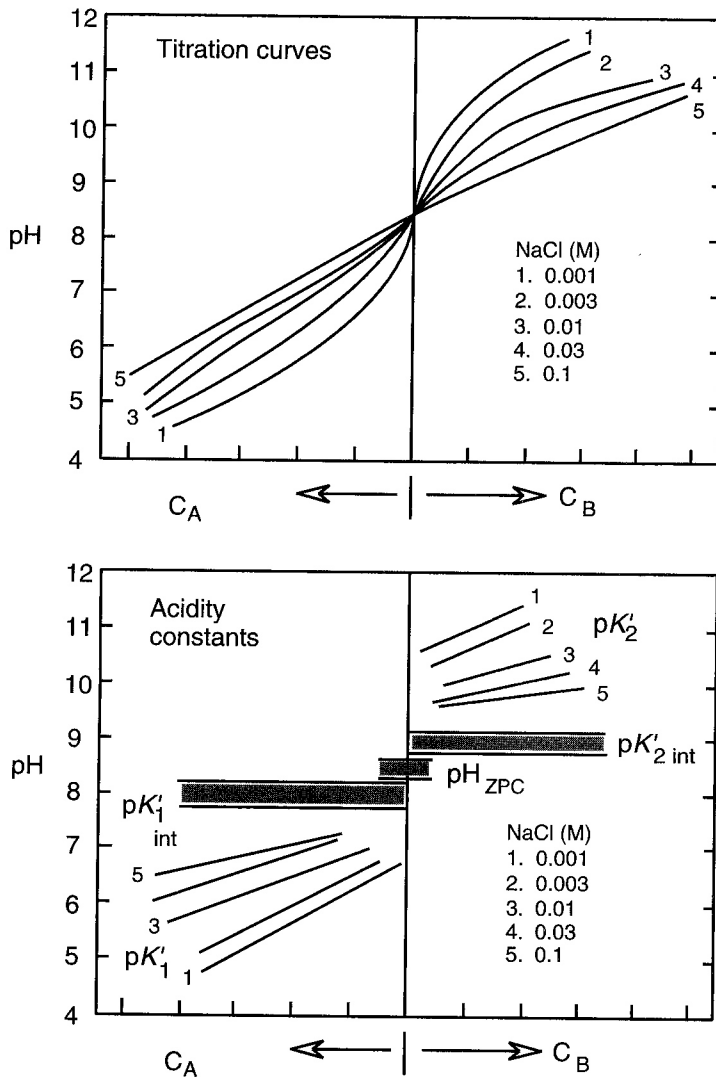
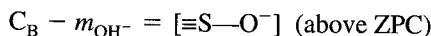


FIGURE 5-6 Titration curves in different concentrations of NaCl background electrolyte and corresponding acidity constants for hydrous $\gamma\text{-Al}_2\text{O}_3$ (1.56 g/l). The uncorrected acidity constants (pK'_1 and pK'_2) are calculated from the corresponding individual points on the titration curves. They vary as a function of surface charge whereas the corresponding intrinsic constants (pK_1^{intr} and pK_2^{intr}) do not; they all plot in the shaded areas on the figure. The titration curves all intersect at the ZPC (after Huang and Stumm, 1973). Reprinted with permission of Academic Press, Inc.

and titration with base above the ZPC yields



$[\equiv\text{S}-\text{OH}_2^+]$ and $[\equiv\text{S}-\text{O}^-]$ can thus be measured as a function of pH from the titration curves. If the total concentration of sites is known (by deuterium exchange or titration to

extreme pH, for example) then the values of K_{a1} and K_{a2} can be calculated. Plotting these values and extrapolating to the ZPC (Fig. 5-6) gives the intrinsic constants K_{a1}^{intr} and K_{a2}^{intr} .

Adsorption of Metal Cations

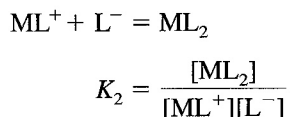
Analogous intrinsic constants can be written for formation of complexes between a metal and the surface. For example, constants for Eq. (5-1) and (5-2) can be written

$$K_M^{\text{intr}} = \frac{[\equiv\text{S}-\text{OM}^+][\text{H}^+]}{[\equiv\text{S}-\text{OH}][\text{M}^{2+}]} \exp\left(\frac{-\Delta z F \Psi_{(\text{surface})}}{RT}\right)$$

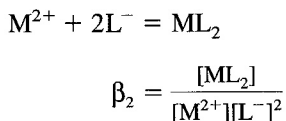
and

$$\beta_{2(\text{M})}^{\text{intr}} = \frac{[(\equiv\text{S}-\text{O})_2\text{M}][\text{H}^+]^2}{[(\equiv\text{S}-\text{OH})_2][\text{M}^{2+}]} \exp\left(\frac{-\Delta z F \Psi_{(\text{surface})}}{RT}\right)$$

The convention for writing equilibrium constants follows that of Sillén and Martell (1971): when a metal forms a constant with more than one ligand, K_n refers to individual steps and β_n refers to a cumulative reaction. For formation of a complex ML_2 , K_2 would refer to the reaction



whereas β_2 would refer to the reaction



The coulombic term is written with Δz rather than z . Δz represents the net change in the charge on the surface corresponding to the adsorption reaction as written (Dzombak and Morel, 1990). For reaction (5-1), Δz would be +1 (one M^{2+} gained, one H^+ lost). For reaction (5-2), Δz would be zero (one M^{2+} gained, two H^+ lost). Intrinsic constants for surface complexation reactions can be measured by methods analogous to surface titrations for adsorbed H^+ (Davis and Kent, 1990; Dzombak and Morel, 1990). Dzombak and Morel give an extensive compilation of constants for hydrous ferric oxide, the most important substrate for adsorption of heavy metals in natural systems.

It is useful to distinguish between *inner sphere* and *outer sphere* surface complexes (Fig. 5-7), analogous to inner- and outer-sphere complexes in solution (Chapter 2). In an outer-sphere complex, the ion remains surrounded by a hydration shell so it does not bind directly to the surface. Adsorption is essentially electrostatic, caused by attraction between a positively charged ion in solution and a negatively charged surface (or between an anion in solution and a positively charged surface). In an inner sphere complex, the ion bonds directly to the surface groups. The bond is generally stronger and does not depend on electrostatic attraction: a cation can adsorb to a positively charged surface.

Adsorption of cations can be regarded as a competition between cations and H^+ for surface sites. At low pH, adsorption of cations is minimal. As the pH rises, there is a relatively

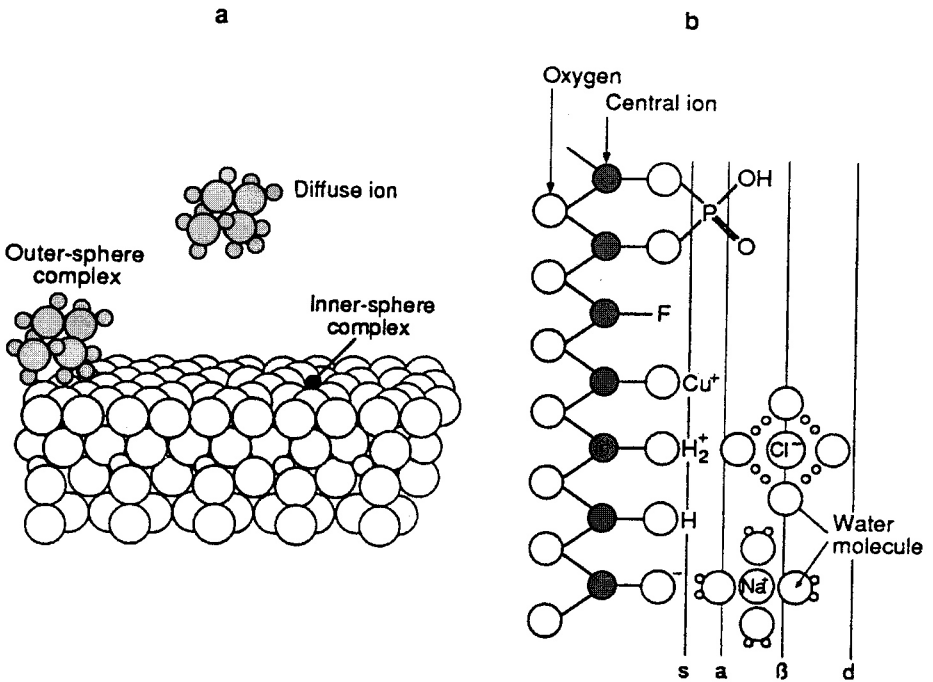
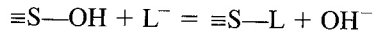


FIGURE 5-7 Schematic representation of inner-sphere (phosphate, fluoride, copper) and outer-sphere (sodium, chloride) complexes. The labels on the layers correspond to the triple-layer model (discussed in text) (after Stumm, 1992).

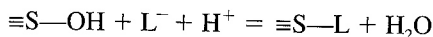
narrow interval (about 2 pH units) over which adsorption changes from essentially zero to essentially complete (Fig. 5-8) (assuming the amount of cation present is small compared to the number of available surface sites). This pH interval is different for different metal cations and for different solid substrates.

Adsorption of Anions

Equations for the adsorption of anions are very similar to those for adsorption of cations. For example



or, written in terms of H^+ rather than OH^- :



$$K_{\text{L}^-}^{\text{intr}} = \frac{[\equiv\text{S}-\text{L}]}{[\equiv\text{S}-\text{OH}][\text{L}^-][\text{H}^+]} \exp\left(\frac{-\Delta z F \Psi_{(\text{surface})}}{RT}\right)$$

In this particular instance Δz would be zero (no net change in surface charge). Other possible anion adsorption reactions would result in non-zero values for Δz . As with cations, anions may adsorb as inner-sphere or outer-sphere complexes.

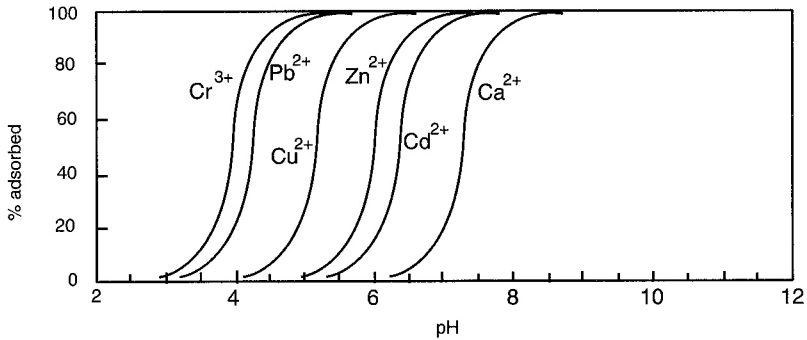


FIGURE 5-8 Adsorption of metal cations on hydrous ferric oxide as a function of pH (data from Dzombak and Morel, 1990).

Anions are essentially competing with OH^- for adsorption sites, so their behavior is the mirror image of cation adsorption (Fig. 5-9). Adsorption increases from essentially zero at high pH to essentially complete at low pH. The transition occurs over a relatively narrow pH range which is specific to the anion and the oxide surface. The adsorption of anions is often complicated by a change in speciation of the solute as a function of pH. For example, at low pH the dominant form of dissolved arsenic in oxidizing environments is H_3AsO_4 . As the pH rises, this acid dissociates into, progressively, H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} . Each species has different adsorption properties, so the overall adsorption behavior is quite complex.

The Electric Double Layer

The treatment so far has been quite general. We have developed a series of equations that describe the adsorption of ions at the surface of an oxide in terms of measurable equilibrium constants and an electrostatic term involving the electrical potential, Ψ , at the surface of the solid. Before we can apply this modeling approach to a real system, we need to be able to calculate Ψ . Ψ itself is a function of surface charge, so it is a function of the extent

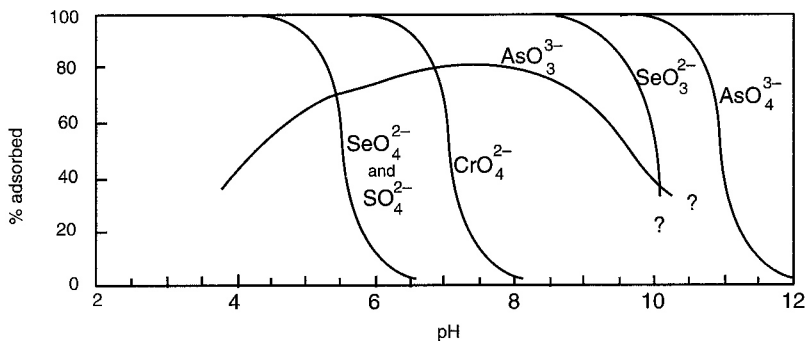


FIGURE 5-9 Adsorption of selected anions on hydrous ferric oxide as a function of pH (data from Dzombak and Morel, 1990).

of protonation–deprotonation reactions and the extent of the adsorption of ions from solution. It is thus a function of solution composition. The electrostatic potential at the surface of the solid and the surface charge are mathematically related

$$\sigma = f(\Psi) \quad (5-9)$$

where σ is the charge on the surface in units of coulombs/m². It is the form of the functional relationship, f , that distinguishes the various surface complexation models discussed below. It is more convenient to express σ in molar units; the conversion is

$$T_\sigma = \frac{S_A C_s}{F} \sigma$$

where T_σ is the surface charge in moles per liter of solution, S_A is the specific surface area of the solid (m²/g), C_s is the concentration of the solid (g solid/l of solution), and F is Faraday's constant. T_σ is zero at the ZPC and represents the net charge (adsorbed cations—adsorbed anions) away from the ZPC.

The Constant Capacitance Model (CCM). In this model it is assumed that the double layer can be represented by a parallel plate capacitor (Fig. 5-10).

1. Only one plane in the interfacial region is considered. All adsorbed protons, negative sites from deprotonation, and specifically adsorbed ions occur in a single plane, defined as the surface of the solid. Ions that do not form inner-sphere complexes (e.g., Na⁺, K⁺, Cl⁻, and NO₃⁻) are assumed to be excluded from this inner plane.

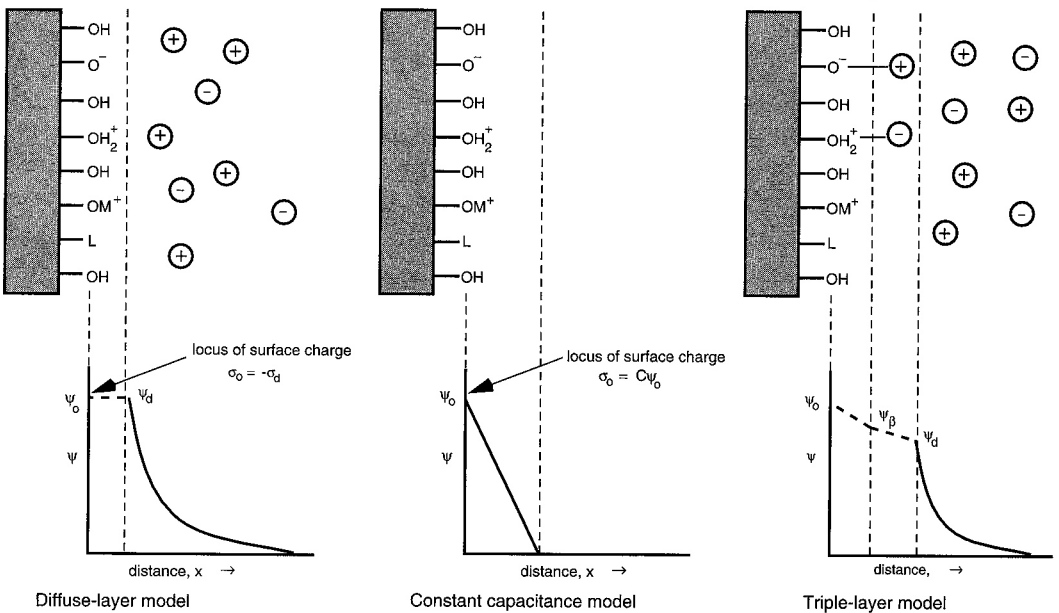


FIGURE 5-10 Idealized distribution of electrical potential (ψ) in the vicinity of a hydrated oxide surface according to (a) the diffuse-layer model; (b) the constant capacitance model; (c) the triple-layer model (after Hayes et al., 1991).

2. The relationship between charge and potential at the surface plane is given by

$$\sigma_{(0)} = C\Psi_{(0)}$$

where C is the capacitance of the double layer (Farads/m²) and is assumed to be a constant. C is essentially a fitting parameter rather than being derived theoretically.

The model is appropriate for solutions of high ionic strength, where the double layer is compressed close to the mineral surface. It has also been widely applied in dilute solution.

The Diffuse Double-Layer Model (DDLDM). The DDLDM is based on the Gouy-Chapman model of the diffuse double layer (for detailed discussions, see Bolt, 1982, and Sposito, 1984). The Gouy-Chapman model was coupled with surface complexation modeling by Stumm et al. (1970) and Huang and Stumm (1973). The approach was extended and modified by Dzombak and Morel (1990). The main difference from the CCM is that the counterions are assumed to form a diffuse layer extending from the surface out into solution, which can be described by Gouy-Chapman theory. In the DDLDM, the relationship between charge and potential is given by

$$\sigma_d = -0.1174\sqrt{I} \sinh \frac{zF\Psi}{RT} \quad (5-10)$$

where the subscript d refers to the diffuse layer and I is the ionic strength (Chapter 2). The electrical potential at the innermost edge of the diffuse layer is assumed to be equal to the surface potential (Fig. 5-10). In this model the capacitance of the double layer is inherently defined by Eq. (5-10); it is a function of solution composition rather than being a fitting parameter. In principle, this model should be appropriate for solutions of low ionic strength and low concentrations of adsorbing ions.

The Triple-Layer Model (TLM). The CCM and the DDLDM both make the assumption that all adsorbed ions are present at a single plane at the surface of the solid. In the TLM (Davis et al., 1978; Hayes et al., 1991) it is assumed that different species are adsorbed at different distances from the surface. Somewhat different versions of the triple-layer model are in use; the description here follows Hayes et al. (1991). In the triple-layer model (Fig. 5-10c), proton and deprotonation reactions occur in a layer directly adjacent to the surface, the o -plane. Inner-sphere complexes are also assigned to the o -plane. Outer-sphere complexes are assigned to a plane (the β -plane) slightly farther from the surface, and all ions that interact only through electrostatic forces are assigned to a diffuse layer outside the β -layer. In the original version of the TLM (Davis et al., 1978), which is the version implemented in MINTEQA2, only proton-deprotonation reactions occurred at the o -plane; inner-sphere complexes were assigned to the β -plane, and outer-sphere complexes were assigned to the diffuse layer. The approach (in both forms) is conceptually reasonable: protons should be attached directly to the surface, physically larger adsorbed species should be centered at a greater distance, and ions that do not bond directly to the surface would form a diffuse layer. The two regions closest to the surface are modeled as a constant capacity layer and the region outside the β -layer as a diffuse (Gouy-Chapman) layer. The advantage of this model is that it is (presumably) a better representation

of reality or, alternatively, it has more fitting parameters, which should result in a better fit to experimental data. The disadvantage is that it is mathematically more complex and requires more parameters to describe the system. It should be stressed, following Westall (1987), that although these models may describe macroscopic data well, they should not be regarded as a literal description of processes occurring at the molecular scale.

Comparison of the Models. The ability of each of the three models (and two others) to describe experimental data from acid-base titrations of hydrous oxides was evaluated rigorously by Westall and Hohl (1980). They showed that each model had sufficient adjustable parameters and that each could describe the experimental titration data equally well. Subsequent comparisons are reviewed by Davis and Kent (1990). They conclude that all surface complexation models can simulate ion adsorption data adequately in simple mineral-water systems, so there is no obvious reason to choose one over the other. Computational complexity is not really an issue because computer codes handle the calculations for all of them. A major limitation is the availability of data to implement any model. The most extensive compilation at present is that of Dzombak and Morel (1990) for hydrous ferric oxide. Dzombak and Morel used a modified DDLM; it is convenient and advisable to maintain consistency by using their model with their data.

Realistically, when it comes to predicting adsorption in field situations, the choice of a specific surface complexation model is likely to be a very minor source of uncertainty. A far greater source of uncertainty is specifying the amount and properties (specific surface area, site density, complexation constants) of the adsorption substrates present in the natural environment.

Modeling Adsorption with MINTEQA2

Conceptually, modeling adsorption is simply an extension of the speciation calculation discussed in Chapter 2. If we were to add a new dissolved component to WATEQ4F or MINTEQA2, we would need to add:

1. An equation for the conservation of the total mass of the component

$$\text{Total concentration} = \text{Sum of concentrations of all species (complexes) containing the component}$$

2. An equilibrium constant for the formation of each species containing the component.

We would thus add n unknowns (the concentration of each complex and the concentration of the free component), and n equations (a total concentration for the component), and $(n - 1)$ equilibrium constant expressions.

Mathematically, if the electrostatic term is omitted, adsorption at a surface site is identical to complex formation in solution. To model adsorption at a single surface site, we need to specify:

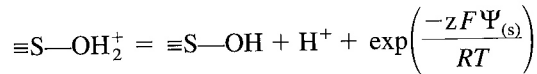
1. The total concentration of "sites" ($[=S-OH]$ in the terminology above) in units of moles/l of solution (MINTEQA2 prompts for the variables shown on the right hand side of Eq. (5-5) above).

2. An equilibrium constant for formation of each complex between the surface site and components in solution. For surface complexation models, these would correspond to the intrinsic constants.

The electrostatic term is modeled mathematically by treating it as an additional component. This “works” because Eq. (5-7),

$$K_{al}^{intr} = \frac{[\equiv\text{S}-\text{OH}][\text{H}^+]}{[\equiv\text{S}-\text{OH}_2^+]} \exp\left(\frac{-zF\Psi_{(s)}}{RT}\right)$$

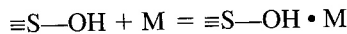
corresponds to the equilibrium constant for the reaction



The electrostatic term is thus analogous to an activity in solution. It is calculated by MINTEQA2 to be consistent with the particular adsorption model chosen. The other equations needed to define the system are an equation for conservation of charge at the surface (at each layer in the triple-layer model), and expressions corresponding to equilibrium constants, which determine the appropriate value for the electrostatic term for each reaction being modeled. These calculations are performed by MINTEQA2 to correspond to the adsorption model chosen. Thus addition of adsorption reactions, including electrostatic effects, is mathematically equivalent to adding additional components in solution and does not require anything fundamentally different from the program.

The adsorption equations available in MINTEQA2 are

1. *The Activity K_d Model.* The model implemented by MINTEQA2 differs slightly from the common usage in that the concentration in solution is expressed as the activity of the free ion rather than as the total concentration of the ion in solution. The relevant equations are:

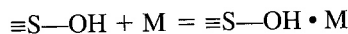


and

$$K_d^{\text{act}} = \frac{[\equiv\text{S}-\text{OH} \cdot \text{M}]}{a_{\text{M}}}$$

where $[\equiv\text{S}-\text{OH} \cdot \text{M}]$ represents the adsorbed concentration of M (which may have any charge, including zero). $[\equiv\text{S}-\text{OH}]$ does not appear in the equation because in the K_d model it is assumed that the number of available sites is infinite and does not change. This is analogous to the assumption that the activity of a solid phase is 1. The only input data needed to implement the model is a numerical value for the K_d for each species of interest. There is no interaction among solutes: adsorption of solute A has no effect on adsorption of solute B.

2. *The Activity Langmuir Model.* As with the activity K_d above, the activity of the relevant species in solution is used rather than the concentration, and the charge of the solute (M) is unimportant. The relevant equations are



and

$$K_{\text{Lang}}^{\text{act}} = \frac{[\equiv\text{S}-\text{OH} \cdot \text{M}]}{a_{\text{M}}[\equiv\text{S}-\text{OH}]} \quad (5-11)$$

If the total concentration of sites is $[\equiv\text{SOH}]_T (= [\equiv\text{S—OH}] + [\equiv\text{S—OH} \cdot \text{M}])$, then Eq. (5–11) can be rewritten in the more familiar Langmuir form:

$$[\equiv\text{S—OH} \cdot \text{M}] = \frac{K_{\text{Lang}}^{\text{act}} [\equiv\text{S—OH}]_T \alpha_{\text{M}}}{1 + K_{\text{Lang}}^{\text{act}} \alpha_{\text{M}}}$$

The input data required to implement the activity Langmuir model are numerical values for $K_{\text{Lang}}^{\text{act}}$ for each species of interest and a numerical value for $[\equiv\text{SOH}]_T$. Because the number of sites is fixed, there is competition among solutes. Adsorption of solute A will tend to decrease the adsorption of solute B.

3. The Activity Freundlich Model. This model is similar to the activity K_d model, with the addition of an exponent n . The concentration/activity of unreacted sites is assumed constant and equal to 1.

$$[\equiv\text{S—OH} \cdot \text{M}] = K_{\text{Freun}}^{\text{act}} \alpha_{\text{M}}^n$$

The required inputs are $K_{\text{Freun}}^{\text{act}}$ and n (somewhat confusingly, MINTEQA2 asks for $1/n$ rather than n). As with the K_d model, there is no interaction among solutes.

4. Ion Exchange Model. This model uses selectivity coefficients, as discussed in Chapter 4. For ions of the same charge,

$$[\equiv\text{S—OH} \cdot \text{M}_1] + \text{M}_2 = [\equiv\text{S—OH} \cdot \text{M}_2] + \text{M}_1$$

$$K_{\text{ex}} (= K_{\text{M}_1\text{M}_2} \text{ in the terminology of Chapter 4}) = \frac{m_{\text{M}_1} [\equiv\text{S—OH} \cdot \text{M}_2]}{m_{\text{M}_2} [\equiv\text{S—OH} \cdot \text{M}_1]}$$

The calculation uses concentrations of free ions (calculated from activity divided by activity coefficient) rather than activities for solutes. The required inputs are a cation exchange capacity and a selectivity coefficient for each pair of ions to be modeled. For ions of different charge, the model implements the Gaines-Thomas equation (Eq. 4–7) discussed in Chapter 4.

5. Constant Capacitance Model, Diffuse-Layer Model, and Triple-Layer Model. The implementation of these models follows the theory outlined above. The necessary inputs are surface area(s) of the solid(s), surface site densities, and intrinsic constants for all species of interest, and a capacitance or capacitances for the double (triple) layers. Five different surfaces (which would correspond to different mineral phases) and can be modeled simultaneously by MINTEQA2, and each surface may have up to two different sites. It is not often that people model more than one surface at a time. There is interaction among solutes both because of competition for a fixed number of sites and because adsorption of any ion affects the electric charge of the surface. MINTEQA2 normally comes with the Dzombak and Morel (1990) data base for calculating adsorption on hydrous ferric oxides with the diffuse double layer model.

REVIEW QUESTIONS

The adsorption properties of ammonium in an aquifer were evaluated by mixing 1 g of an ammonium-saturated sediment with different volumes of ammonium-free groundwater from the aquifer, and the concentration of ammonium in the groundwater was measured. The cation capacity of the sediment was 20 meq/kg.

ml soln/g sediment	0.5	1	2	5	10	20	50	100	200	500	1000
Conc in solution (mM)	6.8	5.0	3.5	2.0	1.3	0.75	0.35	0.186	0.0963	0.03938	0.01984

1. How well do the data fit a Langmuir isotherm? Estimate the values of K_{Lang} and $m_{(\text{ads, max})}$ that best fit the data.
2. What value of K_d would fit the data at low concentration? Up to what concentration is the linear K_d a reasonable fit (say ± 10 percent) to the data?
3. How well do the data fit a Freundlich isotherm? Up to what concentration is the Freundlich isotherm a reasonable fit (say ± 10 percent) to the data? What value of n gives the best fit at low concentration?
4. The data in the table above fit a cation-exchange equation (Eq. 4-3):

$$\frac{m_{\text{A-clay}}}{\text{CEC} - m_{\text{A-clay}}} = K'_{\text{AB}} \frac{m_{\text{A}^+}}{M - m_{\text{A}^+}}$$

with $K'_{\text{AB}} = 6$ and $M = 15 \text{ meq/l}$. How does this equation differ from the Langmuir isotherm? Can you relate the constants in this equation (CEC , K'_{AB} , M) to the constants in the Langmuir isotherm and its linearized equivalent (K_{Lang} , $m_{(\text{ads, max})}$)?

SUGGESTED READING

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