is termed outer-sphere (Sposito, 1989). If there is not a water molecule present between the ion or molecule and the surface functional group to which it is bound this is an inner-sphere complex. One will note in Fig. 5.4 that inner-sphere complexes can be monodentate (metal is bonded to only one oxygen) and bidentate (metal is bonded to two oxygens).

Outer-sphere complexes involve electrostatic coulombic interactions and are thus weak compared to inner-sphere complexes in which the binding is covalent or ionic. Outer-sphere complexation is usually a rapid process that is reversible, and adsorption via this mechanism is affected by ionic strength of the aqueous phase. Adsorption by outer-sphere complexation occurs only on surfaces that are of opposite charge to the adsorbate.

Inner-sphere complexation is usually slower than outer-sphere complexation; it is often not reversible and adsorption by this mechanism is weakly affected by the ionic strength of the aqueous phase. Inner-sphere complexation can increase, reduce, neutralize, or reverse the charge on the sorptive regardless of the original charge. Adsorption of ions via inner-sphere complexation can occur on a surface regardless of the surface charge. It is important to remember that outer- and inner-sphere complexation can, and often do, occur simultaneously.

ADSORPTION ISOTHERMS

One can conduct an adsorption experiment as explained in Box 5.1. The quantity of adsorbate can then be used to determine an adsorption isotherm.

An adsorption isotherm, which describes the relation between the activity or equilibrium concentration of the adsorptive and the quantity of adsorbate on the surface at constant temperature, is usually employed to describe adsorption. One of the first solute adsorption isotherms was described by van Bemmelen (1888), and he later described experimental data using an adsorption isotherm.

Adsorption can be described by four general types of isotherms (S, L, H, and C) that are shown in Fig. 5.6. With an S-type isotherm the slope initially increases with adsorptive concentration, but eventually decreases and becomes zero as vacant adsorbent sites are filled. This type of isotherm indicates that at low concentrations the surface has a low affinity for the adsorptive which increases at higher concentrations. The L-shaped (Langmuir) isotherm is characterized by a decreasing slope as concentration increases since vacant adsorption sites decrease as the adsorbent becomes covered. Such adsorption behavior could be explained by the high affinity of the adsorbent for the adsorptive at low concentrations, which then decreases as concentration increases. The H-type (high affinity) isotherm is indicative of strong adsorbate–adsorptive interactions such as inner-sphere complexes. The C-type isotherms are indicative of a partitioning mechanism whereby adsorptive ions or molecules are distributed or partitioned between the interfacial phase and the bulk solution phase without any specific bonding between the adsorbent and adsorbate (see Box 5.2 for discussion of partition coefficients).

BOX 5.1. Conducting an Adsorption Experiment

Adsorption experiments are carried out by equilibrating (shaking, stirring) an adsorptive solution of a known composition and volume with a known amount of adsorbent at a constant temperature and pressure for a period of time such that an equilibrium (adsorption reaches a steady state or no longer changes after a period of time) is attained. The pH and ionic strength are also controlled in most adsorption experiments.

After equilibrium is reached (it must be realized that true equilibrium is seldom reached, especially with soils), the adsorptive solution is separated from the adsorbent by centrifugation, settling, or filtering, and then analyzed.

It is very important to equilibrate the adsorbent and adsorptive long enough to ensure that steady state has been reached. However, one should be careful that the equilibration process is not so lengthy that precipitation or dissolution reactions occur (Sposito, 1984). Additionally, the degree of agitation that is used in the equilibration process should be forceful enough to effect good mixing but not so vigorous that adsorbent modification occurs (Sparks, 1989). The method that one uses for the adsorption experiment, e.g., batch or flow, is also important. While batch techniques are simpler, one should be aware of their pitfalls, including the possibility of secondary precipitation and alterations in equilibrium states. More details on these techniques are given in Chapter 7.

One can determine the degree of adsorption by using the following mass balance equation,

$$\frac{(C_f\,V_f) - (C_0\,V_0)}{m} = q, \tag{5.1a}$$

where q is the amount of adsorption (adsorbate per unit mass of adsorbent) in mol kg^{-1}, C_f and C_0 are the final and initial adsorptive concentrations, respectively, in mol liter^{-1}, V_f and V_0 are the final and initial adsorptive volumes, respectively, in liters, and m is the mass of the adsorbent in kilograms. Adsorption could then be described graphically by plotting C_f or C (where C is referred to as the equilibrium or final adsorptive concentration) on the x axis versus q on the y axis.

One should realize that adsorption isotherms are purely descriptions of macroscopic data and do not definitively prove a reaction mechanism. Mechanisms must be gleaned from molecular investigations, e.g., the use of spectroscopic techniques. Thus, the conformity of experimental adsorption data to a particular isotherm does not indicate that this is a unique description of the experimental data, and that only adsorption is operational. Thus, one cannot differentiate between adsorption and precipitation using an adsorption isotherm even though this has been done in the soil chemistry literature. For

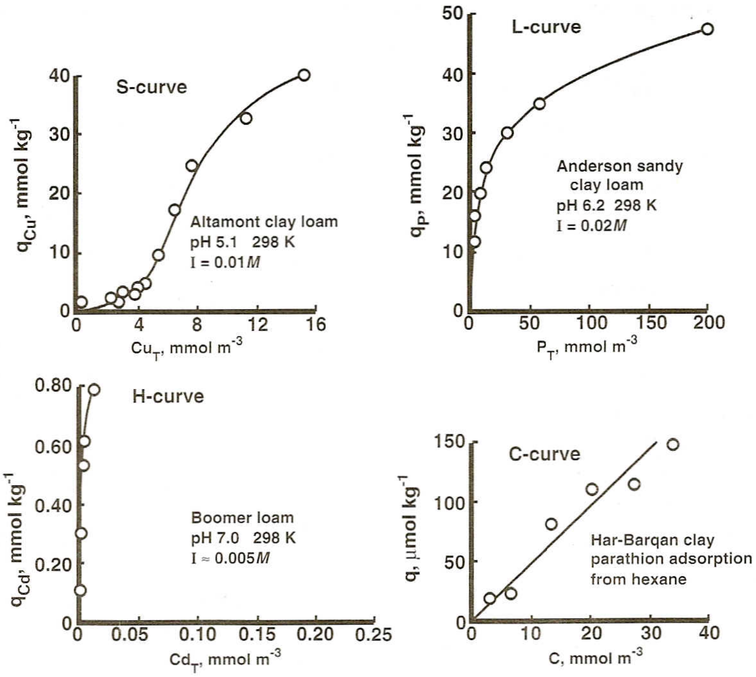

FIGURE 5.6. The four general categories of adsorption isotherms. From Sposito (1984), with permission.

BOX 5.2. Partitioning Coefficients

A partitioning mechanism is usually suggested from linear adsorption isotherms (C-type isotherm, Fig. 5.6), reversible adsorption/desorption, a small temperature effect on adsorption, and the absence of competition when other adsorptives are added, i.e., adsorption of one of the adsorptives is not affected by the inclusion of a second adsorptive.

A partition coefficient, K_p, can be obtained from the slope of a linear adsorption isotherm using the equation

$$q = K_p C, \tag{5.2a}$$

where q was defined earlier and C is the equilibrium concentration of the adsorptive. The K_p provides a measure of the ratio of the amount of a material that is adsorbed to the amount that is in solution.

Partition mechanisms have been invoked for a number of organic compounds, particularly for NOC and some pesticides (Chiou *et al.*, 1977, 1979, 1983).

A convenient relationship between the K_p and fraction of organic carbon (f_{oc}) in the soil is the organic carbon–water partition coefficient, K_{oc}, which can be expressed as

$$K_{oc} = K_p / f_{oc}. \tag{5.2b}$$

example, some researchers have described data using the Langmuir adsorption isotherm and have suggested that one slope at lower adsorptive concentrations represents adsorption and a second slope observed at higher solution concentrations represents precipitation. This is an incorrect use of an adsorption isotherm since molecular conclusions are being made and, moreover, depending on experimental conditions, precipitation and adsorption can occur simultaneously.

EQUILIBRIUM-BASED ADSORPTION MODELS

There are an array of equilibrium-based models that have been used to describe adsorption on soil surfaces. These include the widely used Freundlich equation, a purely empirical model, the Langmuir equation, and double-layer models including the diffuse double-layer, Stern, and surface complexation models that are discussed in the following sections.

Freundlich Equation

The Freundlich equation, which was first used to describe gas phase adsorption and solute adsorption, is an empirical adsorption model that has been widely used in environmental soil chemistry. It can be expressed as

$$q = K_d C^{1/n}, \tag{5.3}$$

where q and C were defined earlier, K_d is the distribution coefficient, and n is a correction factor. By plotting the linear form of Eq. (5.3), log q vs $1/n$ log C + log K_d, the slope is the value of $1/n$ and the intercept is equal to log K_d. If $1/n = 1$, Eq. (5.3) becomes equal to Eq. (5.2a) (Box 5.2), and K_d is a partition coefficient, K_p. One of the major disadvantages of the Freundlich equation is that it does not predict an adsorption maximum. The single K_d term in the Freundlich equation implies that the energy of adsorption on a homogeneous surface is independent of surface coverage. While researchers have often used the K_d and $1/n$ parameters to make conclusions concerning mechanisms of adsorption, and have interpreted multiple slopes from Freundlich isotherms (Fig. 5.7) as evidence of different binding sites, such interpretations are speculative. Plots such as Fig. 5.7 cannot be used for delineating adsorption mechanisms at soil surfaces.

Langmuir Equation

Another widely used sorption model is the Langmuir equation. It was developed by Irving Langmuir (1918) to describe the adsorption of gas molecules on a planar surface. It was first applied to soils by Fried and Shapiro (1956) and Olsen and Watanabe (1957) to describe phosphate sorption on soils. Since that time, it has been heavily employed in many fields to describe sorption on colloidal surfaces. As with the Freundlich equation, it best describes sorption at low sorptive concentrations. However, even here, failure occurs. Beginning in the late 1970s researchers began to question the validity

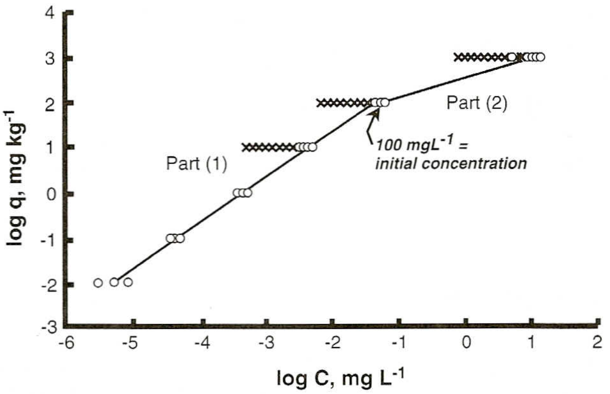

FIGURE 5.7. Use of the Freundlich equation to describe zinc adsorption (x)/desorption (O) on soils. Part I refers to the linear portion of the isotherm (initial Zn concentration < 100 mg L^{-1}) while Part 2 refers to the nonlinear portion of the isotherm. From Elrashidi and O'Connor (1982), with permission.

of its original assumptions and consequently its use in describing sorption on heterogeneous surfaces such as soils and even soil components (see references in Harter and Smith, 1981).

To understand why concerns have been raised about the use of the Langmuir equation, it would be instructive to review the original assumptions that Langmuir (1918) made in the development of the equation. They are (Harter and Smith, 1981): (1) Adsorption occurs on planar surfaces that have a fixed number of sites which are identical and the sites can hold only one molecule. Thus, only monolayer coverage is permitted, which represents maximum adsorption. (2) Adsorption is reversible. (3) There is no lateral movement of molecules on the surface. (4) The adsorption energy is the same for all sites and independent of surface coverage (i.e., the surface is homogeneous), and there is no interaction between adsorbate molecules (i.e., the adsorbate behaves ideally).

Most of these assumptions are not valid for the heterogeneous surfaces found in soils. As a result, the Langmuir equation should only be used for purely qualitative and descriptive purposes.

The Langmuir adsorption equation can be expressed as

$$q = kCb/(1 + kC), \tag{5.4}$$

where q and C were defined previously, k is a constant related to the binding strength, and b is the maximum amount of adsorptive that can be adsorbed (monolayer coverage). In some of the literature x/m, the weight of the adsorbate/unit weight of adsorbent, is plotted in lieu of q. Rearranging to a linear form, Eq. (5.4) becomes

$$C/q = 1/kb + C/b. \tag{5.5}$$

Plotting C/q vs C, the slope is $1/b$ and the intercept is $1/kb$. An application of the Langmuir equation to sorption of zinc on a soil is shown in Fig. 5.8. One will note that the data were described well by the Langmuir equation when the plots were resolved into two linear portions.

A number of other investigators have also shown that sorption data applied

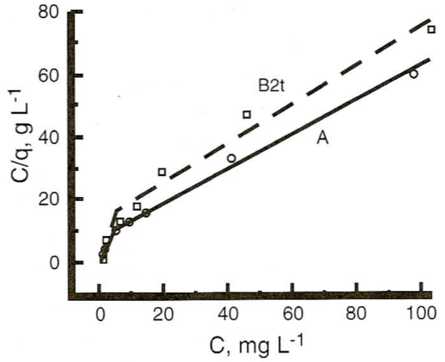

FIGURE 5.8. Zinc adsorption on the A and B2t horizons of a Cecil soil as described by the Langmuir equation. The plots were resolved into two linear portions. From Shuman (1975), with permission.

to the Langmuir equation can be described by multiple, linear portions. Some researchers have ascribed these to sorption on different binding sites. Some investigators have also concluded that if sorption data conform to the Langmuir equation, this indicates an adsorption mechanism, while deviations would suggest precipitation or some other mechanism. However, it has been clearly shown that the Langmuir equation can equally well describe both adsorption and precipitation (Veith and Sposito, 1977). Thus, mechanistic information cannot be derived from a purely macroscopic model like the Langmuir equation. While it is admissible to calculate maximum sorption (b) values for different soils and to compare them in a qualitative sense, the calculation of binding strength (k) values seems questionable. A better approach for calculating these parameters is to determine energies of activation from kinetic studies (see Chapter 7).

Some investigators have also employed a two-site or two-surface Langmuir equation to describe sorption data for an adsorbent with two sites of different affinities. This equation can be expressed as

$$q = \frac{b_1 k_1 C}{1 + k_1 C} + \frac{b_2 k_2 C}{1 + k_2 C}, \tag{5.6}$$

where the subscripts refer to sites 1 and 2, e.g., adsorption on high- and low-energy sites. Equation (5.6) has been successfully used to describe sorption on soils of different physiochemical and mineralogical properties. However the conformity of data to Eq. (5.6) does not prove that multiple sites with different binding affinities exist.

Double-Layer Theory and Models

Some of the most widely used models for describing sorption behavior are based on the electric double-layer theory that was developed in the early part of the 20th century. Gouy (1910) and Chapman (1913) derived an equation describing the ionic distribution in the diffuse layer formed adjacent to a charged surface. The countercharge (charge of opposite sign to the surface charge) can be a diffuse atmosphere of charge, or a compact layer of bound