Chapter 14

SORPTION OF IONIC ORGANIC COMPOUNDS TO CHARGED SURFACES

14.1 Introduction

Many organic compounds exhibit acid or base functionalities and can, therefore, exist as anions or cations in aqueous solutions (Chapter. 4, Section 4.3). As illustrated by Fig. 14.1, despite the fact that charged moieties encourage those ions to stay dissolved in water, one still finds that these organic ions adsorb to natural solids.

Since most natural surfaces are charged when they are submerged in water, this implies we must consider how electrostatic interactions affect adsorption of these charged substances. In this chapter, sorption arising from nonspecific electrostatic attractions to charged surfaces will be referred to as "ion exchange" (Fig. 14.2a). In addition, ionic organic compounds can bond directly with specific atoms exposed on solid surfaces. This adsorptive interaction is called "surface complexation" (Fig. 14.2b).

In Chapter 12, we have already included "ion exchange" in the K_{id} expression:

$$K_{id} = \frac{C_{ioc}f_{oc} + C_{imin}A_{surf} + C_{iex}\sigma_{surf\ ex}A_{surf} + C_{irxn}\sigma_{surf\ rxn}A_{surf}}{C_{iw,neut} + C_{iw,ion}} \quad (12\text{-}11)$$

where A_{surf} is the specific surface area of the relevant solid (m^2 kg^{-1} solid), C_{iex} is the concentration of ionized sorbate drawn towards positions of opposite charge on the solid surface (mol mol^{-1} surface charges), and $\sigma_{surf\ ex}$ is the net concentration of suitably charged sites on the solid surface (mol surface charges m^{-2}) for ion exchange. Likewise, complexation between a sorbate acting as a ligand and surface metals was already included through the product $C_{irxn}\sigma_{surf\ rxn}A_{surf}$ in Eq. 12-11, where C_{irxn} is the concentration of sorbate i bonded in a reversible reaction to the solid (mol mol^{-1} reaction sites) and $\sigma_{surf\ rxn}$ is the concentration of reactive sites on the solid surface (mol reaction sites m^{-2}). In both cases, we need to consider how the structure of the organic sorbate, the nature of the surface, and the pH and ionic composition of the solution affect the extent of adsorption.

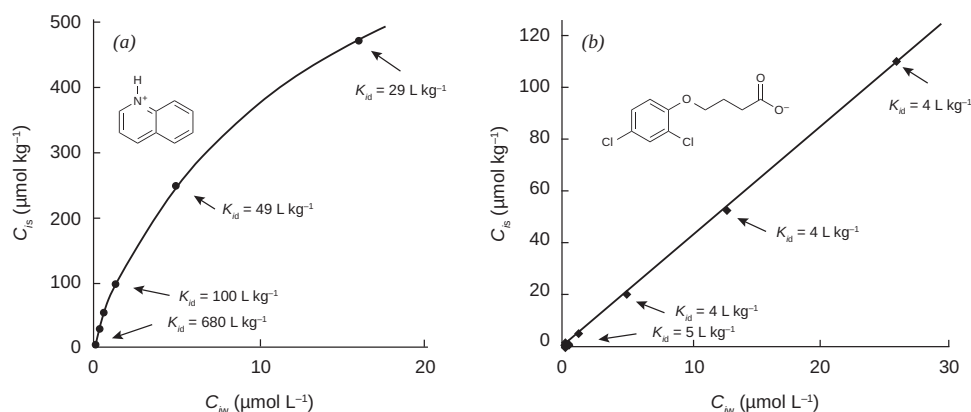

Figure 14.1 Sorption isotherms for some charged organic compounds interacting with natural solids: (a) quinolinium cation on a subsoil of $f_{oc} = 0.0024$ and cation exchange capacity of 84 mmol kg^{-1} (data from Zachara et al. 1986), and (b) sorption of 4-(2,4-dichlorophenoxy)-butyrate anion on a sediment with $f_{oc} = 0.015$ and unknown anion exchange capacity (data from Jafvert 1990).

Figure 14.2 Schematic view of two ways in which an ionic organic chemical i may sorb to natural inorganic solids: (a) adsorption of charged molecules from aqueous solution to complementarily charged surfaces due to electrostatic attractions, and (b) chemisorption due to surface bonding or inner sphere complex formation.
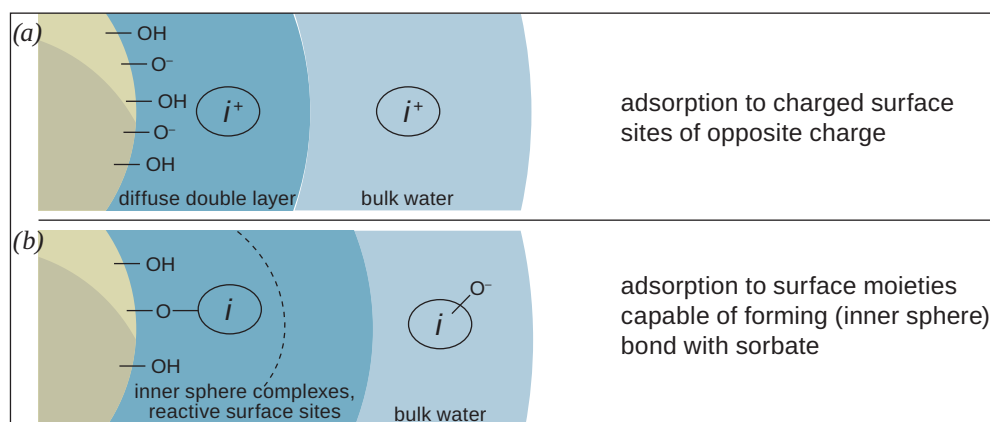
In this chapter, we first examine the extent to which various solids become charged in natural water (Section 14.2). Then we consider adsorption of ionized compounds largely arising from electrostatic attractions to charged mineral surfaces (Section 14.3). We conclude with surface interactions involving sorbate-sorbent bonding or surface complexation (Section 14.4). As we proceed, we identify solid properties like surface area (A_{surf}), surface charge ($\sigma_{surf\ ex}$), and reactive surface sites ($\sigma_{surf\ rxn}$) that are the key sorbent factors used to "tune" the intensity of each interaction for solids of interest. Also, we develop our understanding of how the structures of sorbates dictate their sorption behavior in environments of interest.

14.2   Cation and Anion Exchange Capacities of Solids in Water

Almost all particles are charged in natural waters. If this surface charge is of opposite sign to that of an organic compound, then there will be electrostatic attraction between the organic sorbate in the bulk solution and the particle surface. This is the same interaction energy drawing inorganic cations like Na^+ and Ca^{2+} near a negatively charged surface in water. Therefore, organic ions will accumulate in the thin film of water surrounding the particle as part of the population of charged ions in solution balancing the charges on the solid surface (Fig. 14.3). Conversely, organic molecules with charges of like sign as the surface will be repulsed from the adsorbed near-surface water. These electrostatic effects act similarly for all charged sorbates.

To evaluate the importance of such nonspecific charge-derived interactions, we need to know the "concentration of charges" on the surfaces of solids, called the cation exchange capacity (CEC) if the surface is negatively charged, or the anion exchange capacity (AEC) if the surface is positively charged. In Eq. 12-11, these ion exchange capacities are quantified using the product of the surface charge density, $\sigma_{surf\ ex}$ (e.g., mol charges m^{-2} solid), multiplied by the solid's specific surface area, A_{surf} (e.g., $m^2\ kg^{-1}$). To maintain charge balance, the adjacent layer of water must contain an excess of ions called counter ions (e.g., Cl^- and i^- to balance $\equiv M\text{-}OH_2^+$ in Fig. 14.3) that carry charge equal in magnitude and opposite in sign to that exhibited by the particle surface. The thickness of this ion-rich water layer varies inversely with the ionic strength of the solution (Morel, 1983; Whitehead et al., 2015). For typical ionic compositions of natural waters (ranging from 10^{-3} to 0.5 M), most

Figure 14.3 A positively charged oxide particle in water attracts anionic species including organic ones (e.g., i^-) to the adsorbed near-surface water (arrow 1). M in the solid refers to atoms like Si, Al, or Fe. Binding of the organic chemical to the surface (Section 14.4) is also shown (arrow 2).
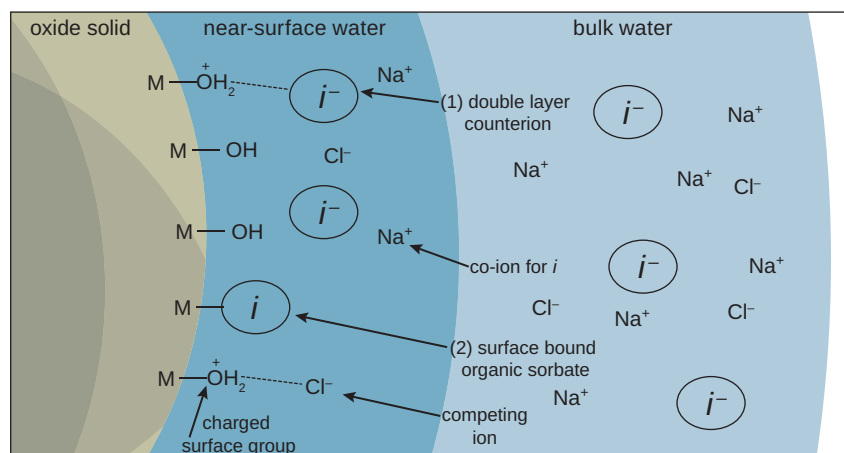
(> 63%) of the counterions are packed into a layer of water between 0.4 and 9 nm thick. This range is very similar to the 1–10 nm range postulated to reflect ordered vicinal water (Drost-Hansen, 1969; Etzler and Fagundus, 1987; Bowen and Yousef, 2003). Therefore, this is a very special microscopic water environment having different properties than the bulk water.

The abundance of charges on particles depends on the surface chemistry of the solid and the nature of the aqueous solution in which it occurs. Several important kinds of surfaces are common in the environment (Table 14.1). Here, we discuss: (1) oxides and oxyhydroxides, (2) aluminosilicates and clay minerals, and (3) carbonates. While absorption into natural organic matter (NOM) was previously discussed in Chapter 13 (Section 13.3), in this chapter NOM is also discussed as an ion exchange sorbent and as a surface reactant.

**Table 14.1** Sorbent Properties of "Pure Solids" Commonly Present in Aquatic Environments[a]

Sorbent	Composition	Specific surface area ($m^2 g^{-1}$)	CEC (pH 7)[b] ($mol\ m^{-2}$)	AEC (pH 7)[b] ($mol\ m^{-2}$)	pK_{a1}^{int}	pK_{a2}^{int}	pH_{zpc}
Oxides							
Quartz	SiO_2	0.2 (10 μm)[b]	0.6 to 5×10^{-4}		(−3)	7	2
Amorphous silica	SiO_2	2 (1 μm)[b]	1 to 4×10^{-4}		(−3)	7	2
Goethite	α-FeOOH	100–300		1 to 4×10^{-7}	6	9	7.5
Amorphous iron hydroxide	$Fe(OH)_3$	600		0.6×10^{-7} (I = 10^{-3} M)[b] 5×10^{-7} (I = 10^{-1} M)[b]	7.4	8.6	8
Gibbsite	$Al(OH)_3$	80–200		2 to 5×10^{-7}	5	8	6.5
Aluminosilicates							
Montmorillonite	$Na_3Al_7Si_{11}O_{30}(OH)_6$	600–800	0.9 to 2×10^{-6}	3 to 4×10^{-7}			2.5
Kaolinite	$Al_2Si_2O_5(OH)_2$	5–30	3 to 20×10^{-6}	0.6 to 2×10^{-5}			4.6
Illite	$KAl_3Si_3O_{10}(OH)_2$	65–100	1 to 6×10^{-6}	3×10^{-7}			
Carbonate							
Calcite	$CaCO_3$	1		9×10^{-6}			8–9.5

[a]Data from Carroll (1959); Parks (1965); Somasundaran and Agar (1967); Grim (1968); Mikhail et al. (1968a, b); Tipping (1981); Davis (1982); Schindler and Stumm (1987); Zullig and Morse (1988); Dzombak and Morel (1990); Kraepiel et al. (1998); Brady and Weil (2002).
[b]Assumed particle size, pH or ionic strength shown in parentheses.

Oxides/Oxyhydroxides

Hydroxyl groups cover the water-wet surface of natural solids that are oxides or oxy-hydroxides (e.g., quartz with M = Si, goethite with M = Fe, and gibbsite with M = Al, see Fig. 14.3). These hydroxyl moieties can undergo proton-exchange reactions with the aqueous solution much like dissolved acids and bases:

$$\equiv M - OH_2^+ \; \rightleftharpoons \; \equiv M - OH + H^+ \tag{14-1}$$
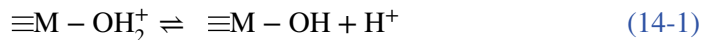
$$\equiv M - OH \rightleftharpoons \; \equiv M - O^- + H^+ \tag{14-2}$$

We may define acid-base equilibrium constants for those acid-base surface reactions (neglecting activity coefficients here):

$$K_{a1} = \frac{[\equiv M - OH][H^+]}{[\equiv M - OH_2^+]} \tag{14-3}$$

$$K_{a2} = \frac{[\equiv M - O^-][H^+]}{[\equiv M - OH]} \tag{14-4}$$

These equilibrium constants differ from their solution counterparts in that they reflect both an intrinsic reactivity of the particular O-H bond (K_a^{int}) and an electrostatic free energy, $\Delta_{elect}G_i = z_i F \Psi_o$, derived from moving the charged ion, H^+, to/from a charged surface with electrical potential, Ψ_o (V), as compared to far from the surface:

$$K_{a1} = K_{a1}^{int} e^{zF\Psi_o/RT} \tag{14-5}$$

$$K_{a2} = K_{a2}^{int} e^{zF\Psi_o/RT} \tag{14-6}$$

where $z = +1$ for the exchanging ion, H^+, in this case; F is the Faraday constant (96,485 C mol^{-1}); Ψ_o is the surface potential relative to the bulk solution (V or J C^{-1}) (see Fig. 14.4); R is the gas constant (8.31 J mol^{-1}K^{-1}); and T is the absolute temperature (K).

At acidic pHs, $[\equiv M - OH_2^+] > [\equiv M - O^-]$, and so the surface has a net positive charge and Ψ_o is positive. In this case, the term $e^{zF\Psi_o/RT}$, mathematically reflects the extra energy associated with moving protons from the bulk solution to the particle surface. At higher and higher pH's, attached protons are lost from the surface and Ψ_o becomes less and less positive as Eq. 14-1 is pushed to the right; Ψ_o eventually becomes negative as Eq. 14-2 continues to the right. This shift in surface charge (from a net positive surface where $[\equiv M - OH_2^+] > [\equiv M - O^-]$ to a net negative one where $[\equiv M - O^-] > [\equiv M - OH_2^+]$) makes it electrostatically more difficult to move H^+ away from the charged oxide surface as solution pH is increased.

Depending on the environmental conditions, it is also possible for some inorganic species (e.g., Fe^{3+} or PO_4^{3-}) to bond to atoms on solid surfaces. In such a case, these inorganic ions, along with H^+ and OH^-, are responsible for establishing the extent of charging on the solid surface. The combination of ions that are responsible for this charge formation are called "potential (Ψ_o) determining" ions. For more information on the effect of such surface reactions on surface charge, the interested reader

Figure 14.4 Simple model of electrostatic potential (mV) as a function of distance from a surface in water. Ψ_o is the surface potential at the solid surface, and this electrostatic potential falls off through the layers of accumulated counter ions. The potential just outside the layer of ions immediately adjacent to the surface is the "Stern potential," and the so-called "zeta potential" is the value measured by observing particle movement in an electric field recognizing that all ions inside the "slipping plane" are moving with the particle. The measured zeta potential only gives an estimate of the true surface potential, Ψ_o.
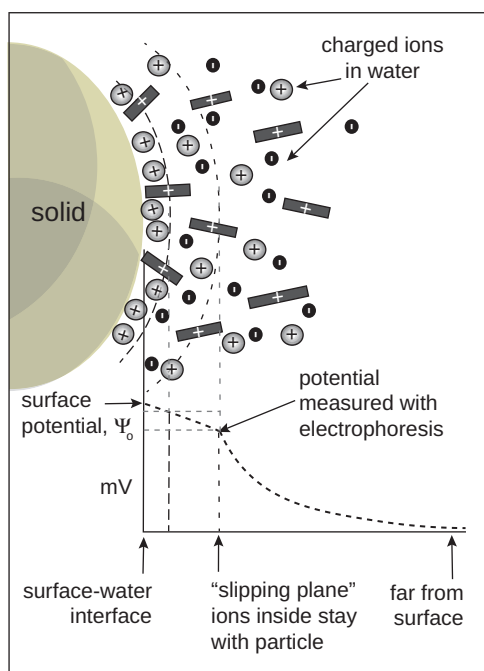
is referred to the literature (e.g., Dzombak and Morel, 1990, for effects of specific adsorption and its impact on surface charge for hydrous ferric oxide).

Focusing now on surface acid-base reactions, it is easy to see that the abundance of $[\equiv M - OH_2^+]$ and $[\equiv M - O^-]$ species on the oxide/oxyhydroxide's surface affects the surface charge. The surface area normalized concentration of this excess surface charge, $\sigma_{\text{surf ex}}$ (mol charges m^{-2}) is:

$$\sigma_{\text{surf ex}} = [\equiv M - OH_2^+] - [\equiv M - O^-] \qquad (14\text{-}7)$$

When these two surface species are present in equal concentrations, the surface exhibits zero net charge (or $\Psi_o = 0$). We call the solution pH that establishes this condition, the pH of zero point of charge or pH_{zpc}. This pH_{zpc} can be calculated if we know the intrinsic acidities of $\equiv M–OH_2^+$ and $\equiv MOH$ since:

$$[\equiv M - OH_2^+] = [\equiv M - O^-] \quad \text{at } pH_{\text{zpc}} \qquad (14\text{-}8)$$

Substituting from Eqs. 14-3 to 14-6 and recalling $\Psi_o = 0$ at pH_{zpc}, we have:

$$\frac{[\equiv M - OH][H^+]_{\text{zpc}}}{K_{a1}^{\text{int}}} = \frac{K_{a2}^{\text{int}}[\equiv M - OH]}{[H^+]_{\text{zpc}}} \qquad (14\text{-}9)$$

$$[H^+]_{\text{zpc}}^2 = K_{a1}^{\text{int}} K_{a2}^{\text{int}} \qquad (14\text{-}10)$$

$$pH_{\text{zpc}} = 0.5(pK_{a1}^{\text{int}} + pK_{a2}^{\text{int}}) \qquad (14\text{-}11)$$

Eq. 14-11 shows that an oxyhydroxide's pH_{zpc} is midway between the intrinsic pK_a's of its surface groups. Table 14.1 shows such intrinsic pK_a's and the corresponding pH_{zpc} values for oxyhydroxides that are common in the environment. At neutral pHs, we see that silicon oxyhydroxides are negatively charged, iron oxyhydroxides are positively charged, and the aluminum oxyhydroxide called gibbsite is nearly uncharged.

Now, when the aqueous solution pH is below the pH_{zpc}, we have the condition $[\equiv M - OH_2^+] > [\equiv M - O^-]$, and the solid exhibits a net positive surface charge and is electrostatically attractive to anions from solution. The concentration of such positive surface charges is called the solid's anion exchange capacity (or AEC). Conversely, when we are above the solid's pH_{zpc}, then $[\equiv M - O^-] > [\equiv M - OH_2^+]$, and the surface is negatively charged. It has a cation exchange capacity (or CEC), and this capacity grows at higher and higher pH. In light of their pH_{zpc} values, we can now understand why siliceous surfaces present in natural systems exhibit a net negative charge and therefore have a pH-dependent CEC, while Fe oxyhydroxides are positively charged and have a pH-dependent AEC (Table 14.1). Typically, surface charge densities in the range of 10^{-4} to 10^{-8} mol m^{-2} are seen for oxides at circumneutral pHs (Table 14.1). This implies that 10^{-4} to 10^{-8} moles of counter ions, including some charged organic molecules, must accumulate in a thin layer of water opposite each meter squared of surface due to electrostatic attractions.

While general values for CECs and AECs for oxyhydroxides are given in Table 14.1 for pH 7, one may need values that correspond to other conditions. To estimate the concentration of excess surface charge for solid oxides as a function of pH (and if necessary considering other solution constituents that chemically bond to oxyhydroxides like CO_3^{-2} or PO_4^{-3}), one can use two approaches. First, computer models (e.g., FITEQL; Westall, 1982) can be used to simultaneously solve for all the surface and solution species in a solution of interest using knowledge of the solid's acid–base site density (e.g., $[\equiv Fe - OH_2^+] + [\equiv Fe - OH] + [\equiv Fe - O^-] = 2 \times 10^{-6}$ mol m^{-2}; Dzombak and Morel, 1990), the solution pH and solid's intrinsic acidity coefficients, and the concentrations of any specifically adsorbing ions and their intrinsic complexation coefficients.

Alternatively, one can measure the total CEC or AEC for representative solid specimens at conditions of interest (e.g., pH). To do this, one saturates a solid with a measurable ion that is not a component of the solids (e.g., ammonium for cations or nitrate for anions), displaces this ion with acid or base, quantifies it, and then normalizes it by the mass or area of solids (e.g., Gillman and Sumpter, 1986; Hendershot and Duquette, 1986).

Solids with Other Surface Potential Determining Ions

Other solid phases like calcium carbonates are also common in nature. One widespread form, calcite ($CaCO_3$), exhibits surface charging due to either excess Ca^{2+} or CO_3^{2-} on the solid's surface. At circumneutral pHs, carbonate (CO_3^{2-}) is typically present at µM levels while calcium concentrations are usually in the millimolar range (see Chapter 5). Hence, such solids typically have calcium in excess on their surfaces

making them positively charged in natural waters. This implies such solids will act as anion exchangers (Table 14.1).

Aluminosilicate Clays
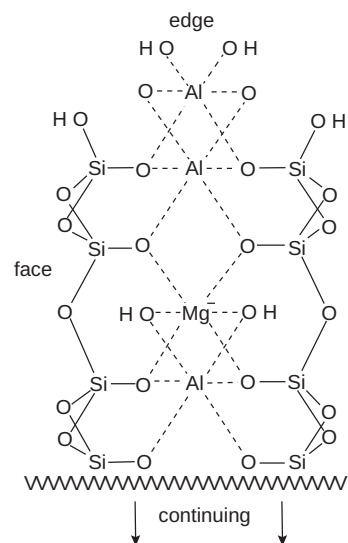
Example of a clay mineral.

Clay minerals present a different case with regard to assessing their surface charge. These mixed aluminum oxides and silicon oxides (thus aluminosilicates) expose two kinds of surface to the external media, and therefore the same particles may exhibit both a CEC and an AEC at the same time (Table 14.1). First, the edges of these flake-shaped minerals act like aluminum oxyhydroxides ($\equiv$Al–OH) and respond to pH changes in the solution much like pure aluminum oxyhydroxides (e.g., pH_{zpc} of kaolinite edge $\sim$7; Williams and Williams, 1978). The consequent anion exchange capacity observed empirically for clay minerals is up to 0.1 mol kg^{-1} for a wide variety of clays (Grim, 1968), but this value changes with solution pH and ionic strength. In contrast, the faces of these particles have a "siloxane" structure (–Si-O–Si–), which does not have free hydroxyl groups ($\equiv$Si–OH) to participate in proton exchange reactions with the bulk solution. Instead, the faces exhibit a charge due to cation substitutions of the aluminum or silicon atoms within the internal structure. These substitutions do not change the overall crystal structure, so they are called "isomorphic." They typically involve cations of lower total positive charge (e.g., Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+}). The result is a fixed permanent charge deficiency that looks like a negative surface charge to the surrounding solution.

As was the case for oxyhydroxides, the overall exchange capacity of aluminosilicate minerals is a function of solution properties like pH and ionic strength, but computational approaches can be employed to deduce how such environmental conditions affect ion exchange capacities (Kraepiel et al., 1998). Empirical measures of this negative surface charge or CEC are made by assessing the maximum concentrations of weakly bound cations such as ammonium, NH_4^+, which can be sorbed. Table 14.1 shows the results of such cation exchange capacity tests on three common clays, montmorillonite, illite, and kaolinite. Three-layer clays like montmorillonite exhibit the highest CEC's near 1 mol kg^{-1} or 1.4×10^{-6} moles of charged sites per meter squared (assuming a specific surface area of 700 m^2 g^{-1}; Grim, 1968). On the other extreme, two-layer kaolinite clays exhibit the lowest CEC's of about 0.1 mol kg^{-1} (Grim, 1968). This is chiefly due to their much smaller specific surface areas as compared to the three-layer clays, since per unit area kaolinites actually have greater charge density, $\sim 10^{-5}$ mol m^{-2}.

Natural Organic Matter

As we pointed out in Chapter 13 (Section 13.3), natural organic matter (DOM, POM, SOM) is also charged in water. This is mostly due to ionization reactions of carboxyl groups (–COOH; see Cabaniss, 1991; Leenheer et al., 1995; Richie and Perdue, 2003). Such acidic moieties occur at about l to 10 mmol per gram of natural organic matter. Carboxyl moieties exhibit pK_a's ranging from about 3 to 6 (Chapter 4, Section 4.3), and so the extent of charging is dependent on the solution pH. However, in general, particulate organic matter is anionic and acts as a cation exchanger. Realizing there will almost always be charges on inorganic and organic particle surfaces submerged

in water, we can now examine their impact with regard to sorbing ionized organic chemicals from solution.

14.3   Ion Exchange: Nonspecific Adsorption of Ionized Organic Chemicals from Aqueous Solutions to Charged Surfaces

Adsorption via Ion Exchange "Reactions"

Due to charging of particles in water, ions from solution must accumulate in the film of water adjacent to those surfaces to balance the excess charges (Fig. 14.2*a*). As solution conditions change, the composition of the ion mixture in the near-surface water also changes via ion exchange "reactions" (e.g., exchanging i^- for Cl^- in Fig. 14.3). Since this water layer remains tightly associated with the solid, any organic ions contained within the layer are "sorbed." This nonspecific surface association is sometimes termed "physisorption" as no bonding or complexation with atoms on the surface is involved.

As previously noted for protons moving between bulk aqueous solution and solid surfaces, ionized organic chemicals are electrostatically attracted (or repulsed) to (from) charged solid surfaces, in addition to any difference in van der Waals and electron donor/acceptor interactions with the surface compared to the bulk aqueous solution. Here, we call this electrostatic interaction energy $\Delta_{elect}G_i$, and it has the magnitude:

$$\Delta_{elect}G_i = z_i F \Psi_o \tag{14-12}$$

where z_i is the charge of the organic sorbate. Additionally, as we saw for nonionic organic compounds (Chapter 11, Section 11.3), the hydrophobic part of an organic sorbate's structure encourages its transfer from bulk aqueous solution into the near-surface water. We will term this free energy contribution $\Delta_{hydrophobic}G_i$. Together, these interactions promote an ion exchange "reaction" (Fig. 14.3):

$$i + \text{competing ion:surf} \rightleftharpoons i\text{:surf} + \text{competing ion} \tag{14-13}$$
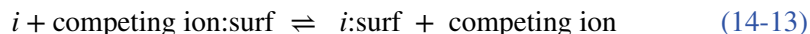
where i is the organic ion participating in the exchange, "surf" represents the charged surface of the solid in water, "competing ion" is the inorganic ion with the same type of charge (positive or negative) as i and thus also attracted to the charged surface. The colons indicate surface association without bonding or complexation.

At low concentrations, the accumulation of organic ions at the surface relative to their concentration in the bulk solution is due to a free energy increment:

$$\Delta_{surf\ water}G_i = z_i F \Psi_o + \Delta_{hydrophobic}G_i \tag{14-14}$$

$$= -RT \ln ([i\text{:surf}]/[i]) \tag{14-15}$$

$$= -RT \ln K_{i\,dex} \tag{14-16}$$

where $K_{i\text{dex}}$ (L kg^{-1}) is the *distribution ratio* of the ionic organic compound accumulated due to ion *ex*change, and we note that we have substituted chemical concentrations for chemical activities (i.e., assumed activity coefficients are 1). Since the displacement of the competing ion results in the "recovery" of its $\Delta_{\text{elect}}G_{\text{competing ion}}$, the overall ion exchange process (i.e., Eq. 14-13) involves an overall free energy change (indicated by subscript, ex):

$$\Delta_{\text{ex}}G_i = (z_i F\Psi_o + \Delta_{\text{hydrophobic}}G_i) - z_{\text{competing ion}}F\Psi_o \qquad (14\text{-}17)$$

Assuming the charged parts of the two competing ions approach the surface to the same extent (since Ψ varies with distance from the solid surface), then the two electrostatic energies are the same, and we have:

$$\Delta_{\text{ex}}G_i \cong \Delta_{\text{hydrophobic}}G_i \qquad (14\text{-}18)$$

$$= -RT\ln([i\text{:surf}][\text{competing ion}]/[i][\text{competing ion:surf}]) \qquad (14\text{-}19)$$

$$= -RT\ln K_{i\text{ex}} \qquad (14\text{-}20)$$

$K_{i\text{ex}}$ is dimensionless for two monovalent ions exchanging, but it does not equal the organic sorbate's sorption coefficient, K_{id} (L kg^{-1}). Rather, it is the ratio of the sorption coefficients of the organic ion and the competing ion:

$$K_{i\text{ex}} = K_{id}/K_{\text{competing ion d}} \qquad (14\text{-}21)$$

In Box 14.1, we derive an expression that relates the concentration of a sorbed organic cation in the near-surface water adjacent to a negatively charged particle's surface at "low" concentrations to its concentration in the bulk aqueous solution.

Box 14.1   Derivation of Ion Exchange Isotherms for a Cationic Organic Compound ($i = $ BH$^+$) Competing with Monovalent Inorganic Cations (e.g., Na$^+$)

1. "Ion exchange reaction" at low concentrations:

$$i^+ + \text{Na:surf} \;\rightleftharpoons\; \text{Na}^+ + i\text{:surf} \qquad (14\text{-}22)$$
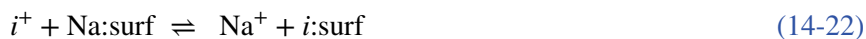
2. Corresponding equilibrium constant:

$$K_{i\text{ex}} = [i\text{:surf}][\text{Na}^+]/[i^+][\text{Na:surf}] \qquad (14\text{-}23)$$

3. Sum of cations must equal cation exchange capacity (CEC):

$$\text{CEC} = [i\text{:surf}] + [\text{Na:surf}] \qquad (14\text{-}24)$$

4. Substituting for [Na:surf] in Eq. 14-23:

$$K_{iex} = \frac{[i:surf][Na^+]}{[i^+](CEC - [i:surf])} \tag{14-25}$$

5. And rearranging one finds a hyperbolic or Langmuir isotherm:

$$[i:surf] = \frac{(CEC)K_{iex}}{[Na^+] + K_{iex}[i^+]}[i^+] \tag{14-26}$$

6. At low concentrations of $[i^+](\ll[Na^+]/K_{iex})$, this implies a linear isotherm behavior:

$$K_{id} = \frac{[i:surf]}{[i^+]} \cong \frac{(CEC)K_{iex}}{[Na^+]} \tag{14-27}$$

7. At high concentrations, that is where $K_{iex}[i^+]$ > [competing ion], continued sorption of $[i^+]$ may be encouraged by interactions between i^+ sorbates. Consequently, the Langmuir isotherm (Eq. 14-26) may no longer be followed.

Let us complete this theoretical treatment by considering some sorption observations for a small organic cation, ethyl ammonium (i = EA; $pK_{ia} \sim 10$), associating with a single charged solid surface, Na-saturated montmorillonite (Fig. 14.5). Before any EA is added to the montmorillonite suspension, the negative charges on the surface of the clay are balanced by sodium cations accumulated in the thin film of water surrounding the particles. When a small quantity of EA is added to the suspension, an ion exchange reaction occurs resulting in some of the EA^+ cations exchanging with Na^+ near the solid's surface. This ion exchange can be expressed:

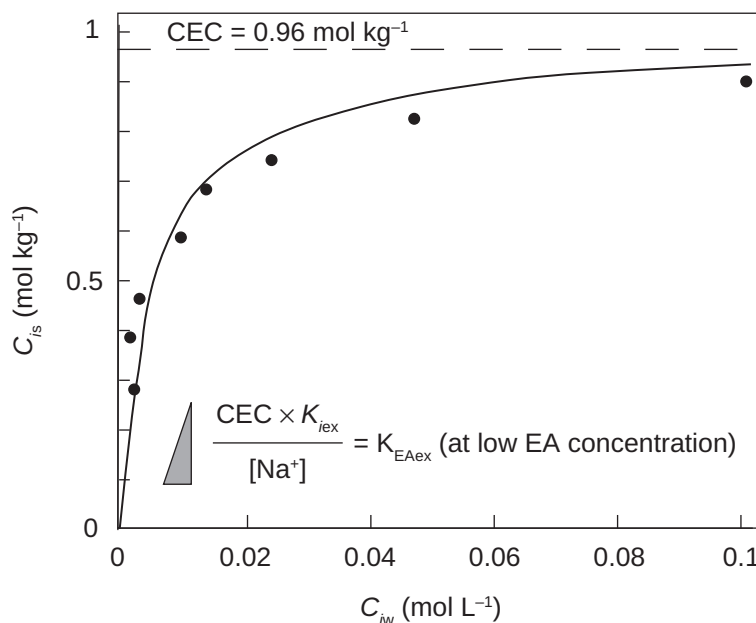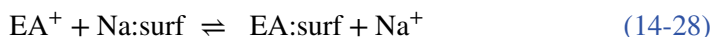$$EA^+ + Na:surf \rightleftharpoons EA:surf + Na^+ \tag{14-28}$$

Figure 14.5 Ion exchange of ethyl ammonium (EA) to montmorillonite (CEC measured to be 0.96 mol kg^{-1}) from a 10 mM aqueous NaCl solution; a Langmuir isotherm with best fit K_{EAex} = 2 matches the experimental data well (data from Cowan and White, 1958).

where again the colons in the bound reactant and product indicate association without specific bond formation. The sorbed concentration of the EA changes as a function of the dissolved EA^+ concentration, the concentration of the competing ion (Na^+), and the CEC of the solid. At low organic cation concentrations, that is where $K_{EAex}[EA^+] \ll [Na^+]$, typical in many environmental situations, the bound-to-dissolved ratio is constant (Fig. 14.4):

$$K_{id}(L\ kg^{-1}) = CEC \times K_{iex}/[Na^+] \qquad (14\text{-}29)$$

In this particular case (Cowan and White, 1958), the observed slope of the isotherm (i.e., K_{EAd}) at low $[EA^+]$ was about 200 L kg^{-1}. With the CEC = 0.96 mol kg^{-1} and $[Na^+]$ = 0.01 mol L^{-1}, one can deduce that K_{EAex} was about 2. This implies EA^+ enjoys a small $\Delta_{hydrophobic}G_{EA}$ (see Eqs. 14-18 to 14-20).

From this example, we can see the important factors dictating the extent of accumulation of organic ions near the charged particle surface. First, the greater the ion exchange capacity, the larger is the maximum extent of sorption. Further, K_{EAex} is near one for EA since its R– group (CH_3CH_2-) is not very hydrophobic (low $\Delta_{hydrophobic}G_{EA}$). At elevated EA^+ levels, the isotherm is hyperbolic and the bound-versus-dissolved distribution ratio (K_{EAd}) declines. We also deduce that for EA^+ concentrations less than about 10^{-2} M (i.e., less than the Na^+ concentration), we have a constant K_{EAd} of about 200 (mol kg^{-1})/(mol L^{-1}) for this montmorillonite in a 10 mM Na^+ solution.

Effects of the Ionic Organic Sorbate's Structure

The remaining problem involves the question of how the rest of the structure of a charged organic sorbate influences its sorption (i.e., the magnitude of K_{iex}). Presumably, the sorbate's chemical structure contributes to the $\Delta_{hydrophobic}G_i$, which dictates the preference of the ionic sorbate for the near-particle water region versus the bulk solution. Cowan and White (1958) also investigated the sorption of a series of alkyl ammonium ions to the same Na-montmorillonite (Fig. 14.6). A very clear pattern emerged: the longer the alkyl chain, the steeper was the initial isotherm slope. Exactly parallel results have been seen for sorption of other amphiphiles, such as negatively charged *n*-alkyl benzene sulfonates binding to positively charged alumina particles (Somasundaran et al., 1984), phenyl alkenoates sorbing to goethite (Evanko and Dzombak, 1999), and cationic surfactants associating with negatively charged silica (Atkin et al., 2003). Such effects are due to the increasing hydrophobicity of the "R–" groups involved (i.e., $\Delta_{hydrophobic}G_i$). By favoring chemical partitioning to the near surface from the bulk solution, hydrophobic effects augment the electrostatic forces and thereby enhance the tendency of the sorbates to collect near the particle surface (Somasundaran et al., 1984; Droge and Goss, 2013a).

This effect has been captured using a pp-LFER analysis of sorption data. Droge and Goss (2013a) measured the K_{id} (L kg^{-1}) values of a large set of organic ammonium cations sorbing to three clays: kaolinite, illite, and bentonite. For many of these sorbates, they found similar values of the ratio, K_{id}/CEC, for all three clays. These ratios
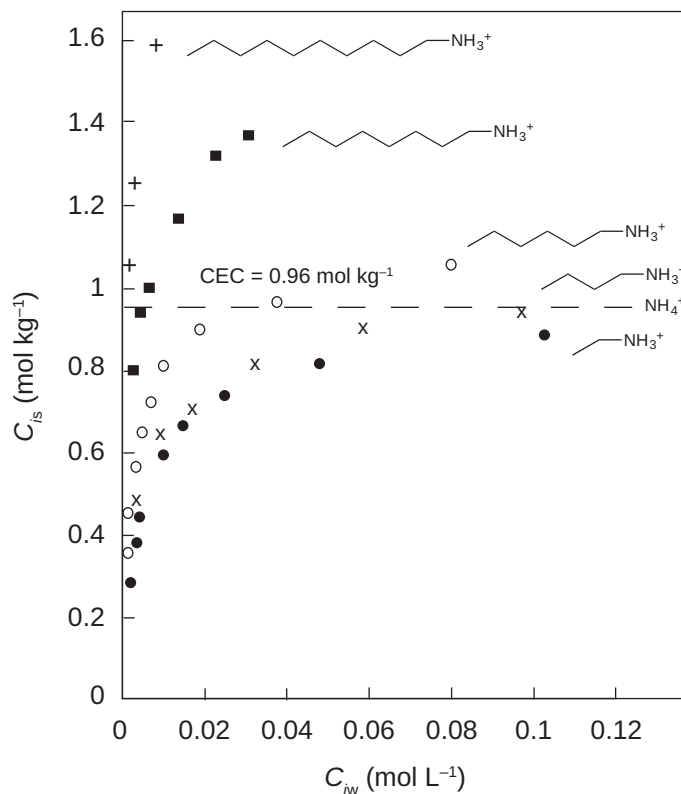
Figure 14.6 Adsorption isotherms for a series of alkyl ammonium compounds on sodium montmorillonite (adapted from Cowan and White, 1958). The horizontal line indicates the cation exchange capacity of the clay, which is exceeded for the longer chain alkyl ammonium compounds.

could be converted to $K_{i\text{ex}}$ values by multiplying by the corresponding competing ion concentrations (see Eq. 14-27 in Box 14.1).

Finally, one can use Abraham solute parameters (Abraham and Acree, 2010) for organic ions given in Appendix Table C.2 to elucidate which chemical interactions are controlling this partitioning of the organic ions (see Section 7.3 for more information about individual solute parameters). The V_i values of the ionized organic compounds are assumed to be nearly the same as their nonionic counterparts since protonation/deprotonation does not change molecular size much. Not surprisingly, when one protonates an amine, the B_i value decreases. It is also worth noting that the ionic organic species now include a new term reflecting their charging (i.e., J^+ for organic cations and J^- for organic anions).

Since an ion exchange reaction involves adsorbing the organic cation and desorbing the competing ion (e.g., Na^+), one may write:

$$\log K_{i\text{ex}} = \log([i{:}\text{surf}][Na^+]/[i^+][Na{:}\text{surf}]) = \log K_{i\text{d}} - \log K_{Na\text{d}} \qquad (14\text{-}30)$$

and then use the corresponding Abraham parameters for each $K_{i\text{d}}$ term:

$$\log K_{i\text{ex}} = v(V_i - V_{Na^+}) + e(E_i - E_{Na^+}) + s(S_i - S_{Na^+}) + a(A_i - A_{Na^+})$$
$$+b(B_i - B_{Na^+}) + j(J_i^+ - J_{Na^+}^+) + (\text{constant}_i - \text{constant}_{Na^+}) \qquad (14\text{-}31)$$

Figure 14.7 Comparison of the average log $K_{iex,clays}$ values found for organic ammonium compounds sorbing to kaolinite, illite, and bentonite from 15 mM NaCl solutions (data from Droge and Goss, 2013b) with estimates of these values made using Eq. 14-33.

or:
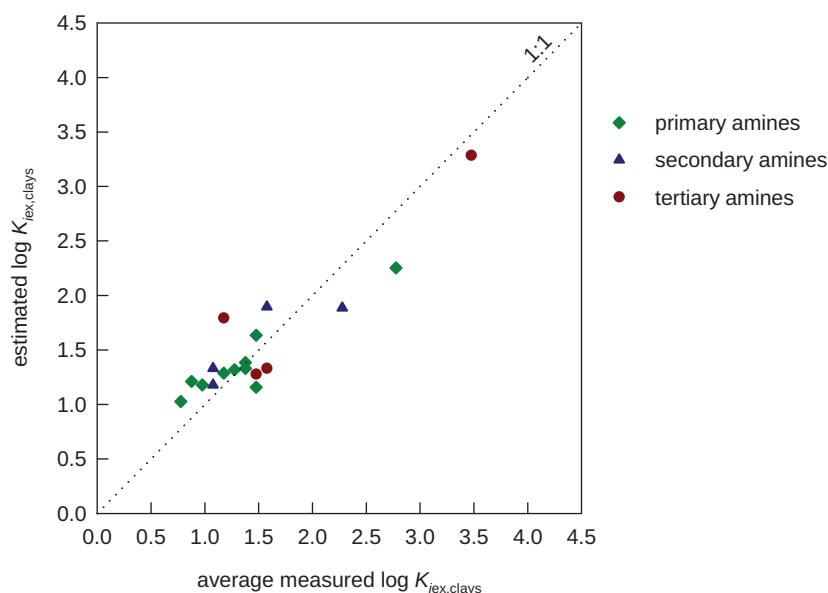
$$\log K_{iex} = v(\Delta V) + e(\Delta E) + s(\Delta S) + a(\Delta A) + b(\Delta B) + j(\Delta J^+) + (\Delta \text{constant})$$

(14-32)

Using the subset of data from Droge and Goss (2013a) for which ion exchange of organic ammonium compounds to all three clays was consistent on a CEC-normalized basis, and the Abraham parameters for the corresponding organic ions and sodium ion (Appendix Table C.2), one finds a best-fit pp-LFER (Fig. 14.7), which is:

$$\log K_{iex,clays} = 1.08(\pm 0.07)\Delta V - 0.56(\pm 0.23)\Delta B$$
$$(\text{number of chemicals} = 18; r^2 = 0.97; \text{S.D.} = 0.30)$$

(14-33)

This means that the ΔJ^+ term is not important, implying that the $\Delta_{elect}G_i - \Delta_{elect}G_{Na^+}$ is not very far from zero, as previously assumed. As was noted by Droge and Goss (2013a), the greater the organic ion's V_i term, the stronger the organic ammonium compounds affinity for the near surface environment over the bulk aqueous solution. Conversely, a larger B_i term discourages surface association. Presumably, this implies breaking hydrogen bonds with water is not fully replaced by making new bonds with electron acceptors in the environment near a charged particle's surface. An illustrating application of this approach is given in Box 14.2.

Natural Organic Matter and Ion Exchange

Natural organic matter is also commonly negatively charged at circumneutral pHs due to the ionization of carboxyl groups. As a result, this material is attractive to cations, while also absorbing the nonionic amine. Droge and Goss (2012; 2013b) reported K_{id} values for organic ammonium compounds for the well-characterized Pahokee peat (see Section 13.2). For primary ammonium sorbates, the K_{iex} values (= K_{id} [competing ion]/CEC) were similar to average values found for clays (Fig. 14.8). However,

---

Box 14.2   Estimation of $K_{i\mathrm{d}}$ for an Organic Amine Adsorbing to Kaolinite

We consider the sorption of naphthyl-methyl-amine (NMA) from water at pH 6 and having an ionic composition of 15 mM NaCl to kaolinite (CEC = 40 mmol kg^{-1}). The following data can be found for this compound: $pK_{\mathrm{NMAH^+a}}$ = 9.05; V_i = 1.35 and B_i = 0.08.

naphthyl-methyl-amine
(NMA)
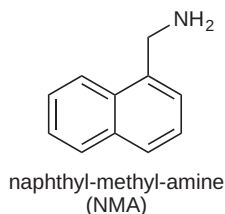
To estimate the sorption coefficient, you assume the cation near the charged kaolinite surface is the only sorbed species, while both protonated NMA and its conjugate base are in the aqueous solution. This leads to a sorption coefficient expression:

$$K_{\mathrm{NMA\,d}} = \frac{[\mathrm{NMAH^+{:}surf}]}{[\mathrm{NMAH^+}] + [\mathrm{NMA}]}$$

where [NMAH:surf] is the sorbed concentration (mol kg^{-1} kaolinite), [NMAH$^+$] is the dissolved concentration of the protonated amine (mol L^{-1} water), and [NMA] is the dissolved concentration of the nonionic amine (mol L^{-1} water). Dividing both the numerator and denominator by [NMAH$^+$], one finds:

$$K_{\mathrm{NMA\,d}} = \frac{[\mathrm{NMAH^+{:}surf}]}{[\mathrm{NMAH^+}]} \frac{1}{1 + [\mathrm{NMA}]/[\mathrm{NMAH^+}]}$$

The first term reflects the ion exchange process and can be estimated using Eq. 14-27. The second term reflects the dissolved phase acid-base equilibrium of the NMA and its conjugate acid, NMAH$^+$, and thus can be found from the solution pH and this acid's $pK_{\mathrm{NMAH^+a}}$:

$$K_{\mathrm{NMAd}} = \frac{(\mathrm{CEC})(K_{\mathrm{NMAH^+ex}})}{[\mathrm{Na^+}]} \frac{1}{1 + 10^{-pK_{\mathrm{NMAH+a}}}/10^{-\mathrm{pH}}}$$

1. First, you find the ratio of [NMA]/[NMAH$^+$] = $10^{(\mathrm{pH}-pK_{\mathrm{NMAH+a}})}$ = 0.0089, so the right-hand term is equal to 0.999. This, of course, tells you that at pH 6, the nonionic [NMA] $\ll$ [NMAH$^+$] and can be neglected here.

2. Next, you use Eq. 14-33 to estimate $K_{i\mathrm{ex}}$ fro NMAH$^+$ using the competing ion's values of V_{Na} = 0.033 and B_{Na} = 0.00:
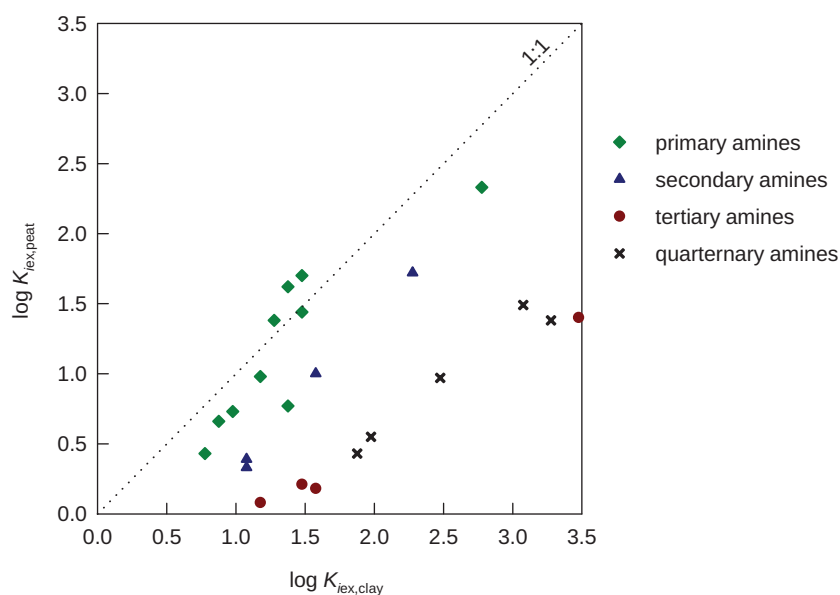
$$\log K_{i\mathrm{ex}} = 1.08(1.35 - 0.033) - 0.56(0.08 - 0.00) = 1.38; K_{i\mathrm{ex}} = 24$$

3. Finally, combining everything:

$$K_{\mathrm{NMAd}} \approx (40 \text{ mmol kg}^{-1})(24)(0.999)/(15 \text{ mmol L}^{-1}) = 64 \text{ L kg}^{-1}$$

We note that testing by Droge and Goss (2013a) found K_{NMAd} = 40 L kg^{-1}.

Figure 14.8 Comparison of ion exchange coefficients for aluminosilicate clays with those for Pahokee peat; data from Droge and Goss (2012; 2013a).

secondary amines had about a factor of 3 lower $K_{i\text{ex,clays}}$ than $K_{i\text{ex,OM}}$, and tertiary and quaternary amines were still lower by an order of magnitude or greater. This may mean that the more heavily substituted organic cations cannot get as near to the charged sites in organic matter as they can for aluminosilicates (i.e., thereby invalidating the assumption that counterions like Na^+ and organic ions experience the same surface potential Ψ value).

Nonetheless, the data suggest that natural organic matter should be seen as both an absorbent ("f_{oc} model") and as an ion exchanger ("CEC model"). This expanded role implies that K_{id} estimates for ionizable organic compounds should consider (1) acid-base equilibria, (2) nonionic species uptake into the organic matter, plus (3) ion exchange of cationic species:

$$K_{id}(\text{L kg}^{-1}) = [(\text{B in OM}) + (\text{BH}^+ \text{ near charged OM} + \text{BH}^+ \text{ near charged clay})]/$$
$$([\text{B}]_w + [\text{BH}^+]_w)$$

or:

$$\frac{f_{oc}K_{ioc}[\text{B}]_w + \{(\text{CEC}_{oc} + \text{CEC}_{clay})K_{iex}[\text{BH}^+]_w/[\text{Na}^+]\}}{[\text{B}]_w + [\text{BH}^+]_w} \tag{14-34}$$

Therefore, the result depends on sorbate properties (K_{ioc}, pK_{ia}, K_{iex}), solution properties (pH, competing ions), and sorbent properties (f_{oc}, CEC).

Adsorption of Organic Ions at High Sorbate Concentrations

One does not usually have especially high concentrations of organic ions in the environment, but sometimes these conditions occur, for example, at spills. Also, high concentrations are found in some engineered situations. For example, such conditions may apply in applications like surfactant-mediated particle floatation (Zhang and Somasundaran, 2006) or subsurface remediation (Paria, 2008). Under these conditions, the sorption process for charged organic sorbates can change dramatically as

a result of the organic sorbates interacting with one another on the sorbent surface. For example, at about eight methylenes ($-CH_2-$) in a hydrophobic chain, the extent of sorption for alkyl amines can far exceed a clay's cation exchange capacity (Cowan and White, 1958, Fig. 14.6). Likewise, Vasudevan et al., (2013) found that aromatic amines can adsorb beyond a clay's CEC. Moreover, one finds that the isotherms no longer conform to the Langmuir model (recall Box 14.1). These observations imply the sorption mechanism must be changing as the hydrophobic portions of the sorbates get larger. This "extra" transfer to the solid surface occurs because the hydrophobic portion of the organic ion strongly prefers to escape the bulk water and move into the near surface water, particularly when like hydrophobic molecules are already abundant there. Such partitioning causes "co-ions" (i.e., oppositely charged inorganic ions like Cl^-) to also move from aqueous solution, and this has also been seen for partitioning of very hydrophobic organic ions into organic solvents (Jafvert et al., 1990).

Thus, we may anticipate little difference in sorption for ionic organic chemicals due to moieties of like charge (e.g., $-COO^-$ versus $-SO_3^-$), so long as these charged functional groups do not react with the surface, since the electrostatic attraction to a surface is fairly nonselective. However, we do expect substantial variations between sorbates if they differ in the hydrophobicity of their nonpolar parts. This sorption behavior is not surprising if one considers the large enrichment of ions near a charged surface due to the $\Delta_{elect}G_i$. In addition, the hydrophobic free energy advantage of the organic sorbate ($\Delta_{hydrophobic}G_i$) causes the local concentration of the organic sorbate i in the solution adjacent to the particle surface to be very high. At high concentrations near the surface, two phenomena influence the organic sorbate's continued partitioning to the surface. First, there is a negative feedback associated with the limited number of ion exchange sites attracting counterions. This tends to cause the isotherm to level out at the CEC for cations or AEC for anions. Secondly, for organic ions with substantial hydrophobic parts in their structures (i.e., large $\Delta_{hydrophobic}G_i$), the association with the particle surface can exceed the particle's ion exchange capacity (Fig. 14.9). In fact, so much i can accumulate at the surface that the macroscopic properties of the surface change. A classic observation is that so much organic ion accumulation occurs at the surface that one sees the surface charge of the particle "reverse" (Fig. 14.9, Fuerstenau, 1971).

It should be noted that electroneutrality requires no net charge build up in the near-surface area. Thus additional organic ion sorption requires the co-transfer of a "co-ion" of opposite charge to i (e.g., Na^+ combined with i^- in Fig. 14.9). Since the transfer of these oppositely charged co-ions against the electrostatic potential requires $-z_iF\Psi_o$ (note that $z_{co\text{-}ion} = -z_i$), their accumulation in the near-surface water is given by (focusing on the monovalent case here):

$$[\text{co-ion:surf}] = [\text{co-ion}] \exp(-z_iF\Psi o/RT) = [\text{co-ion}]\exp(\Delta_{hydrophobic}G_i/RT)$$

$$\text{(14-35)}$$

This means, in the case of the sorption of the alkyl ammonium ions to Na-montmorillonite (Fig. 14.6), the charge balance equation in the near surface region must be:

$$RNH_3\text{:surf} + Na\text{:surf} = CEC + Cl\text{:surf} \qquad \text{(14-36)}$$

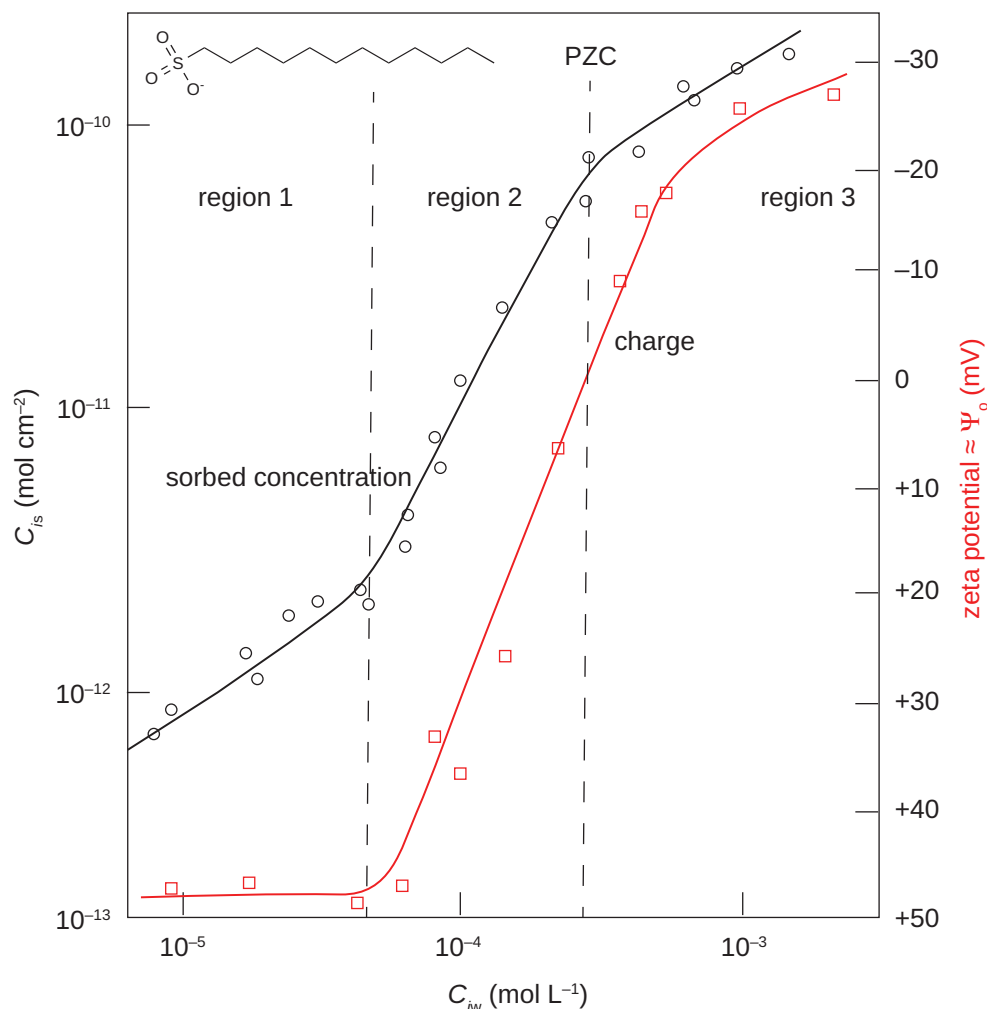**Figure 14.9** The sorption isotherm of dodecyl sulfonate (circles) on α-alumina (15 m² g⁻¹) suspended in water at pH 7.2 and 2 mM NaCl. Electrophoretic mobilities (squares), a measure reflecting Ψ, show the corresponding changes in the particles' zeta potential from positive 50 mV with only Na⁺ sorbed to –30 mV when the sorbed ions are predominantly dodecyl sulfonate. Adapted from Wakamatsu and Fuerstenau (1968) and Fuerstenau (1971).

This model explains why the total sorbed concentrations of organic ions can exceed the solid's CEC (Fig. 14.6) and why the isotherms of all the alkyl amines are not well fit with a series of simple Langmuir isotherms.

To provide an estimate of $K_{i\text{ex}}$ for use in these cases, let us try to isolate the contribution of the sorbate's hydrophobicity using some available data. For the alkyl ammonium ions exchanging with sodium cations in the data of Cowan and White (1958), one has:

$$-RT \ln K_{id} = +z_i F \Psi_\text{o} + \Delta_{\text{hydrophobic}} G_i \qquad (14\text{-}37)$$

implying:

$$-RT \ln K_{id} = +z_i F \Psi_\text{o} - RT \ln K_{i\text{ex}} \qquad (14\text{-}38)$$

Thus, if we examine the variation in $-RT \ln K_{id}$ for a series of alkyl amines participating in ion exchange, we should see how R– groups affect the value of $-RT \ln K_{i\text{ex}}$ while the product, $z_i F \Psi_\text{o}$, remains constant. Since this hydrophobic effect appears to regularly increase with the size of the nonpolar part of the chemical structure (Cowan and White, 1958; Somasundaran et al., 1984, Teppen and Aggarwal, 2007; Samaraweera

et al., 2014), we may reasonably propose this energy term is composed of "excess free energy of solution in water" contributions from each of the nonpolar parts of the structure. Consequently, we expect for the alkyl ammonium ions:

$$- RT \ln K_{i\text{ex}} = \Delta_{\text{hydrophobic}} G_i \approx m\Delta_{\text{hydrophobic}} G_{\text{CH}_2} \qquad (14\text{-}39)$$

and together with the electrostatic term, we have:

$$- RT \ln K_{id} = +z_i F\Psi_o + (m\Delta_{hydrophobic} G_{\text{CH}_2}) \qquad (14\text{-}40)$$

where m is the number of methylene ($-CH_2-$) groups in each sorbate's alkyl chain, and $\Delta_{\text{hydrophobic}} G_{\text{CH2}}$ is the hydrophobic contribution made by each methylene driving these sorbates into the near surface water layer. Using Cowan and White's (1958) observed variation of $-RT \ln K_{id}$ for the alkyl ammonium ions, when these organic sorbates are present at levels much less than Na^+, as a function of the number of methylenes in the alkyl chains, one can examine the hydrophobic and electrostatic energy effects. A least-squares correlation line through the K_{id} data yields:

$$- RT\ ln\ K_{id} = -10.9 - m(0.75 \text{ kJ mol}^{-1}) \qquad (14\text{-}41)$$

The intercept in this fitted result implies that the alkyl ammonium ions experienced an electrostatic attraction to the clay surface corresponding to:

$$z_i F\Psi_o \approx -11 \text{ kJ mol}^{-1} \qquad (14\text{-}42)$$

which corresponds to $\Psi_o \approx -0.11$ V, a typical surface potential. Also, we see $\Delta_{\text{hydrophobic}} G_{\text{CH2}} = -0.75$ kJ mol^{-1}. Somasundaran et al. (1984) noted that inclusion of the phenyl group in alkyl aryl sulfonates increases the ion exchange sorption tendency of these amphiphiles to a degree corresponding to lengthening the alkyl chain by 3-4 methylene groups. This is consistent with increasing the nonpolar structure's hydrophobicity to the same extent [i.e., $\Delta\log K_{\text{ow}}$(phenyl) ~ 1.68 and $\Delta\log K_{\text{ow}}$(3-4 methylenes] ~ 1.59 to 2.12). Thus, there is little doubt that hydrophobic phenomena are playing an important role in determining the extent of amphiphilic sorption.

Notably, the phenomena described occurs in cases involving ionic organic compounds that form micelles/hemimicelles (Fuerstenau, 1956; Somasundaran et al., 1964; Chandar et al., 1983, 1987; Atkin et al., 2003) and inorganic salt precipitates (Jafvert and Heath, 1991). Micelle/hemimicelle formation plays a critical role in amphiphile "sorption" to minerals when the organic ions are present at relatively high dissolved concentrations, about 0.001-0.01 of their critical micelle concentrations (CMC, i.e., the level at which they self-associate in the bulk solution). When the organic sorbate levels are low, the sorption mechanism is like the discussed ion exchange mechanism (Fig. 14.10). However, at some point in the isotherm, micelles form in the near surface, presumably due to both electrostatic and hydrophobic effects enhancing the near-surface concentrations. This in turn allows rapid coagulation of the resultant micelle with the oppositely charged particle surface. Such aggregation smothers that subarea of the particle's surface charge with what have been called hemimicelles. Electrophoretic mobility measurements clearly demonstrate the neutralization of the particle's charges in this steep portion of the isotherm, even going so far as
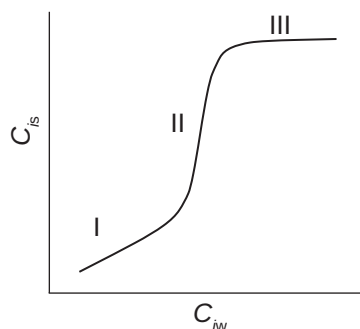
Figure 14.10 Relationship between sorbed and dissolved amphiphile concentrations (upper isotherm plot). These different parts of the isotherm reflect changes in the solid surface as sorption proceeds, possibly explainable by the following: in portion (I) with low dissolved concentrations, sorption occurs via ion exchange and related mechanisms. At some point, sufficient near-surface concentration enhancement occurs that micelles form (IIa) and rapid coagulation between oppositely charged micelles and the surface follows (IIb). When the surface becomes fully coated with such micelles, additional sorption is stopped (III). In portion III, the solid surface charge is converted from one sign to the other, implying sorbates must become physically associated with the particle surface, as opposed to simply being present in the diffuse double layer or the vicinal water layer.
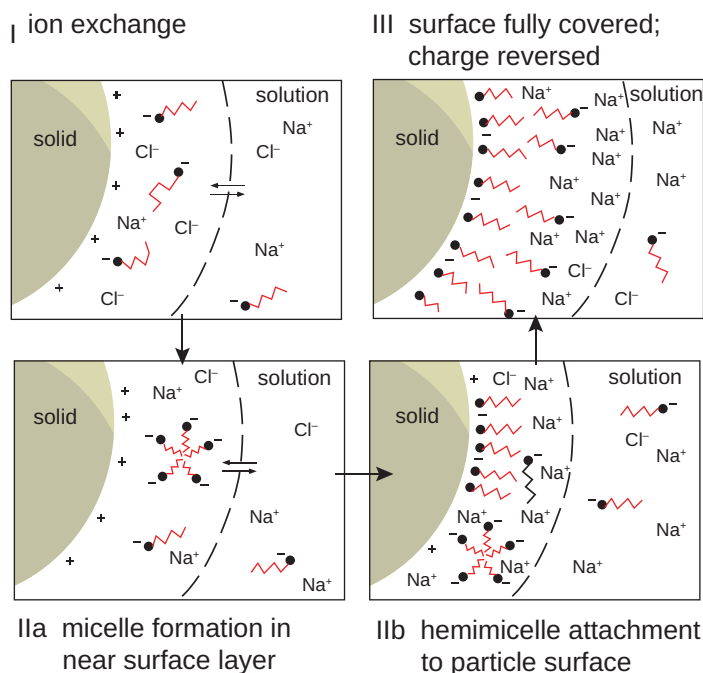
to reverse the surface charge (e.g., Chander et al., 1987; Atkin et al., 2003). The onset of this particle coating by hemimicelles occurs at different dissolved concentrations for various amphiphiles, but is near millimolar levels ($\sim$100 mg L^{-1}) for decyl-substituted amphiphiles and is near micromolar levels ($\sim$100 µg L^{-1}) for octadecyl derivatives. Elevated near-surface concentrations, derived from accumulation of these amphiphiles in the thin film of water near the particle surface by factors of 100 or more, are compensating just enough to achieve critical micelle concentrations in this near-surface water layer. Finally, the entire particle surface is covered with a bilayer of amphiphile molecules; the particle's surface charge is now that of the surfactant, and the addition of still more amphiphile to the solution does not yield any higher sorbed loads. This especially extensive degree of sorption may cause macroscopic phenomena such as dispersion of coagulated colloids and particle flotation.

Impacts of Multiple Sorption Mechanisms on Isotherms of Ionic Organic Sorbates

Finally, we note that work performed using the mix of solids that occur in "real world" soils and sediments suggests the heterogeneity of the natural sorbents is very

Figure 14.11 Observed sorption of dodecylpyridinium on a soil exhibiting an overall cation exchange capacity of 0.135 mol kg^{-1}. Two Langmuir isotherms are placed on the data to illustrate how different portions of the observed isotherm may reflect the influence of different materials in the complex soil sorbent or possibly different mechanisms (data from Brownawell et al. 1990).
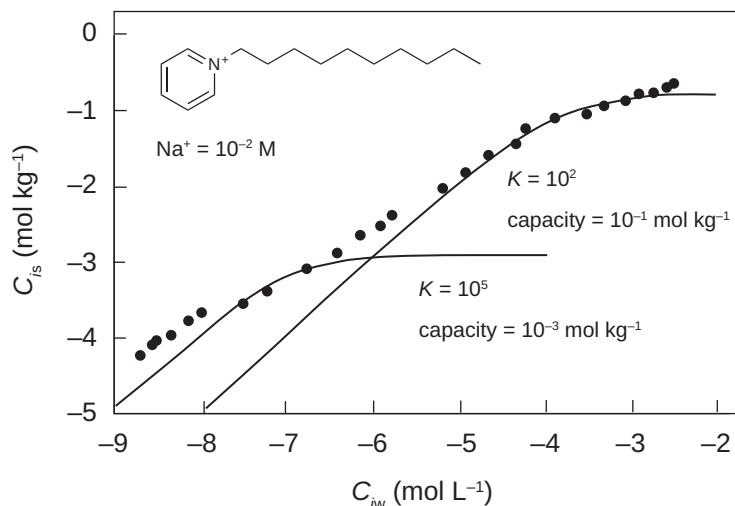
important to charged organic species (Brownawell et al., 1990; Droge and Goss, 2013c). It appears that one sees the influence of more than one solid surface type at the same time. Thus, fitting sorption isotherms for real world solids may require using combinations of isotherms. For example, two Langmuir isotherms may be superimposed to fit the experimental data (Fig. 14.11). Presumably, each isotherm reflects the association of the organic sorbate with different solid materials that make up the complex medium we simply call a soil, subsoil, or sediment.

14.4   Surface Complexation: Specific Bonding of Organic Compounds with Solid Phases in Water

In contrast to nonspecific ion exchange, ions sometimes bond to specific atoms on a solid surface, displacing other ligands. This "chemisorption" or "surface complexation" forms a sorbed species, which is distinct from organic ions simply dissolved in the near-surface water (i.e., $M–i$ is not the same as $M–OH_2^+$ with i^- nearby in the diffuse double layer, Fig. 14.3, path 1). One or both of these sorbed species may co-exist in significant proportions (Stone et al., 1993; Whitehead et al., 2015). Some organic substances form covalent bonds with the NOM in a sediment or soil; other organic sorbates serve as ligands for metals on the surfaces of inorganic solids.
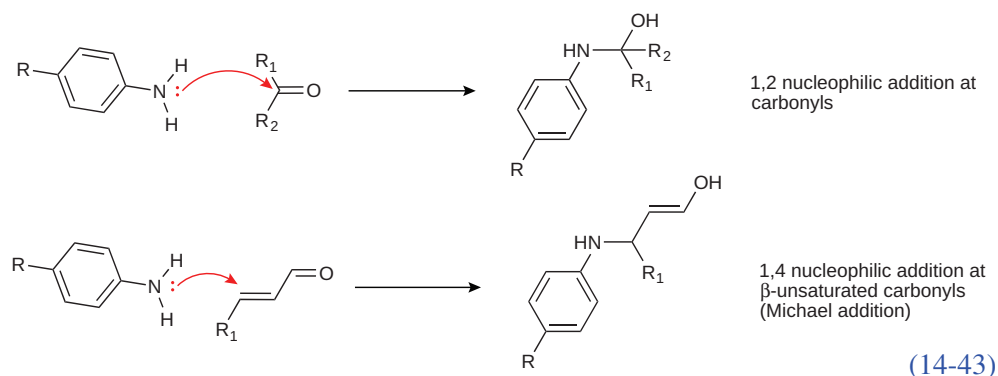
Organic Sorbate-Natural Organic Matter Reactions

First, some organic sorbates can react with organic moieties contained within the natural organic matter of a particulate phase. Especially prominent in this regard are organic bases like substituted anilines (Hsu and Bartha, 1974, 1976; Fabrega-Duque et al., 2000; Li et al., 2000; Weber et al., 2001; Chen and Nyman 2007; Gulkowska et al., 2012). When compounds like 3,3′-dichlorobenzidine are mixed with sediment, they become irretrievable using organic solvents that are capable of recovering them from absorbed positions within natural organic matter or using salt solutions that should displace them from ion exchange sites (Appleton et al., 1980; Weber et al.,

2001, Chen and Nyman 2009). Conditions that promote hydrolysis (see Chapter 22) do release much of the sorbed amines. Thus, it appears that reactions between the basic amine and carbonyl functionalities in the natural organic matter explain the strong sorption seen (Stevenson, 1976; Chen and Nyman, 2009).
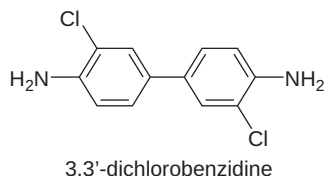
Due to their low pK_{ia} values (~ 5), the aromatic amines can be largely deprotonated at natural water pH's. Thus, the nitrogen's nonbonded electrons can nucleophilically attack carbonyl moieties or carbon double bonds in β-unsaturated carbonyls such as present in quinone moieties:

3,3'-dichlorobenzidine

1,2 nucleophilic addition at carbonyls

1,4 nucleophilic addition at β-unsaturated carbonyls (Michael addition)

$$(14\text{-}43)$$

Observations indicate that the importance of such reactions increases with pH, and modeling suggests such reactive carbonyls occur at tens of millimoles per kg of organic carbon (Chen and Nyman, 2009). These reactions often proceed slowly over hours, days, and even years, so the extent of this chemisorption is difficult to predict as it may be kinetically controlled. Furthermore, such bond-forming sorption is sometimes irreversible on the timescales of interest, and we might not wish to include these effects in a K_{id} expression reflecting sorption equilibrium. Nevertheless, this condensation-type sorption is very important to reducing the mobility and bioavailability of such compounds (Li et al., 2000; Weber et al., 2001).

### Organic Sorbate-Inorganic Solid Surface Reactions

A second type of surface reaction involves bonding of organic sorbates with metals exposed on the surface of the solid. This process is often referred to as formation of "inner sphere complexes," in contract to cases in which the organic ion is separated from the metals by other ligands or water (see Fig. 14.12). In these cases, the organic sorbate bonds to one or two metals (i.e., mononuclear or binuclear) using either one or two functional groups (i.e., monodentate or bidentate).

In these sorption reactions, we may consider that a ligand such as a hydroxyl bound to a metal on the solid is displaced by the organic sorbate:

$$\equiv M - OH + i^- \rightleftharpoons \ \equiv M - i + OH^- \qquad (14\text{-}44)$$
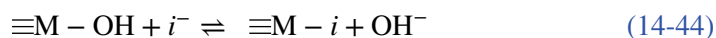
Based on spectral evidence, such surface bonding (or inner sphere complexation) reactions occur on oxyhydoxides of metals like Fe, Al, and Ti (Boily et al., 2000;

Figure 14.12 Illustration of possible adsorption mechanisms of organic acids to mineral surfaces illustrated by phthalate. Adapted from Hwang and Lennart (2009).
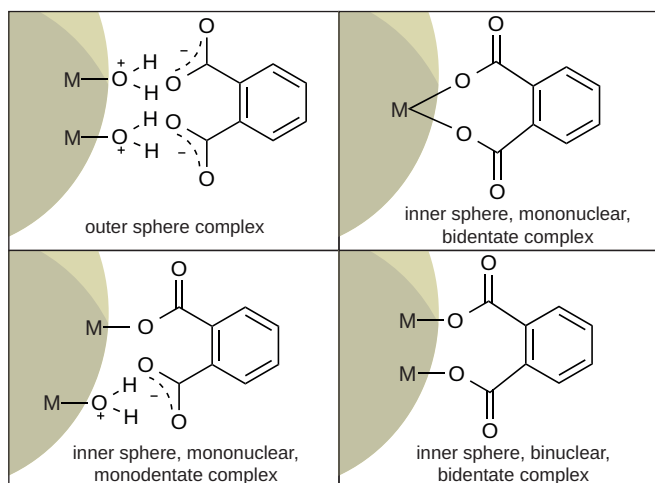
Roddick-Lanzilotta and McQuillan, 2000; Sverjensky et al., 2008; Hwang and Lenhart, 2009; Lindegren et al., 2009; Hanna et al., 2014). Carboxylic acids and phenols are common reactive moieties of such sorbates.

Often, the resultant bound species is not known with certainty, but is only assumed as part of a modeling fit. Surface complexation modeling is used to interpret sorption as a function of solution properties like pH and ionic strength, and these efforts suggest unique surface-associated species. However, at the present time, it is difficult to clearly distinguish the continuum from inner sphere bound sorbates to outer sphere hydrogen-bonded sorbates to outer sphere diffuse double layer counter ions.

Given such additional sorption mechanisms, multiple sorption equilibria may need to be modeled (Stone et al., 1993; Evanko and Dzomback, 1999; Whitehead et al., 2015). The sorption coefficient may include ionic species held near the solid surface by outer sphere interactions and also by inner sphere bonding:

$$K_{id,\text{ion exchange and surface reaction}} = \frac{\begin{bmatrix} \text{organic counterion} \\ \text{near the surface} \end{bmatrix} + \begin{bmatrix} \text{organic ion bound} \\ \text{to the surface} \end{bmatrix}}{\begin{bmatrix} \text{neutral organic H}i \\ \text{in solution} \end{bmatrix} + \begin{bmatrix} \text{organic ion } i^- \\ \text{in solution} \end{bmatrix}} \quad (14\text{-}45)$$

The denominator in this expression can be simplified by using an acid-base relation relating Hi in solution to its conjugate base, i^-, to give (Hi + i^-) = ($10^{-\text{pH}}/10^{-\text{pK}_{ia}}$ + 1)(i^-), so that Eq. 14-45 becomes:

$$K_{id,\text{ion exchange and surface reaction}} = \left(\frac{\begin{bmatrix} \text{organic} \\ \text{counterion} \end{bmatrix}}{[i^- \text{ in solution}]} + \frac{\begin{bmatrix} \text{organic ion bound} \\ \text{to surface} \end{bmatrix}}{[i^- \text{ in solution}]} \right) (10^{-\text{pH}}/10^{-\text{pK}_{ia}} + 1)^{-1}$$

$$(14\text{-}46)$$

For low sorbate levels, we can use Eq. 14-26 to estimate the first term on the right hand side of Eq. 14-46. Now our task is to develop an expression to predict the last term. To do this, we begin by writing the reaction involved:

$$i\text{:surface} + \text{L} - \text{M}\!\equiv\; \rightleftharpoons\; i\!-\!\text{M}\!\equiv\; + \text{L:surface} \tag{14-47}$$
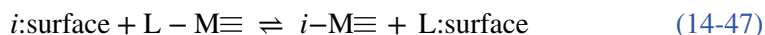
where $i\!-\!\text{M}\!\equiv$ and $\text{L} - \text{M}\!\equiv$ represent species in which an organic compound and an inorganic ligand are directly bonded to at least one metal atom on the surface of the solid. One should note that such inner sphere bonding could involve monodentate or bidentate bonding, as well as association with one or two metals (see Fig. 14.12). Such surface complexation reflects a free energy change that we refer to as $\Delta_{\text{rxn}}G_i$ and a corresponding equilibrium expression:

$$K_{i\text{rxn}} = \frac{[i\!-\!\text{M}\!\equiv][\text{L:surface}]}{[i\text{:surface}][\text{L} - \text{M}\!\equiv]} \tag{14-48}$$

The species L:surface and i:surface represent near-surface ions already accumulated in the water near the solid surface.

Recalling Eq. 12-11, we can assume that there are a finite number of key reactive sites on the solid, $\sigma_{\text{surf rxn}}$ (mol m^{-2}), so we have:

$$\sigma_{\text{surf rxn}}A_{\text{surf}} = [i\!-\!\text{M}\!\equiv] + [\text{L} - \text{M}\!\equiv] \tag{14-49}$$

with A_{surf} equal to the specific particle surface area (m^2 kg^{-1}). Therefore, we can rewrite Eq. 14-48:

$$K_{i\text{rxn}} = \frac{[i\!-\!\text{M}\!\equiv][\text{L:surface}]}{[i\text{:surface}](\sigma_{\text{surf rxn}}A_{\text{surf}} - [i\!-\!\text{M}\!\equiv])} \tag{14-50}$$

As discussed in Section 14.3, the concentrations of ions in the layer of water next to the particle surface can be related to the corresponding species in the bulk solution:

$$[\text{L:surface}] = [\text{L}^-]_{\text{bulk}}e^{-\Delta_{\text{elect}}G_i/RT} \tag{14-51}$$

and:

$$[i\text{:surface}] = [i]_{\text{bulk}}e^{-\Delta_{\text{elect}}G_i/RT}e^{-\Delta_{\text{hydrophobic}}G_i/RT} \tag{14-52}$$

Using these relations in Eq. 14-50, we have:

$$\begin{aligned}
K_{i\text{rxn}} &= \frac{[i\!-\!\text{M}\!\equiv][\text{L}^-]_{\text{bulk}} \cdot e^{-\Delta_{\text{elect}}G_i/RT}}{(\sigma_{\text{surf ex}}A_{\text{surf}} - [i\!-\!\text{M}\!\equiv])[i]_{\text{bulk}} \cdot e^{-\Delta_{\text{elect}}G_i/RT} \cdot e^{-\Delta_{\text{hydrophobic}}G_i/RT}} \\
&= \frac{[i\!-\!\text{M}\!\equiv][\text{L}^-]_{\text{bulk}}}{(\sigma_{\text{surf ex}}A_{\text{surf}} - [i\!-\!\text{M}\!\equiv])[i^-]_{\text{bulk}}K_{i\text{ex}}}
\end{aligned} \tag{14-53}$$

where $K_{i\text{ex}}$ is equal to $\exp(-\Delta_{\text{hydrophobic}}G_i/RT)$, as discussed in Section 14.3. Rearranging, we then find:

$$[i-M\equiv] = \frac{\sigma_{\text{surf rxn}}A_{\text{surf}}K_{i\text{ex}}K_{i\text{rxn}}[i^-]_{\text{bulk}}}{[L^-]_{\text{bulk}} + K_{i\text{ex}}K_{i\text{rxn}}[i^-]_{\text{bulk}}} \tag{14-54}$$

Thus, another Langmuir isotherm is expected with the maximum bound concentrations equal to $\sigma_{\text{surf rxn}} A_{\text{surf}}$. Returning to our overall K_{id} expression for organic ions (Eq. 14-46), we can now write:

$$K_{\substack{id,\text{ionexchange}\\ \text{andsurface}\\ \text{reaction}}} = \frac{\sigma_{\text{surf ex}}A_{\text{surf}}K_{i\text{ex}}}{[\text{comp.ion}] + K_{i\text{ex}}[i^-]} + \frac{\sigma_{\text{surf rxn}}A_{\text{surf}}K_{i\text{ex}}K_{i\text{rxn}}}{[\text{comp.ligand}] + K_{i\text{ex}}K_{i\text{rxn}}[i^-]} \tag{14-55}$$

As for nonreacting organic ions, we need information on the ion exchange tendency of the chemical of interest ($K_{i\text{ex}}$ or $\Delta_{\text{hydrophobic}} G_i$), and we need to assess $K_{i\text{rxn}}$ or $\Delta_{\text{rxn}} G_i$.

Various investigators have utilized surface complexation modeling along with reasonable hypotheses concerning the surface species formed (and hence the adsorption reaction stoichiometry) to extract values of the product, $K_{i\text{ex}} K_{i\text{rxn}}$, for cases of interest (e.g., Mesuere and Fish, 1992; Ali and Dzombak, 1996; Vasudevan and Stone, 1996; Evanko and Dzombak, 1998, 1999). For example, Evanko and Dzombak (1999) fitted data for carboxylic acids and phenols sorbing to goethite from 10 mM NaCl solutions. They considered a sorption reaction of the form:

$$\equiv\text{Fe} - \text{OH} + i^- + H^+ \rightleftharpoons \ \equiv\text{Fe} - i + \text{H}_2\text{O} \tag{14-56}$$
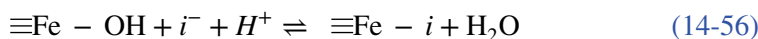
and fitted an "intrinsic" equilibrium constant, K_1^{int}, after accounting for electrostatic contributions:

$$K_1^{\text{int}} = \frac{[\equiv\text{Fe} - i]}{\gamma_i'[i^-]\gamma_{H^+}'[H^+][\equiv\text{Fe} - \text{OH}]} \tag{14-57}$$

Adding the reaction, $\text{H}_2\text{O} = H^+ + \text{OH}^-$ with $K_w = 10^{-14}$, this sorption reaction is equivalent to a ligand exchange with OH$^-$ being replaced by i^-:
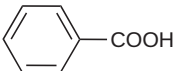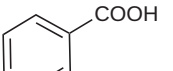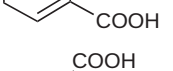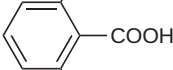
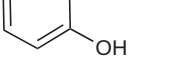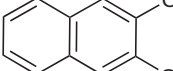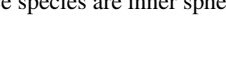$$\equiv\text{Fe} - \text{OH} + i^- \rightleftharpoons \ \equiv\text{Fe} - i + \text{OH}^- \tag{14-58}$$
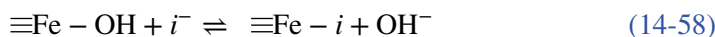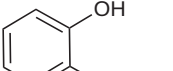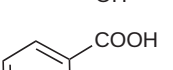
For this reaction, the equilibrium constant is the product, $K_{i\text{ex}}K_{i\text{rxn}}$, since i^- must partition from bulk solution into the near-surface water and then undergo the complexation reaction. Thus, this product ($K_{i\text{ex}}K_{i\text{rxn}}$) is related to the previous "intrinsic" constant from reaction 14-56:

$$K_{i\text{ex}}K_{i\text{rxn}} = 10^{-14}K_1^{\text{int}} \tag{14-59}$$

$K_{i\text{ex}}K_{i\text{rxn}}$ values depend on the sorbate's structure (see examples given in Table 14.2). First, $K_{i\text{ex}}K_{i\text{rxn}}$ values increase with the addition of moieties like carboxyl groups (compare hemimellitate to phthalate to benzoate). Also, functional groups positioned to allow multiple bonds with surface metals enhance the equilibrium values (compare

4

Table 14.2 Examples of Equilibrium Coefficients for Non-Charged Surface Species Binding to Goethite[a,b]

| Organic sorbate (i)	pK_{ia}	Structure	Sorption reaction	$\log(K_{iex}K_{irxn})^c$
benzoic acid	4.12		$\equiv Fe-OH + i^- \rightleftharpoons \equiv Fe-i + OH^-$	$10^{-6.1}$
phthalic acid	2.87 5.23		$\equiv Fe-OH + Hi^- \rightleftharpoons \equiv Fe-iH + OH^-$	$10^{-3.75}$
hemimellitic acid	2.79 4.49 6.95		$\equiv Fe-OH + H_2i^- \rightleftharpoons \equiv Fe-iH_2 + OH^-$	$10^{-2.97}$
catechol	9.34 13.24		$\equiv Fe-OH + Hi^- \rightleftharpoons \equiv Fe-iH + OH^-$	$10^{0.12}$
salicylic acid	2.88 13.56		$\equiv Fe-OH + Hi^- \rightleftharpoons \equiv Fe-iH + OH^-$	$10^{-5.45}$
3-hydroxy-2-naphthoic acid	2.65 12.72		$\equiv Fe-OH + Hi^- \rightleftharpoons \equiv Fe-iH + OH^-$	$10^{-4.54}$

[a]Deduced from data and complexation modeling in Evanko and Dzombak (1999).
[b]Note that one cannot assume the surface species are inner sphere "surface complexes."
[c]Equation 14-54 with $L^- = OH^-$.

1-naphthoic acid

3,5-dihydroxybenzoic acid

phenyl hexanoic acid

salicylate to benzoate). Values of $K_{iex}K_{irxn}$ increase for ligands with greater pK_{ia} values (Vasudevan and Stone, 1996). This may be interpreted as the greater the tendency to "hold" a proton (i.e., greater pK_{ia}), the greater will be the affinity for bonding to a metal on an oxide surface.

For the four mono carboxylic acids (benzoic acid, 1-naphthoic acid, 3,5-dihydroxy benzoic acid, and 6-phenyl hexnoic acid) also investigated by Evanko and Dzombak (1998, 1999), a value of $K_{iex}K_{irxn} \approx 10^{-6}$ was always found. The product was a little higher for the acids with larger "R-" groups (ranging from benzoic acid at $10^{-6.1}$ to phenyl hexanoate at $10^{-5.32}$). This range is consistent with our expectations from the K_{iex} contribution, since K_{iex} (benzoic acid) should be about 10 times less than K_{iex} (phenyl hexanoate) given the latter's five methylenes ($-CH_2-$) (see Eq. 14-39).

Returning to our effort to anticipate the overall sorption of organic compounds that may act both as counter ions and surface ligands, we can recognize all the terms in the second half of Eq. 14-55:

$$\sigma_{\text{surf rxn}} A_{\text{surf}} = [\equiv Fe-OH] \tag{14-60}$$
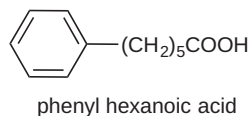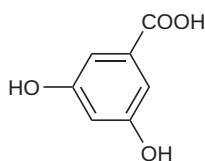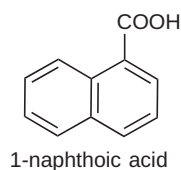
and:

$$[\text{comp.ligand}] = [\text{OH}^-] \qquad (14\text{-}61)$$

With the empirical measures of K_1^{int} reported in the literature and understandings of the "stoichiometries" of both the ion exchange and ligand exchange processes, we can now estimate the solid–water distribution ratios of such ionic organic sorbates.

We should point out that many organic sorbates, and especially bidentate ones like phthalate and salicylate, can apparently form more than one bound surface species. The relative importance of these surface species varies greatly as a function of pH. Hence, accurate predictions of the sorption of such organic ligands on mineral oxides requires applying more than one empirical surface reaction equilibrium constant to calculate the contributes of each bound species (see Evanko and Dzombak, 1999).

Finally, we can also evaluate $K_{i\text{rxn}}$ recognizing that the tendency to form chemical linkages to solid surface atoms correlates with the likelihood of forming comparable complexes in solution (Stumm et al., 1980; Schindler and Stumm, 1987; Dzombak and Morel, 1990). That is, the free energy change associated with the exchange shown by Eq. 14-48 appears energetically similar to that for a process occurring between two dissolved components:

$$\text{M} - \text{L}^{z+} + i^- \;\rightleftharpoons\; \text{M} - i^{z+} + \text{L}^- \qquad (14\text{-}62)$$
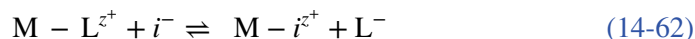
where $z+1$ would be the charge of the free metal in aqueous solution. This entirely solution-phase exchange reaction is characterized by an equilibrium constant:
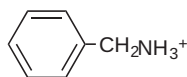
$$K_{i\substack{\text{ligand exchange} \\ \text{in solution}}} = \frac{[\text{M} - i^{z+}][\text{L}^-]}{[\text{M} - \text{L}^{z+}][i^-]} \qquad (14\text{-}63)$$

A substantial database is available to quantify such solution equilibria (e.g., Martell and Smith, 1997; Morel, 1983).
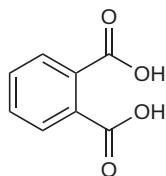
The procedure for other charged organic chemicals is analogous. By using such complexation results in Eq. 14-56, we begin to build an overall estimate of charged organic chemical sorption to minerals. We may now anticipate even a small degree of adsorption, which can be important (e.g., to the rate of heterogeneous transformations, Ulrich and Stone, 1989).
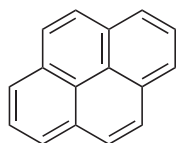
14.5   Questions and Problems

Special note: Problem solutions are available on the book's website. Solutions to problems marked with an asterisk are available for everyone. Unmarked problems have solutions only available to teachers, practitioners, and others with special permission.
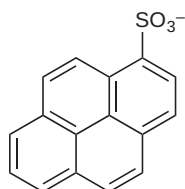
Questions

Q 14.1

For what kind of compounds and in which environmentally relevant cases is adsorption of organic chemicals to inorganic surfaces in water important? Give five examples.

Q 14.2

What intermolecular interactions and corresponding free energy contributions (ΔG_i) would you suspect to be important for the following sorbate:sorbent:solution combinations:

(a) benzyl ammonium between water and quartz sand? See structure in margin.

(b) *ortho*-phthalic acid between water and quartz sand? See structure in margin.

Indicate in each case the intermolecular interaction forces, key structural features of the sorbate, and the environmental parameters influencing sorption.

Q 14.3

Why do minerals have charges when they are submerged in water?

Q 14.4

Indicate whether the following solids are positively charged, neutral, or negatively charged when they occur in water at pH **7** (neglect specific adsorbates like phosphate or ferric iron species):

(a) quartz (SiO_2)

(b) natural organic matter

(c) goethite (FeOOH)

(d) gibbsite ($Al(OH)_3$)

(e) kaolinite

Q 14.5

Which of the two compounds do you think would sorb more to kaolinite in water at pH 6? See structures in margin.

(a) pyrene or pyrene sulfonate?

(b) butyl ammonium or butyrate?

(c) propyl ammonium or octyl ammonium?
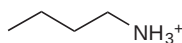
benzyl ammonium
$pK_{ia} = 9.33$

ortho-phthalic acid
$pK_{ia1} = 2.89$
$pK_{ia2} = 5.51$

pyrene

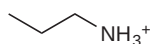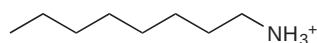pyrene sulfonate

butyl ammonium
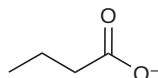
butyrate

propyl ammonium

octyl ammonium

Q 14.6

How can organic ions accumulate in excess of the ion exchange capacity near a pure mineral solid submerged in water?

Q 14.7

If organic ions are not bonded to a mineral's surface, why do they still not migrate past the minerals in a groundwater flow?

Problems

P 14.1 *Evaluating the Sorption of an Organic Anion, 2,4-Dichlorophenoxy-Butyrate, to Negatively Charged Natural Solids*

In Fig. 14.1*b*, a sorption isotherm shows that an organic anion, 2,4-dichlorophenoxybutyrate (DB$^-$), will sorb to a sediment from water of pH 7.9, despite the sediment's overall negative charge (as evidenced by its CEC of about 140 mmol kg^{-1}; Jafvert, 1990).

DB characteristics

$M_i = 246$ g mol^{-1}
$pK_{i\text{a}} = 4.95$
$K_{i\text{ow}} = 2.5 \times 10^3$

(a) The sediment also contained 1.5% organic carbon ($f_{oc} = 0.015$). Given a $pK_{i\text{a}}$ of 4.95 for this acid, can you account for the observed $K_{i\text{d}}$ values near 4 to 5 L kg^{-1}, assuming the neutral DB species partitioned into the NOM of the sediment? What $K_{i\text{d}}$ value (L kg^{-1}) do you expect from such absorption?

(b) You suspect the hydrophobicity of this organic anion also causes it to accumulate near the mineral surface *against the electrostatic repulsion* it feels:

$$\text{DB}^- + \text{Na}^+ \rightleftharpoons \text{DB:surf} + \text{Na:surf} \quad K_{\text{DBex}}(\text{L kg}^{-1})$$
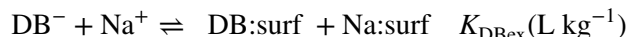
(i) Write a charge balance equation for the near-surface water assuming a solution composition of 20 mM NaC1.

(ii) Write an equilibrium equation (i.e., relating K_{DBex} to chemical concentrations) for the exchange reaction shown above.

(iii) Derive an isotherm equation describing [DB:surfl as a function of [DB$^-$] by combining the equilibrium quotient relation with your near-surface charge balance equation.

(iv) What value of K_{DBex} would be necessary to account for the observed K_{DBd} values (i.e., [DB:surf]/ [DB$^-$]) if the solution composition was 20 mM NaCl?

(v) Would such a K_{DBex} be "reasonable"? Explain your reasoning in light of electrostatic and hydrophobic energies required.

P 14.2 *Designing a Reactor to Remove Aniline from a Wastewater*

You have been charged with removing the aniline present at 100 ppm in the water of a 100 m^3 tank.

(a) One colleague suggests you add alum (A1$_2$(SO$_4$)$_3$) and NaOH to make a 100 mg L^{-1} suspension of negatively charged amorphous aluminum hydroxide (Al(OH)$_3$)
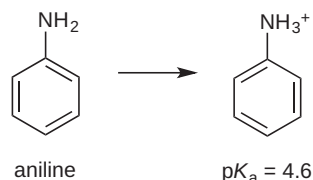
particles at pH 10 and 10 mM Na_2SO_4. Assume the surface density of $\equiv Al–OH$ is 6×10^{-6} mol m^{-2}, a specific surface area of 800 m^2 g^{-1}, and $pK_{a1}^{int} = 7$ and $pK_{a2}^{int} = 9$.

Will the aniline sorb to these negatively charged aluminum hydroxide particles and be carried to the bottom of the tank? Calculate the fraction of aniline sorbed to the particles before settling.

(b) Another colleague suggests you add Na:montmorillonite clay and HCl to make a 100 mg L^{-1} suspension of clay particles at pH 3 and 10 mM NaCl. Assume a CEC of 1×10^{-6} mol m^{-2} and AEC of 5×10^{-7} mol m^{-2} at pH 3, a specific surface area of 7×10^5 m^2 kg^{-1}, and a pH$_{zpc}$ = 2.5.

Will the aniline sorb to these mixed-charge clay particles and be carried to the bottom of the tank? Calculate the fraction of aniline sorbed to the particles before settling.

aniline $pK_a = 4.6$

P 14.3 *Transport of Di-Isopropanol-Amine (DIPA) in Ground Water from a Sour Gas Processing Plant*

Di-isopropanol-amine (DIPA) was used to remove hydrogen sulfide from natural gas supplies (Goar, 1971). Unfortunately, this compound has been found as a groundwater contaminant at a total concentration of about 1 mM levels near such a sour gas processing plant. Estimate the retardation factor for DIPA the nearby aquifer.

Aquifer characteristics

mineralogy: 70% quartz, 5% calcite, 25% montmorillonite, 0.2% organic matter

cation exchange capacity: CEC = 90 mmol kg^{-1}

density of aquifer material: $\rho_s = 2.6$ kg L^{-1}

total aquifer porosity: $\phi = 0.40$

groundwater composition: pH = 8.0; $[Na^+]$ = 20 mM; $[Ca^{+2}]$ = 1 mM; $[Cl^-]$ = 20 mM; $[HCO_3^-]$ = 1 mM

di-isopropanol-amine (DIPA)
$pK_{DIPAH+a} = 8.88$
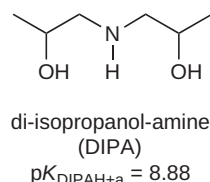
P 14.4 *What Mechanism Accounts for the Benzidine Sorption in Sediments and Soils?*

Zierath et al. (1980) measured sorption isotherm data for benzidine on sediments and soils. Using Missouri River sediment with f_{oc} = 0.023 kg oc kg^{-1} solid, CEC = 190 mmol kg^{-1}, and a specific surface area A_{surf} = 131 m^2 g^{-1}, they obtained the following sorption data:
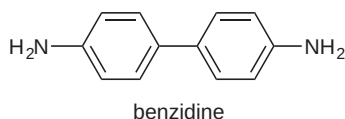
benzidine

Benzidine Sorption to Missouri River Sediment[a]

C_{iw} (μmol L^{-1})	C_{is} (μmol kg^{-1})
20	1500
30	3000
120	5300
200	7600
340	9300

[a]Data from Zierath et al. (1980).

You are interested in discerning what mechanism or mechanisms were responsible for the benzidene sorption observed with Missouri River sediment. To examine this question, you assume the tests used 1 g of soil per 10 mL of water and had a pH of 6 and a salt content of 1 mM NaCl. Given these assumptions, what sorption mechanism would predominate? Justif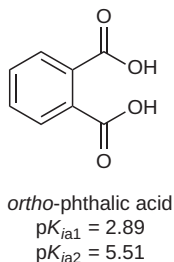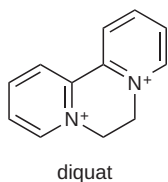y your answer using estimates of K_{id} (a) first assuming absorption into organic matter predominates and (b) then assuming adsorption to ion exchange sites predominates.

P 14.5 *Impact of Diquat Sorption on Its Biodegradation*

diquat

The presence of montmorillonite in microbial cultures has been seen to reduce the rate of diquat (D) biodegradation (Weber and Coble, 1968). It has been hypothesized that this is due to significant diquat adsorption to the clay. What fraction (%) of the diquat in 1 μM diquat solutions would be adsorbed to a 10 mg L^{-1} montmorillonite suspension (assume CEC = 1 mol kg^{-1}) at pH 7 and 10^{-2} M NaCl and assuming $K_{Dex} = [D:surf_2] [Na^+]^2 / [D^{2+}] [Na:surf]^2 = 3$ kg L^{-1}. *(Hint: $(1 - \varepsilon)^{0.5} \approx 1 - \varepsilon/2$ for small values of ε).*

P 14.6 *Adsorption of Organic Ions to Iron Oxides from Seawater*

ortho-phthalic acid
pK_{ia1} = 2.89
pK_{ia2} = 5.51

Balistrieri and Murray (1987) evaluated the sorption of organic acids to positively charged goethite (FeOOH) particles suspended at 6.6 g L^{-1} in 0.53 M NaCl solutions to mimic seawater salt. They observed the adsorption trend for *ortho*-phthalic acid added at 200 μM as shown in the table. Why is the extent of adsorption largest near pH 4?

Ortho-phthalic Acid Sorption to Goethite[a]

pH	% adsorbed
3	60
4	65
5	50
6	25
7	5
8	5

[a]Data from Balistrieri and Murray (1987).

14.6   Bibliography

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