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5 PHASE INTERACTIONS

5.1. CHEMICAL INTERACTIONS INVOLVING SOLIDS, GASES, AND WATER

Homogeneous chemical reactions occurring entirely in aqueous solution are rather rare in natural waters and wastewaters. Instead, most significant chemical and biochemical phenomena in water involve interactions between species in water and another phase. Some of these important interactions are illustrated in Figure 5.1. Several examples of phase interactions in water illustrated by the figure are the following: production of solid biomass through the photosynthetic activity of algae occurs within a suspended algal cell and involves exchange of dissolved solids and

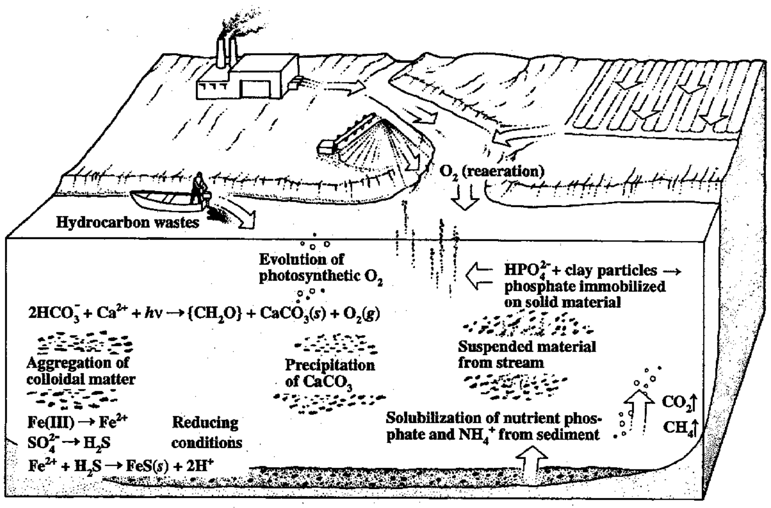


Figure 5.1. Most important environmental chemical processes in water involve interactions between water and another phase.

gases between the surrounding water and the cell. Similar exchanges occur when bacteria degrade organic matter (often in the form of small particles) in water. Chemical reactions occur that produce solids or gases in water. Iron and many important trace-level elements are transported through aquatic systems as colloidal chemical compounds or are sorbed to solid particles. Pollutant hydrocarbons and some pesticides may be present on the water surface as an immiscible liquid film. Sediment can be washed physically into a body of water.

This chapter discusses the importance of interactions among different phases in aquatic chemical processes. In a general sense, in addition to water, these phases may be divided between *sediments* (bulk solids) and *suspended colloidal material.* The ways in which sediments are formed and the significance of sediments as repositories and sources of aquatic solutes are discussed. Mentioned in earlier chapters, solubilities of solids and gases (Henry's law) are covered here in some detail.

Much of this chapter deals with the behavior of colloidal material, which consists of very fine particles of solids, gases, or immiscible liquids suspended in water. Colloidal material is involved with many significant aquatic chemical phenomena. It is very reactive because of its high surface-area-to-volume ratio.

5.2. IMPORTANCE AND FORMATION OF SEDIMENTS

Sediments are the layers of relatively finely divided matter covering the bottoms of rivers, streams, lakes, reservoirs, bays, estuaries, and oceans. Sediments typically consist of mixtures of fine-, medium-, and coarse-grained minerals, including clay, silt, and sand, mixed with organic matter. They may vary in composition from pure mineral matter to predominantly organic matter. Sediments are repositories of a variety of biological, chemical, and pollutant detritus in bodies of water. Of particular concern is the transfer of chemical species from sediments into aquatic food chains via organisms that spend significant parts of their life cycles in contact with or living in sediments. Among the sediment-dwelling organisms are various kinds of shellfish (shrimp, crayfish, crab, clams) and a variety of worms, insects, amphipods, bivalves, and other smaller organisms that are of particular concern because they are located near the bottom of the food chain.

Although the classic picture of pollutant transfer from sediments to organisms invokes an intermediate stage in water solution, it is now believed that direct transfer from sediments to organisms occurs to a large extent. This is probably particularly important for poorly-water-soluble organophilic pollutants, such as organohalide pesticides. The portion of substances held in sediments that is probably most available to organisms is that contained in **pore water**, contained in microscopic pores within the sediment mass. Pore water is commonly extracted from sediments for measurements of toxicity to aquatic test organisms.

Formation of Sediments

Physical, chemical, and biological processes may all result in the deposition of sediments in the bottom regions of bodies of water. Sedimentary material may be simply carried into a body of water by erosion or through sloughing (caving in) of the shore. Thus, clay, sand, organic matter, and other materials may be washed into a lake and settle out as layers of sediment.

Sediments may be formed by simple precipitation reactions, several of which are discussed below. When a phosphate-rich wastewater enters a body of water containing a high concentration of calcium ion, the following reaction occurs to produce solid hydroxyapatite:

$$5Ca^{2+} + H_2O + 3HPO_4^{2-} \rightarrow Ca_5OH(PO_4)_3(s) + 4H^+ \qquad (5.2.1)$$

Calcium carbonate sediment may form when water rich in carbon dioxide and containing a high level of calcium as temporary hardness (see Section 3.5) loses carbon dioxide to the atmosphere,

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2(g) + H_2O \qquad (5.2.2)$$

or when the pH is raised by a photosynthetic reaction:

$$Ca^{2+} + 2HCO_3^- + h\nu \rightarrow \{CH_2O\} + CaCO_3(s) + O_2(g) \qquad (5.2.3)$$

Oxidation of reduced forms of an element can result in its transformation to an insoluble species, such as occurs when iron(II) is oxidized to iron(III) to produce a precipitate of insoluble iron(III) hydroxide:

$$4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3(s) + 8H^+ \qquad (5.2.4)$$

A decrease in pH can result in the production of an insoluble humic acid sediment from base-soluble organic humic substances in solution (see Section 3.17).

Biological activity is responsible for the formation of some aquatic sediments. Some bacterial species produce large quantities of iron(III) oxide (see Section 6.14) as part of their energy-extracting mediation of the oxidation of iron(II) to iron(III). In anaerobic bottom regions of bodies of water, some bacteria use sulfate ion as an electron receptor,

$$SO_4^{2-} \rightarrow H_2S \qquad (5.2.5)$$

whereas other bacteria reduce iron(III) to iron(II):

$$Fe(OH)_3(s) \rightarrow Fe^{2+} \qquad (5.2.6)$$

The net result is a precipitation reaction producing a black layer of iron(II) sulfide sediment:

$$Fe^{2+} + H_2S \rightarrow FeS(s) + 2H^+ \qquad (5.2.7)$$

This frequently occurs during the winter, alternating with the production of calcium carbonate by-product from photosynthesis (Reaction 5.2.3) during the summer. Under such conditions, a layered bottom sediment is produced composed of alternate layers of black FeS and white CaCO3 as shown in Figure 5.2.

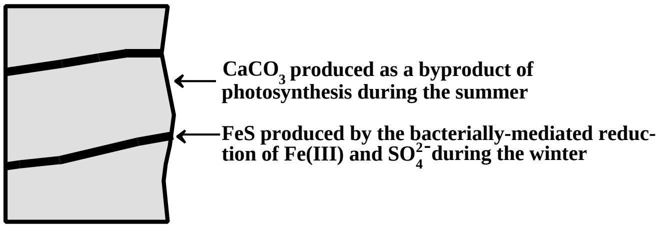


Figure 5.2. Alternate layers of FeS and $CaCO_3$ in a lake sediment. This phenomenon has been observed in Lake Zürich in Switzerland.

The preceding are only a few examples of reactions that result in the formation of bottom sediments in bodies of water. Eventually these sediments may become covered and form sedimentary minerals.

5.3. SOLUBILITIES

The formation and stabilities of nonaqueous phases in water are strongly dependent upon solubilities. Calculations of the solubilities of solids and gases are addressed in this section.

Solubilities of Solids

Generally, the solubility of a solid in water is of concern when the solid is slightly soluble, often having such a low solubility that it is called “insoluble.” In section 3.11 the solubility of lead carbonate was considered. This salt can introduce toxic lead ion into water by reactions such as

$$PbCO_3(s) \leftrightarrows Pb^{2+} + CO_3^{2-} \qquad (3.10.13)$$

A relatively straightforward calculation of the solubility of an ionic solid can be performed on barium sulfate,[1] which dissolves according to the reaction

$$BaSO_4(s) \leftrightarrows Ba^{2+} + SO_4^{2-} \qquad (5.3.1)$$

for which the equilibrium constant is the following:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.23 \times 10^{-10} \qquad (5.3.2)$$

An equilibrium constant in this form that expresses the solubility of a solid that forms ions in water is a **solubility product** and is designated K_{sp}. In the simplest cases a solubility product can be used alone to calculate the solubility of a slightly soluble salt in water. The solubility (S, moles per liter) of barium sulfate is calculated as follows:

$$[Ba^{2+}] = [SO_4^{2-}] = S \qquad (5.3.3)$$

$$[Ba^{2+}][SO_4^{2-}] = S \times S = K_{sp} = 1.23 \times 10^{-10} \tag{5.3.4}$$

$$S = (K_{sp})^{1/2} = (1.23 \times 10^{-10})^{1/2} = 1.11 \times 10^{-5} \tag{5.3.5}$$

Even such a simple calculation may be complicated by variations in activity coefficients resulting from differences in ionic strength.

Intrinsic solubilities account for the fact that a significant portion of the solubility of an ionic solid is due to the dissolution of the neutral form of the salt and must be added to the solubility calculated from K_{sp} to obtain the total solubility, as illustrated below for the calculation of the solubility of calcium sulfate. When calcium sulfate dissolves in water the two major reactions are

$$CaSO_4(s) \leftarrow\rightarrow CaSO_4(aq) \tag{5.3.6}$$

$$[CaSO_4(aq)] = 5.0 \times 10^{-3}\text{ M} \quad (25^\circ C) \tag{5.3.7}$$

(Intrinsic solubility of $CaSO_4$)

$$CaSO_4(s) \leftarrow\rightarrow Ca^{2+} + SO_4^{2-} \tag{5.3.8}$$

$$[Ca^{2+}][SO_4^{2-}] = K_{sp} = 2.6 \times 10^{-5} \quad (25^\circ C) \tag{5.3.9}$$

and the total solubility of $CaSO_4$ is calculated as follows:

$$S = \underset{\substack{\uparrow \\ \text{Contribution to solubility} \\ \text{from solubility product}}}{[Ca^{2+}]} + \underset{\substack{\uparrow \\ \text{Contribution to solubility} \\ \text{from intrinsic solubilty}}}{[CaSO_4(aq)]} \tag{5.3.10}$$

$$\begin{aligned} S &= (K_{sp})^{1/2} + [CaSO_4(aq)] = (2.6 \times 10^{-5})^{1/2} + 5.0 \times 10^{-3} \\ &= 5.1 \times 10^{-3} + 5.0 \times 10^{-3} = 1.01 \times 10^{-2}\text{ M} \end{aligned} \tag{5.3.11}$$

It is seen that, in this case, the intrinsic solubility accounts for half of the solubility of the salt.

In Section 3.15 it was seen that solubilities of ionic solids can be very much affected by reactions of cations and anions. It was shown that the solubility of $PbCO_3$ is increased by the chelation of lead ion by NTA,

$$Pb^{2+} + T^{3-} \leftarrow\rightarrow PbT^{-} \tag{3.15.6}$$

increased by reaction of carbonate ion with H^+,

$$H^+ + CO_3^{2-} \leftarrow\rightarrow HCO_3^{-} \tag{5.3.12}$$

and decreased by the presence of carbonate ion from water alkalinity:

$$CO_3^{2-}(\text{from dissociation of } HCO_3^{-}) + Pb^{2+} \leftarrow\rightarrow PbCO_3(s) \tag{5.3.13}$$

These examples illustrate that reactions of both cations and anions must often be considered in calculating the solubilities of ionic solids.

Solubilities of Gases

The solubilities of gases in water are described by Henry's Law which states that *at constant temperature the solubility of a gas in a liquid is proportional to the partial pressure of the gas in contact with the liquid.* For a gas, "X," this law applies to equilibria of the type

$$X(g) \leftarrow\rightarrow X(aq) \tag{5.3.14}$$

and does not account for additional reactions of the gas species in water such as,

$$NH_3 + H_2O \leftarrow\rightarrow NH_4^+ + OH^- \tag{5.3.15}$$

$$SO_2 + HCO_3^- \text{ (From water alkalinity) } \leftarrow\rightarrow CO_2 + HSO_3^- \tag{5.3.16}$$

which may result in much higher solubilities than predicted by Henry's law alone. Mathematically, Henry's Law is expressed as

$$[X(aq)] = K P_X \tag{5.3.17}$$

where $[X(aq)]$ is the aqueous concentration of the gas, P_X is the partial pressure of the gas, and K is the Henry's Law constant applicable to a particular gas at a specified temperature. For gas concentrations in units of moles per liter and gas pressures in atmospheres, the units of K are $\text{mol} \times L^{-1} \times \text{atm}^{-1}$. Some values of K for dissolved gases that are significant in water are given in Table 5.1.

Table 5.1. Henry's Law Constants for Some Gases in Water at 25˚C.

Gas	K, $\text{mol} \times L^{-1} \times \text{atm}^{-1}$
O_2	1.28×10^{-3}
CO_2	3.38×10^{-2}
H_2	7.90×10^{-4}
CH_4	1.34×10^{-3}
N_2	6.48×10^{-4}
NO	2.0×10^{-4}

In calculating the solubility of a gas in water, a correction must be made for the partial pressure of water by subtracting it from the total pressure of the gas. At 25˚C the partial pressure of water is 0.0313 atm; values at other temperatures are readily obtained from standard handbooks. The concentration of oxygen in water saturated with air at 1.00 atm and 25˚C may be calculated as an example of a simple gas solubility calculation. Considering that dry air is 20.95% by volume oxygen, factoring in the partial pressure of water gives the following:

$$P_{O_2} = (1.0000 \text{ atm} - 0.0313 \text{ atm}) \times 0.2095 = 0.2029 \text{ atm} \qquad (5.3.18)$$

$$\begin{aligned}[O_2(aq)] &= K \times P_{O_2} = 1.28 \text{ x } 10^{-3} \text{ mol} \times L^{-1} \times \text{atm}^{-1} \times 0.2029 \text{ atm} \\ &= 2.60 \times 10^{-4} \text{ mol} \times L^{-1} \end{aligned} \qquad (5.3.19)$$

Since the molecular weight of oxygen is 32, the concentration of dissolved oxygen in water in equilibrium with air under the conditions given above is 8.32 mg/L, or 8.32 parts per million (ppm).

The solubilities of gases decrease with increasing temperature. Account is taken of this factor with the **Clausius-Clapeyron** equation,

$$\log\frac{C_2}{C_1} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (5.3.20)$$

where C_1 and C_2 denote the gas concentration in water at absolute temperatures of T_1 and T_2, respectively; ΔH is the heat of solution; and R is the gas constant. The value of R is 1.987 $\text{cal} \times \text{deg}^{-1} \times \text{mol}^{-1}$, which gives ΔH in units of cal/mol.

5.4. COLLOIDAL PARTICLES IN WATER

Many minerals, some organic pollutants, proteinaceous materials, some algae, and some bacteria are suspended in water as very small particles. Such particles, which have some characteristics of both species in solution and larger particles in suspension, which range in diameter from about 0.001 micrometer (µm) to about 1 µm, and which scatter white light as a light blue hue observed at right angles to the incident light, are classified as **colloidal particles**. The characteristic light-scattering phenomenon of colloids results from their being the same order of size as the wavelength of light and is called the **Tyndall effect**. The unique properties and behavior of colloidal particles are strongly influenced by their physical-chemical characteristics, including high specific area, high interfacial energy, and high surface/charge density ratio.

Occurrence of Colloids in Water

Colloids composed of a variety of organic substances (including humic substances), inorganic materials (especially clays), and pollutants occur in natural water and wastewater.[2] These substances have a number of effects, including effects on organisms and pollutant transport. The characterization of colloidal materials in water is obviously very important, and a variety of means are used to isolate and characterize these materials. The two most widely used methods are filtration and centrifugation, although other techniques including voltammetry, gels, and field-flow fractionation can be used.[3]

Kinds of Colloidal Particles

Colloids may be classified as *hydrophilic colloids*, *hydrophobic colloids*, or *association colloids*. These three classes are briefly summarized below.

Hydrophilic colloids generally consist of macromolecules, such as proteins and synthetic polymers, that are characterized by strong interaction with water resulting in spontaneous formation of colloids when they are placed in water. In a sense, hydrophilic colloids are solutions of very large molecules or ions. Suspensions of hydrophilic colloids are less affected by the addition of salts to water than are suspensions of hydrophobic colloids.

Hydrophobic colloids interact to a lesser extent with water and are stable because of their positive or negative electrical charges as shown in Figure 5.3. The charged surface of the colloidal particle and the **counter-ions** that surround it compose an **electrical double layer**, which causes the particles to repel each other.

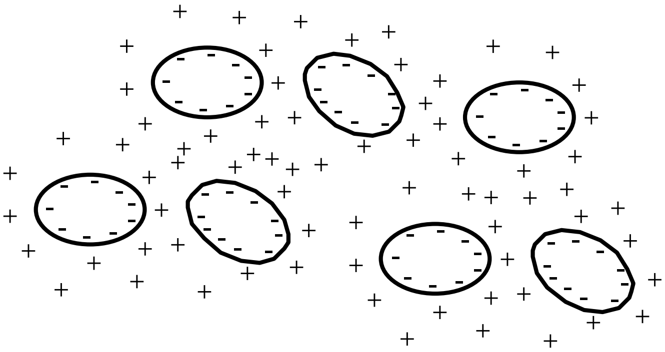
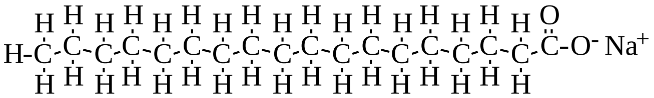


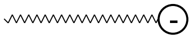
Figure 5.3. Representation of negatively charged hydrophobic colloidal particles surrounded in solution by positively charged counter-ions, forming an electrical double layer. (Colloidal particles suspended in water may have either a negative or positive charge.)

Hydrophobic colloids are usually caused to settle from suspension by the addition of salts. Examples of hydrophobic colloids are clay particles, petroleum droplets, and very small gold particles.

Association colloids consist of special aggregates of ions and molecules called **micelles**. To understand how this occurs, consider sodium stearate, a typical soap with the structural formula shown below:



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O^{-}\ Na^{+}}$$

Represented as 

The stearate ion has both a hydrophilic $-CO_2^-$ head and a long organophilic tail, $CH_3(CH_2)_{16}^-$. As a result, stearate anions in water tend to form clusters consisting of as many as 100 anions clustered together with their hydrocarbon “tails” on the inside of a spherical colloidal particle and their ionic “heads” on the surface in contact with water and with Na^+ counterions. This results in the formation of **micelles** as illustrated in Figure 5.4. Micelles can be visualized as droplets of oil about 3-4 nanometers (nm) in diameter and covered with ions or polar groups. According to this model, micelles form when a certain concentration of surfactant species, typically around 1×10^{-3}, is reached. The concentration at which this occurs is called the **critical micelle concentration**.

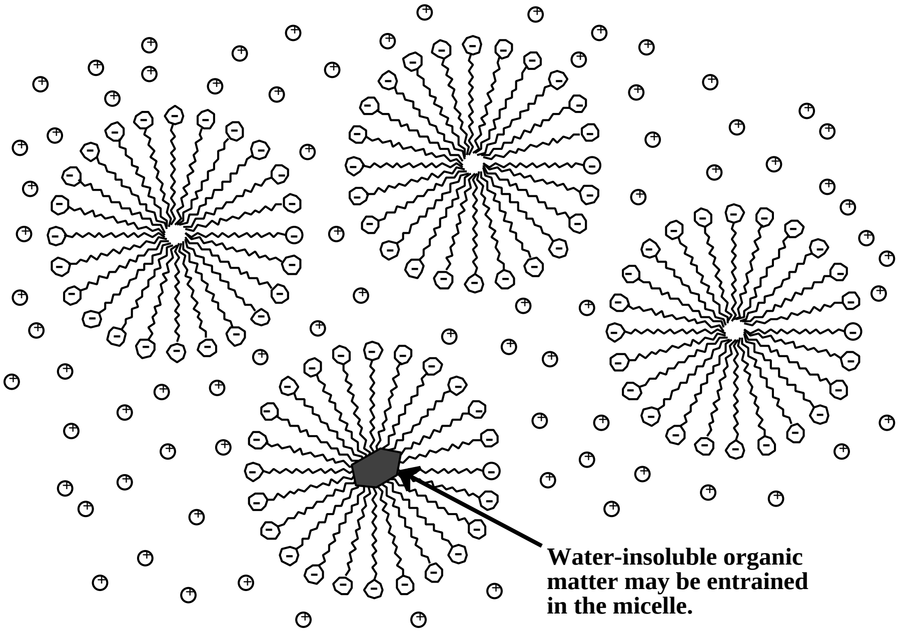


Figure 5.4. Representation of colloidal soap micelle particles.

Colloid Stability

The stability of colloids is a prime consideration in determining their behavior. It is involved in important aquatic chemical phenomena including the formation of sediments, dispersion and agglomeration of bacterial cells, and dispersion and removal of pollutants (such as crude oil from an oil spill).

Discussed above, the two main phenomena contributing to the stabilization of colloids are **hydration** and **surface charge**. The layer of water on the surface of hydrated colloidal particles prevents contact, which would result in the formation of larger units. A surface charge on colloidal particles may prevent aggregation, since like-charged particles repel each other. The surface charge is frequently pH-dependent; around pH 7 most colloidal particles in natural waters are negatively charged. Negatively charged aquatic colloids include algal cells, bacterial cells, proteins, and colloidal petroleum droplets.

One of the three major ways in which a particle may acquire a surface charge is by **chemical reaction at the particle surface**. This phenomenon, which frequently involves hydrogen ion and is pH-dependent, is typical of hydroxides and oxides and is illustrated for manganese dioxide, MnO_2, in Figure 5.5.

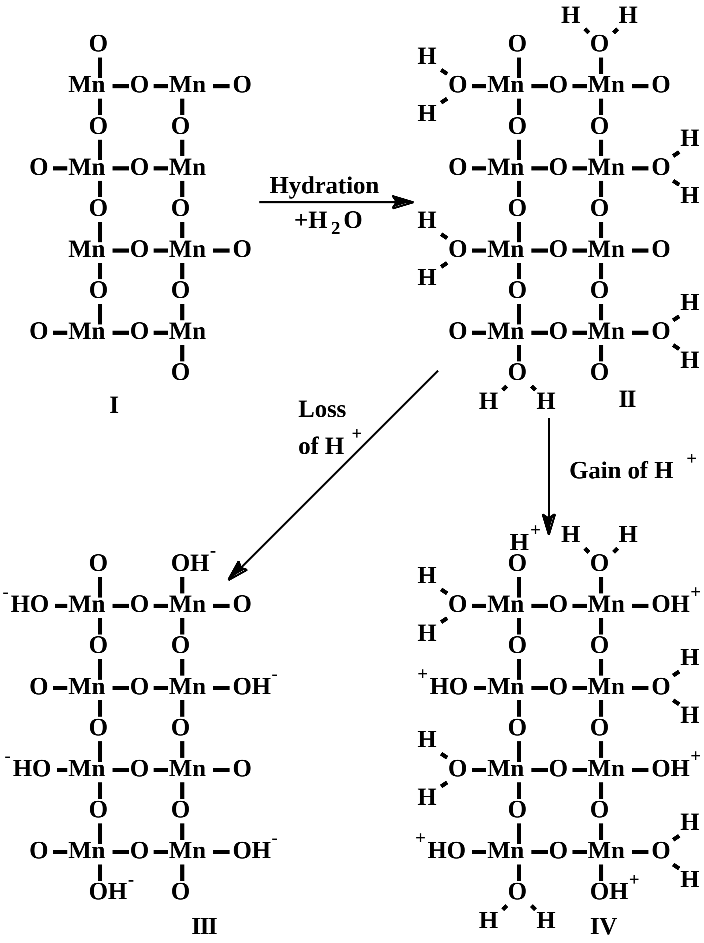


Figure 5.5. Acquisition of surface charge by colloidal MnO_2 in water. Anhydrous MnO_2 (I) has two O atoms per Mn atom. Suspended in water as a colloid, it binds to water molecules to form hydrated MnO_2 (II). Loss of H^+ from the bound H_2O yields a negatively charged colloidal particle (III). Gain of H^+ by surface O atoms yields a positively charged particle (IV). The former process (loss of H^+ ion) predominates for metal oxides.

As an illustration of pH-dependent charge on colloidal particle surfaces, consider the effects of pH on the surface charge of hydrated manganese oxide, represented by the chemical formula $MnO_2(H_2O)(s)$. In a relatively acidic medium, the reaction

$$MnO_2(H_2O)(s) + H^+ \rightarrow MnO_2(H_3O)^+(s) \tag{5.4.1}$$

may occur on the surface giving the particle a net positive charge. In a more basic medium, hydrogen ion may be lost from the hydrated oxide surface to yield negatively charged particles:

$$MnO_2(H_2O)(s) \rightarrow MnO_2(OH)^-(s) + H^+ \tag{5.4.2}$$

At some intermediate pH value, called the **zero point of charge (ZPC)**, colloidal particles of a given hydroxide will have a net charge of zero, which favors aggregation of particles and precipitation of a bulk solid:

$$\text{Number of } MnO_2(H_3O)^+ \text{ sites} = \text{Number of } MnO_2(OH)^- \text{ sites} \qquad (5.4.3)$$

Individual cells of microorganisms that behave as colloidal particles have a charge that is pH-dependent. The charge is acquired through the loss and gain of H^+ ion by carboxyl and amino groups on the cell surface:

$$\underset{\text{low pH}}{{}^+H_3N(+\text{ cell})CO_2H} \quad \underset{\text{intermediate pH}}{{}^+H_3N(\text{neutral cell})CO_2^-} \quad \underset{\text{high pH}}{H_2N(-\text{ cell})CO_2^-}$$

Ion absorption is a second way in which colloidal particles become charged. This phenomenon involves attachment of ions onto the colloidal particle surface by means other than conventional covalent bonding, including hydrogen bonding and London (Van der Waal) interactions.

Ion replacement is a third way in which a colloidal particle may gain a net charge; for example, replacement of some of the Si(IV) with Al(III) in the basic SiO_2 chemical unit in the crystalline lattice of some clay minerals as shown in Equation 5.4.4,

$$[SiO_2] + Al(III) \rightarrow [AlO_2^-] + Si(IV) \qquad (5.4.4)$$

yields sites with a net negative charge. Similarly, replacement of Al(III) by a divalent metal ion such as Mg(II) in the clay crystalline lattice produces a net negative charge.

5.5. THE COLLOIDAL PROPERTIES OF CLAYS

Clays constitute the most important class of common minerals occurring as colloidal matter in water. The composition and properties of clays are discussed in some detail in Section 15.7 (as solid terrestrial minerals) and are briefly summarized here. **Clays** consist largely of hydrated aluminum and silicon oxides and are **secondary minerals**, which are formed by weathering and other processes acting on primary rocks (see Sections 15.2 and 15.8). The general formulas of some common clays are given below:

- Kaolinite: $Al_2(OH)_4Si_2O_5$
- Montmorillonite: $Al_2(OH)_2Si_4O_{10}$
- Nontronite: $Fe_2(OH)_2Si_4O_{10}$
- Hydrous mica: $KAl_2(OH)_2(AlSi_3)O_{10}$

Iron and manganese are commonly associated with clay minerals. The most common clay minerals are illites, montmorillonites, chlorites, and kaolinites. These clay minerals are distinguished from each other by general chemical formula, structure, and chemical and physical properties.

Clays are characterized by layered structures consisting of sheets of silicon oxide alternating with sheets of aluminum oxide. Units of two or three sheets make up **unit layers**. Some clays, particularly the montmorillonites, may absorb large quantities of water between unit layers, a process accompanied by swelling of the clay.

As described in Section 5.4, clay minerals may attain a net negative charge by ion replacement, in which Si(IV) and Al(III) ions are replaced by metal ions of similar size but lesser charge. This negative charge must be compensated by association of cations with the clay layer surfaces. Since these cations need not fit specific sites in the crystalline lattice of the clay, they may be relatively large ions, such as K^+, Na^+, or NH_4^+. These cations are called **exchangeable cations** and are exchangeable for other cations in water. The amount of exchangeable cations, expressed as milliequivalents (of monovalent cations) per 100 g of dry clay, is called the **cation-exchange capacity**, **CEC**, of the clay and is a very important characteristic of colloids and sediments that have cation-exchange capabilities.

Because of their structure and high surface area per unit weight, clays have a strong tendency to sorb chemical species from water. Thus, clays play a role in the transport and reactions of biological wastes, organic chemicals, gases, and other pollutant species in water. However, clay minerals also may effectively immobilize dissolved chemicals in water and so exert a purifying action. Some microbial processes occur at clay particle surfaces and, in some cases, sorption of organics by clay inhibits biodegradation. Thus, clay may play a role in the microbial degradation or nondegradation of organic wastes.

5.6. AGGREGATION OF PARTICLES

The processes by which particles aggregate and precipitate from colloidal suspension are quite important in the aquatic environment. For example, the settling of biomass during biological waste treatment depends upon the aggregation of bacterial cells. Other processes involving the aggregation of colloidal particles are the formation of bottom sediments and the clarification of turbid water for domestic or industrial use. Particle aggregation is complicated and may be divided into the two general classes of *coagulation* and *flocculation*. These are discussed below.

Colloidal particles are prevented from aggregating by the electrostatic repulsion of the electrical double layers (adsorbed-ion layer and counter-ion layer). **Coagulation** involves the reduction of this electrostatic repulsion such that colloidal particles of identical materials may aggregate. **Flocculation** uses **bridging compounds,** which form chemically bonded links between colloidal particles and enmesh the particles in relatively large masses called **floc networks.**

Hydrophobic colloids are often readily coagulated by the addition of small quantities of salts that contribute ions to solution. Such colloids are stabilized by electrostatic repulsion. Therefore, the simple explanation of coagulation by ions in solution is that the ions reduce the electrostatic repulsion between particles to such an extent that the particles aggregate. Because of the double layer of electrical charge surrounding a charged particle, this aggregation mechanism is sometimes called **double-layer compression.** It is particularly noticeable in estuaries where sediment-laden fresh water flows into the sea, and is largely responsible for deltas formed where large rivers enter oceans.

The binding of positive ions to the surface of an initially negatively charged colloid can result in precipitation followed by colloid restabilization as shown in Figure 5.6. This kind of behavior is explained by an initial neutralization of the negative surface charge on the particles by sorption of positive ions, allowing coagulation to occur. As more of the source of positive ions is added, their sorption results in the formation of positive colloidal particles.

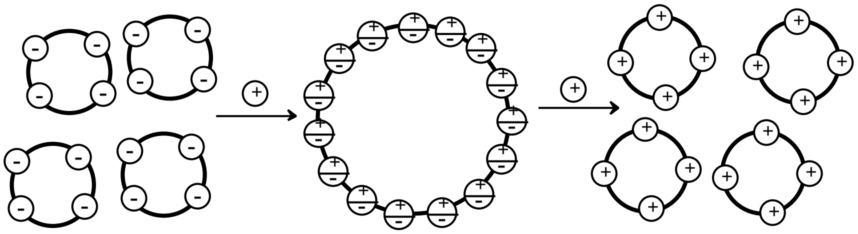


Figure 5.6. Aggregation of negatively charged colloidal particles by reaction with positive ions, followed by restabilization as a positively charged colloid.

Flocculation of Colloids by Polyelectrolytes

Polyelectrolytes of both natural and synthetic origin may cause colloids to flocculate. Polyelectrolytes are polymers with a high formula weight that normally contain ionizable functional groups. Typical examples of synthetic polyelectrolytes are shown in Table 5.2.

It can be seen from Table 5.2 that anionic polyelectrolytes have negatively charged functional groups, such as $–SO_3^-$ and $–CO_2^-$. Cationic polyelectrolytes have positively charged functional groups, normally H^+ bonded to N. Nonionic polymers that serve as flocculants normally do not have charged functional groups.

Somewhat paradoxically, *anionic* polyelectrolytes may flocculate *negatively charged* colloidal particles. The mechanism by which this occurs involves bridging between the colloidal particles by way of the polyelectrolyte anions. Strong chemical bonding has to be involved, since both the particles and the polyelectrolytes are negatively charged. However, the process does occur and is particularly important in biological systems, for example, in the cohesion of tissue cells, clumping of bacterial cells, and antibody-antigen reactions.

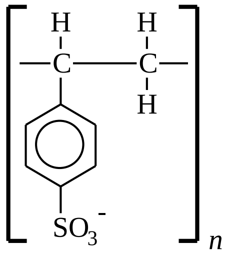
The flocculation process induced by anionic polyelectrolytes is greatly facilitated by the presence of a low concentration of a metal ion capable of binding with the functional groups on the polyelectrolyte. The positively charged metal ion serves to form a bridge between the negatively charged anionic polyelectrolytes and negatively charged functional groups on the colloidal particle surface.

Flocculation of Bacteria by Polymeric Materials

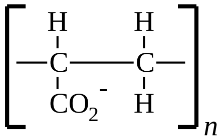
The aggregation and settling of microorganism cells is a very important process in aquatic systems and is essential to the function of biological waste treatment systems. In biological waste treatment processes, such as the activated sludge process (Chapter 8), microorganisms utilize carbonaceous solutes in the water to produce biomass. The primary objective of biological waste treatment is the removal of carbonaceous material and, consequently, its oxygen demand. Part of the carbon is evolved from the water as CO_2, produced by the energy-yielding metabolic processes of the bacteria. However, a significant fraction of the carbon is removed as **bacterial floc**, consisting of aggregated bacterial cells that have settled from the water. The formation of this floc is obviously an important phenomenon in biological waste treatment. Polymeric substances, including polyelectrolytes, that are formed by the bacteria induce bacterial flocculation.

Table 5.2. Synthetic Polyelectrolytes and Neutral Polymers Used as Flocculants

Anionic polyelectrolytes

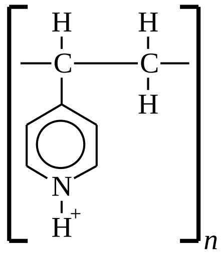


Polystyrene sulfonate

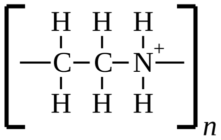


Polyacrylate

Cationic polyelectrolytes

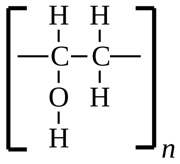


Polyvinyl pyridinium

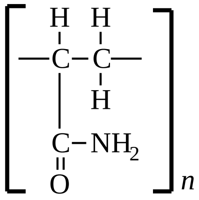


Polyethylene imine

Nonionic polymers



Polyvinyl alcohol



Polyacrylamide

Within the pH range of normal natural waters (pH 5-9), bacterial cells are negatively charged. The ZPC of most bacteria is within the pH range 2-3. However, even at the ZPC, stable bacterial suspensions may exist. Therefore, surface charge is not necessarily required to maintain bacterial cells in suspension in water, and it is likely that bacterial cells remain in suspension because of the hydrophilic character of their surfaces. As a consequence, some sort of chemical interaction involving bridging species must be involved in bacterial flocculation.

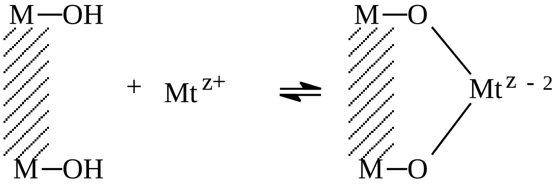
5.7. SURFACE SORPTION BY SOLIDS

Many of the properties and effects of solids in contact with water have to do with the sorption of solutes by solid surfaces. Surfaces in finely divided solids tend to have excess surface energy because of an imbalance of chemical forces among surface atoms, ions, and molecules. Surface energy level may be lowered by a reduction in surface area. Normally this reduction is accomplished by aggregation of particles or by sorption of solute species.

Some kinds of surface interactions can be illustrated with metal oxide surfaces binding with metal ions in water. (Such a surface, its reaction with water, and its subsequent acquisition of a charge by loss or gain of H^+ ion were shown in Figure 5.5 for MnO_2.) Other inorganic solids, such as clays, probably behave much like solid metal oxides. Soluble metal ions, such as Cd^{2+}, Cu^{2+}, Pb^{2+}, or Zn^{2+}, may be bound with metal oxides such as $MnO_2 \bullet xH_2O$ by nonspecific ion exchange adsorption, complexation with surface –OH groups, coprecipitation in solid solution with the metal oxide, or as a discrete oxide or hydroxide of the sorbed metal.[4] Sorption of metal ions, Mt^{z+}, by complexation to the surface is illustrated by the reaction

$$\text{M–OH} + \text{Mt}^{z+} \rightleftharpoons \text{M-OMt}^{z-1} + \text{H}^+ \qquad (5.7.1)$$

and chelation by the following process:



(5.7.2)

A metal ion complexed with a ligand, L, may bond by displacement of either H^+ or OH^-:

$$\text{M–OH} + \text{MtL}^{z+} \rightleftharpoons \text{M-OMtL}^{(z-1)} + \text{H}^+ \qquad (5.7.3)$$

$$\text{M–OH} + \text{MtL}^{z+} \rightleftharpoons \text{M-(MtL)}^{(z+1)} + \text{OH}^- \qquad (5.7.4)$$

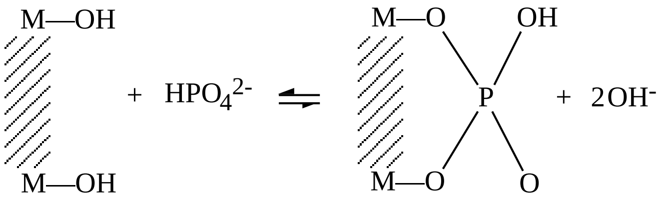
Furthermore, in the presence of a ligand, dissociation of the complex and sorption of the metal complex and ligand must be considered as shown by the scheme below in which “(sorbed)” represents sorbed species and “(aq)” represents dissolved species:

$$\begin{tikzcd}
\text{Mt}^{z+}(\textit{sorbed}) \arrow[r, shift left, "\rightarrow"] & \text{Mt}^{z+}(\textit{aq}) \arrow[l, shift left] \\
\text{MtL}^{z+}(\textit{sorbed}) \arrow[u, shift left] \arrow[r, shift left] & \text{MtL}^{z+}(\textit{aq}) \arrow[u, shift left] \arrow[l, shift left] \\
\text{L}(\textit{sorbed}) \arrow[u, shift left] \arrow[r, shift left] & \text{L}(\textit{aq}) \arrow[u, shift left] \arrow[l, shift left]
\end{tikzcd}$$

Some hydrated metal oxides, such as manganese(IV) oxide and iron(III) oxide, are especially effective in sorbing various species from aquatic solution. The sorption ability is especially pronounced for relatively fresh metal hydroxides or hydrated oxides such as colloidal MnO_2. This oxide usually is produced in natural waters by the oxidation of Mn(II) present in natural waters placed there by the bacterially-mediated reduction of manganese oxides in anaerobic bottom sediments. Colloidal hydrated manganese(II) oxide can also be produced by the reduction of manganese(VII), which often is deliberately added to water as an oxidant in the form of permanganate salts to diminish taste and odor or to oxidize iron(II).

Freshly precipitated MnO_2 may have a surface area as large as several hundred square meters per gram. The hydrated oxide acquires a charge by loss and gain of H^+ ion and has a ZPC in an acidic pH range between 2.8 and 4.5. Since the pH of most normal natural waters exceeds 4.5, hydrous MnO_2 colloids are usually negatively charged.

The sorption of anions by solid surfaces is harder to explain than the sorption of cations. Phosphates may be sorbed on hydroxylated surfaces by displacement of hydroxides (ion exchange):



(5.7.5)

The degree of anion sorption varies. As with phosphate, sulfate may be sorbed by chemical bonding, usually at a pH less than 7. Chloride and nitrate are sorbed by electrostatic attraction, such as occurs with positively charged colloidal particles in soil at a low pH. More specific bonding mechanisms may be involved in the sorption of fluoride, molybdate, selenate, selenite, arsenate, and arsenite anions.

5.8. ION EXCHANGE WITH BOTTOM SEDIMENTS

Bottom sediments are important sources of inorganic and organic matter in streams, fresh-water impoundments, estuaries, and oceans. It is incorrect to consider bottom sediments simply as wet soil. Normal soils are in contact with the atmosphere and are aerobic, whereas the environment around bottom sediments is usually anaerobic, so sediments are subjected to reducing conditions. Bottom sediments undergo continuous leaching, whereas soils do not. The level of organic matter in sediments is generally higher than that in soils.

One of the most important characteristics of bottom sediments is their ability to exchange cations with the surrounding aquatic medium. **Cation-exchange capacity** (CEC) measures the capacity of a solid, such as a sediment, to sorb cations. It varies with pH and with salt concentration. Another parameter, **exchangeable cation status** (ECS), refers to the amounts of specific ions bonded to a given amount of sediment. Generally, both CEC and ECS are expressed as milliequivalents per 100 g of solid.

Because of the generally anaerobic nature of bottom sediments, special care must be exercised in their collection and treatment. Particularly, contact with atmospheric oxygen rapidly oxidizes exchangeable Fe^{2+} and Mn^{2+} to nonexchangeable oxides containing the metals in higher oxidation states as Fe_2O_3 and MnO_2. Therefore, sediment samples must be sealed and frozen as soon as possible after they are collected.

A common method for the determination of CEC consists of: (1) treating the sediment with a solution of an ammonium salt so that all exchangeable sites are occupied by NH_4^+ ion; (2) displacing the ammonium ion with a solution of NaCl; and (3) determining the quantity of displaced ammonium ion. The CEC values may then be expressed as the number of milliequivalents of ammonium ion exchanged per 100 g of dried sample. Note that the sample must be dried *after* exchange.

The basic method for the determination of ECS consists of stripping all of the exchangeable metal cations from the sediment sample with ammonium acetate. Metal cations, including Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Na^+, K^+, Ca^{2+}, and Mg^{2+}, are then determined in the leachate. Exchangeable hydrogen ion is very difficult to determine by direct methods. It is generally assumed that the total cation exchange capacity minus the sum of all exchangeable cations except hydrogen ion is equal to the exchangeable hydrogen ion.

Freshwater sediments typically have CEC values of 20-30 milliequivalents/100 g. The ECS values for individual cations typically range from less than 1 to 10-20 milliequivalents/100 g. Sediments are important repositories of metal ions that may be exchanged with surrounding waters. Furthermore, because of their capacity to sorb and release hydrogen ions, sediments have an important buffering effect in some waters.

Trace-Level Metals in Suspended Matter and Sediments

Sediments and suspended particles are important repositories for trace amounts of metals such as chromium, cadmium, copper, molybdenum, nickel, cobalt, and manganese. These metals may be present as discrete compounds, ions held by cation-exchanging clays, bound to hydrated oxides of iron or manganese, or chelated by insoluble humic substances. The form of the metals depends upon pE. Examples of specific trace-metal-containing compounds that may be stable in natural waters under oxidizing and reducing conditions are given in Table 5.3. Solubilization of metals from sedimentary or suspended matter is often a function of the complexing agents present. These include amino acids, such as histidine, tyrosine, or cysteine; citrate ion; and, in the presence of seawater, chloride ion. Suspended particles containing trace elements may be in the submicrometer size range. Although less available than metals in true solution, metals held by very small particles are more accessible than those in sediments. Among the factors involved in metal availability are the identity of the metal, its chemical form (type of binding, oxidation state), the nature of the suspended material, the type of organism taking up the metal, and the physical and chemical conditions in the water. The pattern of trace-metal occurrence in suspended matter in relatively unpolluted water tends to correlate well with that of the parent minerals from which the suspended solids originated; anomalies appear in polluted waters where industrial sources add to the metal content of the stream.

Table 5.3. Inorganic Trace Metal Compounds That May be Stable under Oxidizing and Reducing Conditions.

	Discrete compound that may be present	
Metal	Oxidizing conditions	Reducing conditions
Cadmium	$CdCO_3$	CdS
Copper	$Cu_2(OH)_2CO_3$	CuS
Iron	$Fe_2O_3 \bullet x(H_2O)$	FeS, FeS_2
Mercury	HgO	HgS
Manganese	$MnO_2 \bullet x(H_2O)$	MnS, $MnCO_3$
Nickel	$Ni(OH)_2$, $NiCO_3$	NiS
Lead	$2PbCO_3 \bullet Pb(OH)_2$, $PbCO_3$	PbS
Zinc	$ZnCO_3$, $ZnSiO_3$	ZnS

The toxicities of heavy metals in sediments and their availability to organisms are very important in determining the environmental effects of heavy metals in aquatic systems. Many sediments are anaerobic, so that microbial reduction of sulfate to sulfide leads to a preponderance of metal sulfides in sediments. The very low solubilities of sulfides tend to limit bioavailability of metals in anaerobic sediments. However, exposure of such sediments to air, and subsequent oxidation of sulfide to sulfate, can release significant amounts of heavy metals. Dredging operations can expose anaerobic sediments to air, leading to oxidation of sulfides and release of metals such as lead, mercury, cadmium, zinc, and copper.[5]

Phosphorus Exchange with Bottom Sediments

Phosphorus is one of the key elements in aquatic chemistry and is thought to be the limiting nutrient in the growth of algae under many conditions. Exchange with sediments plays a role in making phosphorus available for algae and contributes, therefore, to eutrophication. Sedimentary phosphorus may be classified into the following types:

- **Phosphate minerals**, particularly hydroxyapatite, $Ca_5OH(PO_4)_3$
- **Nonoccluded phosphorus**, such as orthophosphate ion bound to the surface of SiO_2 or $CaCO_3$. Such phosphorus is generally more soluble and more available than occluded phosphorus (below).
- **Occluded phosphorus** consisting of orthophosphate ions contained within the matrix structures of amorphous hydrated oxides of iron and aluminum and amorphous aluminosilicates. Such phosphorus is not as readily available as nonoccluded phosphorus.
- **Organic phosphorus** incorporated within aquatic biomass, usually of algal or bacterial origin.

In some waters receiving heavy loads of domestic or industrial wastes, inorganic polyphosphates (from detergents, for example) may be present in sediments. Runoff from fields where liquid polyphosphate fertilizers have been used might possibly provide polyphosphates sorbed on sediments.

Organic Compounds on Sediments and Suspended Matter

Many organic compounds interact with suspended material and sediments in bodies of water.[6] Colloids can play a significant role in the transport of organic pollutants in surface waters, through treatment processes, and even to a limited extent in groundwater. Settling of suspended material containing sorbed organic matter carries organic compounds into the sediment of a stream or lake. For example, this phenomenon is largely responsible for the presence of herbicides in sediments containing contaminated soil particles eroded from crop land. Some organics are carried into sediments by the remains of organisms or by fecal pellets from zooplankton that have accumulated organic contaminants.

Suspended particulate matter affects the mobility of organic compounds sorbed to particles. Furthermore, sorbed organic matter undergoes chemical degradation and biodegradation at different rates and by different pathways compared to organic matter in solution. There is, of course, a vast variety of organic compounds that get into water. As one would expect, they react with sediments in different ways, the type and strength of binding varying with the type of compound. An indication of the variable nature of the binding of organic compounds to sediments is provided by evidence that release of the compounds from sediments to water often occurs in two stages, the first rapid and the second slow.[7]

The most common types of sediments considered for their organic binding abilities are clays, organic (humic) substances, and complexes between clay and humic substances. Both clays and humic substances act as cation exchangers. Therefore, these materials sorb cationic organic compounds through ion exchange. This is a relatively strong sorption mechanism, greatly reducing the mobility and biological activity of the organic compound. When sorbed by clays, cationic organic compounds are generally held between the layers of the clay mineral structure where their biological activity is essentially zero.

Since most sediments lack strong anion exchange sites, negatively charged organics are not held strongly at all. Thus, these compounds are relatively mobile and biodegradable in water despite the presence of solids.

The degree of sorption of organic compounds is generally inversely proportional to their water solubility. The more water-insoluble compounds tend to be taken up strongly by lipophilic (“fat-loving”) solid materials, such as humic substances (see Section 3.17). Compounds having a relatively high vapor pressure can be lost from water or solids by evaporation. When this happens, photochemical processes (see Chapter 9) can play an important role in their degradation.

The herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) has been studied extensively in regard to sorption reactions. Most of these studies have dealt with pure clay minerals, however, whereas soils and sediments are likely to have a strong clay-fulvic acid complex component. The sorption of 2,4-D by such a complex can be described using an equation of the Freundlich isotherm type,

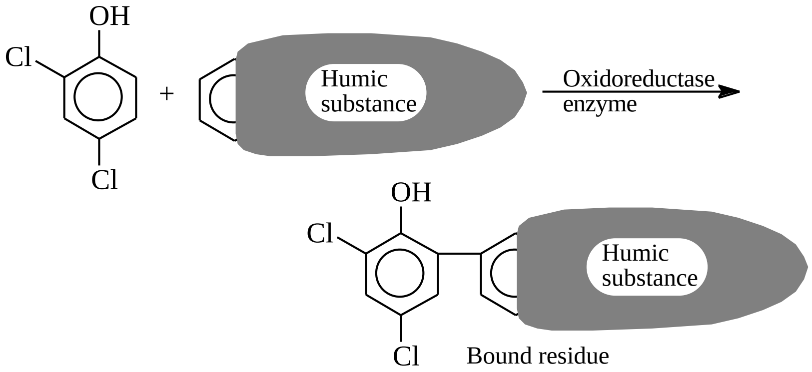
$$X = KC^n \tag{5.8.1}$$

where X is the amount sorbed per unit weight of solid, C is the concentration of 2,4-D in water solution at equilibrium, and n and K are constants. These values are determined by plotting log X versus log C. If a Freundlich-type equation is obeyed, the plot will be linear with a slope of n and an intercept of log K. In a study of the sorption of 2,4-D on an organoclay complex,[8] n was found to be 0.76 and log K was 0.815 at 5˚C; at 25˚C, n was 0.83 and log K was 0.716.

Sorption of comparatively nonvolatile hydrocarbons by sediments removes these materials from contact with aquatic organisms but also greatly retards their biodegradation. Aquatic plants produce some of the hydrocarbons that are found in sediments. Photosynthetic organisms, for example, produce quantities of n-heptadecane. Pollutant hydrocarbons in sediments are indicated by a smooth, chain-length distribution of n-alkanes and thus can be distinguished from hydrocarbons generated photosynthetically in the water. An analysis of sediments in Lake Zug, Switzerland, for example, has shown a predominance of pollutant petroleum hydrocarbons near densely populated areas.

The sorption of neutral species like petroleum obviously cannot be explained by ion-exchange processes. It probably involves phenomena such as Van der Waals forces (a term sometimes invoked when the true nature of an attractive force is not understood, but generally regarded as consisting of induced dipole-dipole interaction involving a neutral molecule), hydrogen bonding, charge-transfer complexation, and hydrophobic interactions.

In some cases pollutant compounds become covalently bound as “bound residues” to humic substances in soil.[9] It is plausible that the same occurs in sediments formed from soil washed into a body of water or directly onto sediments. It is very difficult to remove such residues from humic substances thermally, biochemically, or by exposure to acid or base (hydrolysis). The binding is thought to occur through the action of enzymes from some organisms. These enzymes are extracellular enzymes (those acting outside the cell) that act as oxidoreductases, which catalyze oxidation-reduction reactions. Such enzymes are capable of causing polymerization of aromatic compounds, as illustrated below for the coupling of pollutant 2,4-dichlorophenol to an aryl ring on a humic substance molecule:



(5.8.2)

Obviously, uptake of organic matter by suspended and sedimentary material in water is an important phenomenon. Were it not for this phenomenon, it is likely that pesticides in water would be much more toxic. Biodegradation is generally slowed down appreciably, however, by sorption of a substance to a solid. In certain intensively farmed areas, there is a very high accumulation of pesticides in the sediments of streams, lakes, and reservoirs. The sorption of pesticides by solids and the resulting influence on their biodegradation is an important consideration in the licensing of new pesticides.

The transfer of surface water to groundwater often results in sorption of some water contaminants by soil and mineral material. To take advantage of this purification effect, some municipal water supplies are drawn from beneath the surface of natural or artificial river banks as a first step in water treatment. The movement of water from waste landfills to aquifers is also an important process (see Chapter 19) in which pollutants in the landfill leachate may be sorbed by solid material through which the water passes.

The sorption of dilute solutions of halogenated and aryl hydrocarbons by soil and sand has been studied under simulated water infiltration conditions.[10] The relationship between the sorption equilibria observed may be expressed by the formula

$$S = K_pC \tag{5.8.2}$$

where S and C are the concentrations of hydrocarbons in the solid and liquid phases, respectively, and K_p is the partition coefficient. It was found that the two most important factors in estimating the sorption of nonpolar organic compounds were: (1) the fraction of organic carbon, f_{oc}, in the solid sorbents; and (2) the 1-octanol/water partition coefficient, K_{ow}, of the organic compound. (The K_{ow} value is a measure of the tendency of a solute to dissolve from water into immiscible 1-octanol. This long-chain alcohol mimics lipid (fat) tissue, and K_{ow} is used to indicate a tendency toward bioaccumulation of solutes in water.) The K_p of individual compounds was determined using the following empirical relationship:

$$\text{Log } K_p = 0.72 \log K_{ow} + \log f_{oc} + 0.49 \tag{5.8.3}$$

The sorption was found to be reversible on the solids studied, which included natural aquifer material, river sediment, soil, sand, and sewage sludge. The organic compounds studied included methylbenzene compounds containing from 1 to 4 chlorine atoms, tetrachloroethylene, n-butylbenzene, benzene, acetophenone, tetrachloroethane, naphthalene, parathion, β-BHC, DDT (the latter three compounds are insecticides), pyrene, and tetracene.

5.9. SORPTION OF GASES—GASES IN INTERSTITIAL WATER

Interstitial water or *pore water* consisting of water held by sediments is an important reservoir for gases in natural water systems. Generally, the gas concentrations in interstitial waters are different from those in the overlying water. The results of the analyses of gases in interstitial water in some sediments taken from Chesapeake Bay[11] are given in Table 5.4. Examination of this table shows that CH_4 could not be detected at the sediment surface, which is because the equilibrium concentration of methane in air is very low, and it is biodegradable under aerobic conditions. However, of the gases analyzed, by far the highest concentration at a depth of one meter was that of methane. The methane is produced by the anaerobic fermentation of biodegradable organic matter, $\{CH_2O\}$, (see Section 6.6):

$$2\{CH_2O\} \rightarrow CH_4(g) + CO_2(g) \qquad (5.9.1)$$

The concentrations of argon and nitrogen are much lower at a depth of one meter than they are at the sediment surface. This finding may be explained by the stripping action of the fermentation-produced methane rising to the sediment surface.

Table 5.4. Gases in Interstitial Waters from Chesapeake Bay Sediments.

Gas	Depth	Gas concentration, mL/L
N_2	surface	13.5
N_2	1.00 m	2.4
Ar	surface	0.35
Ar	1.00 m	0.12
CH_4	surface	0.00
CH_4	1.00 m	140

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QUESTIONS AND PROBLEMS

1. A sediment sample was taken from a lignite strip-mine pit containing highly alkaline (pH 10) water. Cations were displaced from the sediment by treatment with HCl. A total analysis of cations in the leachate yielded, on the basis of millimoles per 100 g of dry sediment, 150 mmol of Na^+, 5 mmol of K^+, 20 mmol of Mg^{2+}, and 75 mmol of Ca^{2+}. What is the cation exchange capacity of the sediment in milliequivalents per 100 g of dry sediment?
2. What is the value of $[O_2(aq)]$ for water saturated with a mixture of 50% O_2, 50% N_2 by volume at 25˚C and a total pressure of 1.00 atm?
3. Of the following, the least likely mode of transport of iron(III) in a normal stream is: (a) bound to suspended humic material, (b) bound to clay particles by cation exchange processes, (c) as suspended Fe_2O_3, (d) as soluble Fe^{3+} ion, (e) bound to colloidal clay-humic substance complexes.
4. How does freshly precipitated colloidal iron(III) hydroxide interact with many divalent metal ions in solution?
5. What stabilizes colloids made of bacterial cells in water?
6. The solubility of oxygen in water is 14.74 mg/L at 0˚C and 7.03 mg/L at 35˚C. Estimate the solubility at 50˚C.
7. What is thought to be the mechanism by which bacterial cells aggregate?
8. What is a good method for the production of freshly precipitated MnO_2?
9. A sediment sample was equilibrated with a solution of NH_4^+ ion, and the NH_4^+ was later displaced by Na^+ for analysis. A total of 33.8 milliequivalents of NH_4^+ were bound to the sediment and later displaced by Na^+. After drying, the sediment weighed 87.2 g. What was its CEC in milliequivalents/100 g?
10. A sediment sample with a CEC of 67.4 milliequivalents/100 g was found to contain the following exchangeable cations in milliequivalents/100 g: Ca^{2+}, 21.3; Mg^{2+}, 5.2; Na^+, 4.4; K^+, 0.7. The quantity of hydrogen ion, H^+, was not measured directly. What was the ECS of H^+ in milliequivalents/100 g?

11. What is the meaning of *zero point of charge* as applied to colloids? Is the surface of a colloidal particle totally without charged groups at the ZPC?

12. The concentration of methane in an interstitial water sample was found to be 150 mL/L at STP. Assuming that the methane was produced by the fermentation of organic matter, $\{CH_2O\}$, what weight of organic matter was required to produce the methane in a liter of the interstitial water?

13. What is the difference between CEC and ECS?

14. Match the sedimentary mineral on the left with its conditions of formation on the right:

    (a) FeS(*s*)
    (b) $Ca_5OH(PO_4)_3$
    (c) $Fe(OH)_3$
    (d) $CaCO_3$

    (1) May be formed when anaerobic water is exposed to O_2.
    (2) May be formed when aerobic water becomes anaerobic.
    (3) Photosynthesis by-product.
    (4) May be formed when wastewater containing a particular kind of contaminant flows into a body of very hard water.

15. In terms of their potential for reactions with species in solution, how might metal atoms, M, on the surface of a metal oxide, MO, be described?

16. Air is 20.95% oxygen by volume. If air at 1.0000 atm pressure is bubbled through water at 25˚C, what is the partial pressure of O_2 in the water?

17. The volume percentage of CO_2 in a mixture of that gas with N_2 was determined by bubbling the mixture at 1.00 atm and 25˚C through a solution of 0.0100 M $NaHCO_3$ and measuring the pH. If the equilibrium pH was 6.50, what was the volume percentage of CO_2?

18. For what purpose is a polymer with the following general formula used?