VI. SORPTION

Sorption: "A surface phenomenon which may be either **ab**sorption or **ad**sorption, or a combination of the two. The term is often used when the specific mechanism is not known." (Hawley's Condensed Chemical Dictionary, 11th Ed.).

A. Introduction

Adsorption is the association of an *adsorbate* compound *onto* a surface (*sorbent*), usually in a liquid/solid or vapor-solid system, while *absorption* involves the redistribution of a compound from the aqueous phase *into* a volume of material. In geochemical systems, however, the two are often indistinguishable, and the term *sorption* is almost always used. Sorptive surfaces are ubiquitous, and sorption is a fate mechanism that can be present in virtually any aquatic or ground water system.

Sorption to *immobile* sediments is the basis of concept of *retardation*, and as such is fundamental to an understanding of contaminant-transport.   Sorption to *mobile* sediments is also of critical importance. While it might seem arbitrary to separate *dissolved* compound from compound sorbed onto a micron-sized colloid, the distinction is vital. First, thermodynamic controls on contaminant behavior are based on the *activity* of dissolved solute only, and sorbed molecules are not included. Second, sparingly soluble hydrophobic compounds, such as PNA's, are significantly more mobile sorbed to colloids than they are as dissolved substance. Finally, current wisdom suggests that compound sorbed to a surface is not available to microorganisms for biodegradation, but some surface can accelerate certain abiotic transformation reactions, such as hydrolysis and redox. So sorption can both mobilize and immobilize a dissolved contaminant, enhance and inhibit contaminant degradation.

B. Objectives

1. Learn the basic properties of oxide surfaces and surface charge
2. Distinguish between adsorption and absorption, and their roles in sorption.
3. Examine the basic sorption isotherms, the surface interactions responsible for these isotherms, and where they are encountered in natural systems
4. Determine the relative importance of adsorption on minerals and absorption into soil organic matter in the retardation of contaminant transport.
5. Determine the importance of colloidal organic matter in the mobility of hydrophobic organic contaminants.

C. Molecular basis of sorption

Sorption has traditionally been divided into two extremes: weak physi-sorption, and strong chemi-sorption. Each specific sorption interaction, however, is usually somewhere in-between these two extremes. To understand these terms, however, we must first understand the molecular nature of the surface, and of the sorbate.

Sorption is a broad term that really includes several elementary reactions. Sorption can involve strong electrostatic interactions between ions or dipoles and surfaces, including *ion exchange* type reactions. Sorption can also involve only weak intermolecular forces such as van der Waals interactions. As used by geochemists, sorption to natural surfaces also generally includes **ad**sorption on surfaces and **ab**sorption (partitioning) into SOM. The starting place for sorption therefore should be a description of the surface....

1. The oxide surface:

Figure 6-1: Schematic of a silicate mineral surface. From *Environmental Organic Geochemistry*, Schwarzenbach, R.P., Gschwend, P.M., and Imboden, D.M. Copyright © 1993, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc..
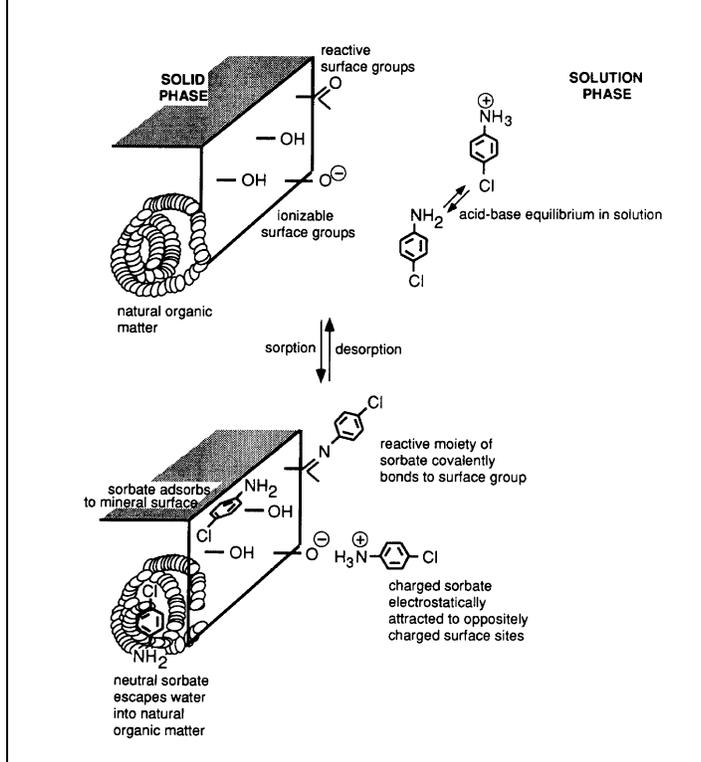
- The *surface* of a solid represents an interface between the gas or solution phase and the mineral crystal. The nature of that interface depends on the nature of both the crystal phase, and the solution or gas phase.

- The solid surface can be represented as a surface of discrete sites, and each one individually participates in a reaction resulting in sorption. Many aquifer materials are silicates or oxides, both described as an oxide.

- The dry oxide surface can be "simply" described as a surface of *amphoteric* hydroxyl sites, each capable of both donating and accepting a proton, resulting in anionic, neutral and cationic sites, depending on pH and hydroxyl pK.

- In aqueous systems, these charged sites strongly attract water (another amphoteric dipole), creating a layer of tightly-bound water at the surface (*vicinal water*). So the adsorbing organic molecule "sees" a charged surface of water, any direct association with that surface must first displace that water.

2. Surface Charge and the double layer

Surface charge on oxide surfaces primarily originates from three sources: protonation and deprotonation of surface hydroxyls, isomorphous substitution of aluminum for silicon in clays, and the sorption of charged species.

a) Variable surface charge

- The surface hydroxyls on oxides and silicates can gain or lose a proton, resulting in a surface charge that varies with changing pH.
    - ⇒ At low pH, surface sites are protonated: $H^+ + =OH \longrightarrow =OH_2^+$ and the surface will be *cationic*, or positively charged.
    - ⇒ At high pH, the surface hydroxyls lose their protons: $=OH \longrightarrow H^+ + =O^-$, and the surface is anionic
    - ⇒ When the concentration of cationic $=OH_2^+$ sites equals the concentration of anionic $=O^-$ sites, the average surface charge is neutral, that pH is known as the ZPC, or zero point of charge.

b) *Fixed surface charge*

- Isomorphous substitution of tetravalent silicon by trivalent aluminum in layer clays results in a permanent negative charge, which must be balanced by a cation. While the fixed charge can't be changed, the counterion is exchangeable.

c) *The double layer*

The electrical double layer at the hydrated oxide surface can be both simple and complex, depending on the need. As an example, we will examine a silica surface in an aqueous system above the ZPC (about pH 2 for silica).
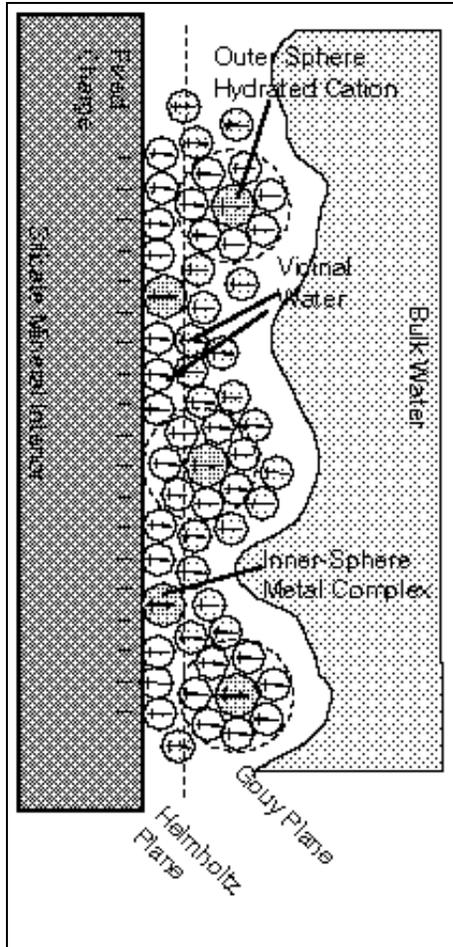
1. The solid surface itself is negatively charged, and the charge density and is constant at constant pH and temperature
2. In pure water, this charged layer would attract oriented water molecules, forming a highly structured inner layer of *vicinal* surface water that more closely resembles ice than water, with a very low dielectric constant (6 vs 78.5 for bulk water).
3. A second layer of less structured water will form with the opposite orientation. This water may have a dielectric constant near 30.
4. Hydrated cations in solution will associate with the surface anionic sites, forming a fairly immobile layer of surface cations (the *Stern* layer). The ability to penetrate to the surface depends on the hydrated radius: $Cs>NH_4>K>Na>Li$. Waters of hydration will add to the vicinal water layer.
5. Anions will loosely associate with the Stern layer, forming a diffuse negative *Gouy layer*. The charge density will decline with distance from the surface until the bulk water composition is regained.
6. The thickness of the double layer decreases with increasing ionic strength.

Figure 6-2: Molecular model of the surface double layer. Modified from Adamson, 1990, pg. 235.

- While the nature of the double layer is most important for characterizing ion exchange and ion adsorption reactions, the structure of this layer strongly influences the adsorption of neutral hydrophobic compounds as well.
- In order to sorb to a hydrated mineral surface, the organic solute must break multiple hydrogen bonds that form the tightly structured vicinal water, while the bonds that are formed are much weaker van der Waals type bonds. This it energetically unfavorable, resulting in low K's of sorption for mineral surfaces.
- At very low moisture contents, less than 2 molecular layers of water, vapor-phase sorption can occur on the vicinal water, or onto non-hydrated patches of mineral surfaces. In this case relatively high K's of sorption are encountered.

3. Sorption of gasses on solid surface:

The original development of sorption isotherms used the gas-solid system, and it is still the easiest way to introduce the important points. Vapor-phase sorption is also important in environmental chemistry as a sink for volatile organic compounds in the vadose zone.

a) *Physisorption*

- **Physisorption** occurs when vapors near their saturation pressures adsorb to a dry surface in a process that resembles condensation. The van der Waals forces and weak dipole interactions present here have heats of adsorption typically a few hundred cal/deg.mol..
    - ⇒ Physisorption is very rapid and reversible, with the equilibrium established quickly as the gas pressure is varied.
    - ⇒ Physisorption is generally considered important only for vapors below their critical temperature, which may include vapor-phase sorption of volatile organic compounds onto soil surfaces in the vadose zone.
    - ⇒ Longer range forces are causing the attraction to occur, therefore multiple layers of adsorbed ions can build up on the surface.

b) *Chemisorption (specific adsorption)*

- **Chemisorption** is often associated with heterogeneous catalysis, and involves strong bonding of the sorbate to the sorbent, often resulting in a change in both the surface and sorbate chemical character.
    - ⇒ Adsorbed species are chemically bound to the surface creating something like a "surface compound" ex. O_2 on a shiny aluminum surface.
    - ⇒ Chemisorption is the result of relatively strong binding forces (>30kcal/mol), and is characterized by high adsorption energies.
    - ⇒ The reactions is likely to be slow, and less readily reversible, in the sense that equilibrium may take longer to achieve.
    - ⇒ Adsorbed species are limited to the formation of a monolayer, because direct interaction between the gas and the surface is required. Once the surface is covered, physisorption can continue

4. Sorption from Solution

- Oxide surfaces in aqueous systems adsorb water molecules via strong electrostatic interactions called *hydrogen bonds*, where the proton on water associates with the surface oxygen at the oxide surface.
- For a solute to chemisorb (form an *inner-sphere complex*) at the aquated oxide surface, the sorbing molecule must displace one of these strongly bound waters, a difficult, and energy-intensive interaction.
    - ⇒ For this reason, the K_{sorp} would be expected to be low for neutral organic compounds, higher for polar compounds that can compete for charged sites.
- When hydrophobic molecules associate with soil organic matter, however, there is no competition with water, and the interactions resembles a dissolution reaction into an organic solvent. This requires much less energy, and the associated K is much higher. For wet oxide surfaces, absorption into SOM is the primary interaction for retardation.

D. The adsorption Isotherm.

- Adsorption isotherms describe the equilibrium relationship between bulk activity of absorbate in solution and the moles adsorbed on the surface, *at constant temperature*. While adsorption as a reaction is a function of temperature and pressure, isotherms are a function of pressure only

- Adsorption isotherm expression are derived at least in part from fundamental principles of the adsorption process, but usually are empirically based.
  ⇒ Experimental data are often successfully fit by an isotherm expressions whether the experimental system satisfies the assumptions of the isotherm derivation or not.

- Brunauer described 5 general types of gas-solid sorption isotherms:

1. Type 1. (Langmuir Type)
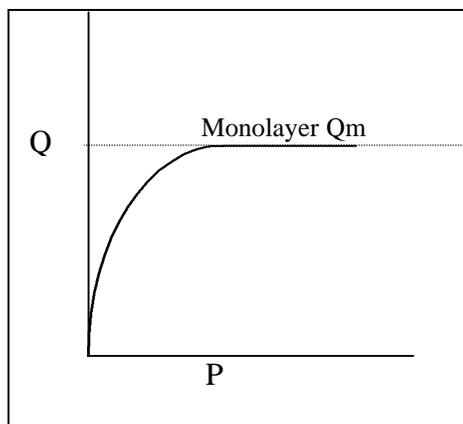
- A good representation of chemisorption, and usually represents the low P portion of other isotherms.
- Adsorption sequentially fills surface sites until mono-layer coverage is achieved. No multi-layer coverage is included. Each site is equivalent in energy.
- Langmuir behavior assumes rapid reversible sorption, and interaction only between sorbate molecules and a surface site.
- The lower portion is linear

The equation for the Langmuir isotherm is usually given as: $Q = \dfrac{Q_m bP}{1 + bP}$ where Q is

the amount sorbed, Qm is the monolayer coverage, Cg is gas phase concentration (P), and b is a constant. While the Langmuir isotherm is rarely useful in real, heterogeneous systems, it illustrates well the concept of monolayer coverage.

2. Type 2 (BET Type)
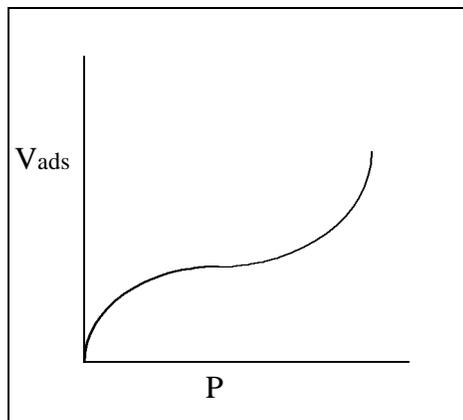
- The BET equation is an extension of the Langmuir relationship that accounts for multilayer coverage.
- Here multiple layers can form before the monolayer is complete, with multiple layers forming as a "condensation" reaction.
- At high P, the adsorbate condenses to a bulk liquid on the surface, the number of layers becomes infinite.
- This isotherm describes well the physisorption of an organic vapor onto very dry surface soils.

VI-5

Here the equation is: $Q = \dfrac{QmcP}{(P^o - P)[1 + (c-1)(P/P^o)]}$; where P° is the saturated vapor pressure, and c is a constant related to the energy (enthalpy) of adsorption. While this is effective in describing vapor-phase adsorption on dry soils, it does not describe electrostatic interactions of ions onto a heterogeneous surface in an aqueous system.

3. Type 3 (Freundlich type)
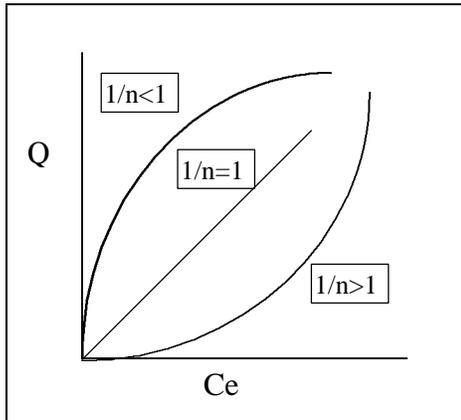
- A well-used empirical isotherm is the Freundlich relationship, which allows for a heterogeneous surface that is more often seen in natural systems.
- When 1/n >1, the sorption constant increases with increasing solution concentration, perhaps reflecting an increase in the hydrophobic character of the surface after a monolayer
- When 1/n<1, K decreases with solution concentration as the low-energy sites are occupied. 1/n slightly greater than 1 is often found for organic solutes

The Freundlich equations is: $Q = K_F C_e^{1/n}$

4. Linear Isotherms

- When 1/n = 1, the isotherm becomes a linear relationship, which often closely describes the *ab*sorption reaction of an organic molecule partitioning into soil organic matter. There is no linear portion in either of the other two cases.

a) Distribution Coefficient

- The K_d expression describes a linear relationship between the dissolved concentration of absorbate ion and the concentration adsorbed to the surface. Linear adsorption best describes systems at low concentration, where the Langmuir relationship is still linear.
- The end result assumes that the amount of a solute sorbed is directly proportional to the concentration in solution. The K_d expression is derived from the Langmuir isotherm, assuming P is very small and KP is << 1:
- The measured K_d value is an operational parameter with no thermodynamic significance, but it is still useful in describing simple systems. The value of the K_d is restricted to the system for which that value was obtained.

E. Factors Affecting Sorption:

1. Surface area,

- Adsorption is a surface phenomena that is directly related to surface area. Increase the surface area, and specific adsorption will increase.
- Often however, sorption is reported as a bulk property on a per gram weight basis. With these units, it has been shown that clays have a much higher sorptive capacity than do other minerals.
- If all else were equal, a unit area of clay has the same sorptive capacity as a the same unit area of goethite. Sorption should **always** be reported on an area basis.
- The definition of surface area, however, is hazy, and often difficult to measure unambiguously. Micro pores and molecular porosity increase the sorptive capacity, but are not necessarily measured.
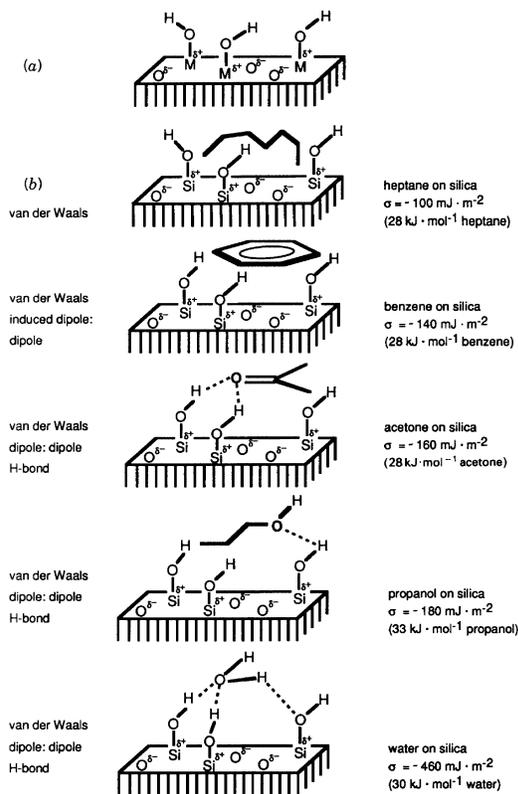

Figure 6-3: Potential sorbent-sorbate interactions. From *Environmental Organic Geochemistry*, Schwarzenbach, R.P., Gschwend, P.M., and Imboden, D.M. Copyright © 1993, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

2. Mineral surface properties.

- Surface charge of an oxide mineral surface in aqueous systems will change with changing pH as a function of the ZPC of that mineral.
- This surface charge creates a surface condition in which there is an uneven charge distribution, creating a double-layer of ions.
- Charged organic solutes may exchange with other counter-ions in the double layer, resulting in physisorption.

3. Organic carbon and the K_{OC}

- It has been found that the sorption of hydrophobic organic compounds is strongly controlled by the presence of soil organic material.
- While the reaction resembles that of sorption, and will fit a sorption isotherm, it is actually partitioning.
- The K_{OC} then is an expression describing the *partitioning* of a solute between the aqueous and organic phases.

4. Solubility:
- As the solubility of a hydrophobic compound decreases, the adsorption coefficient. increases, probably from entropy driven interaction with the surface.

5. Temperature
- Since adsorption is an exothermic process, values of K usually decrease with increasing temperature. A 10% decrease in K_{sorp} would occur with a temperature rise from 20 to 30 C.
- The probable control is the aqueous activity coefficient, with the variation in γ depending on the magnitude of ΔH (e.g. Schwarzenbach et al., 1993):

$$\ln g_w = \frac{\Delta H_s^e}{RT} + C \tag{6-X}$$

$$\Delta H_s^e \cong -RT \ln x_w + T\Delta S_s^e \tag{)6-X}$$

- For large apolar compounds the Δh_{abs} is about -25kJ/mol.

6. pH
- Only chemicals that tend to ionize are much affected by pH, the only influence on neutral molecules would be the change in the character of the surface, For example, at low pH, humic materials are nearly neutral and more hydrophobic.
- Changes in pH will dramatically affect organic acids and bases by changing solubility. Cations resulting from the protonation of an organic base, for example, may more strongly sorb to soils at then the neutral species.
- As pH changes, surface charge also changes, and the sorption of charged species will be affected.

7. Salinity
- An increase in salinity can significantly lower the adsorption coefficient of cations, probably due to replacement/exchange by alkali cations.
- The adsorption of some acid herbicides increases with greater salinity at pH values above the pK_a of the acid. pH therefore influences the affects of salinity.
- Neutral molecules are generally less affected by salinity, but often show an increased adsorption with increasing salt concentration, probably due to the increase in the activity coefficient of neutral molecules and resulting decrease in aqueous solubility, i.e. salting out. (Karickhoff et al., 1979; Eaganhouse and Calder, 1982).
  - For example, pyrene sorption increased 15% with an increase of salinity from 0 to 0.34 M sodium chloride (Karickhoff et al., 1979).
- Increased salinity may also change the interlayer spacing of layer clays, as well as the morphology of soil organic matter.

8. Co-solvents and dissolved organic matter:
- Co-solvents are water soluble organic solvents, such as methanol or acetone. These may be present in the aquifer as a part of a mixed waste. Co solvents can decrease the K_{sorp} by increasing the apparent solubility. The pyrene K_{sorp} for example, decreases by 30% in 10% methanol.
- The presence of dissolved organic matter commonly reduces the adsorption of a chemical. This may be due to the increased solubility of the chemical in such a solution, or to competitive adsorption to organic colloids.

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