

CHAPTER 1 Theoretical Considerations of Partition Uptake of Nonionic Compounds by Soil Organic Matter

1. P. 4 1-1 PARTITION CHARACTERISTICS IN SOLVENT-WATER SYSTEMS

$$\text{Log } K = -\log S_w - \log V_o^* - \log \gamma_o^* - \log (\gamma_w/\gamma_w^o) \quad [1]$$

where: K = solute partition coefficient = $\frac{\text{solute conc. in organic phase}}{\text{solute conc. in water phase}}$

S_w = molar water solubility of solute (mol/L)

V_o^* = molar volume of water-saturated organic phase (L/mol)

γ_o^* = solute activity coefficient in water-saturated solvent phase

γ_w = solute activity coefficient in water

γ_w^* = solute activity coefficient in solvent-saturated water.

2. **Important points for relatively water-insoluble organic solutes:**

Characteristics associated with partitioning of organic compounds into an organic phase:

- (1) Magnitude of K determined primarily by reciprocal of S_w , rather than by solubility in organic solvent (magnitude of γ_o^*).

Therefore: one finds a linear inverse relationship between $\log K_{ow}$ and $\log S_w$ (for a wide range of chemical classes). Table 1 & Fig. 1-1.

- (2) (p. 6) K is largely independent of solute concentration.

Therefore: a linear isotherm (solute conc. in organic phase vs in water phase) should exist over a wide range of solute concentration relative to the solute's solubility. (This provides a basis for distinguishing a partition equilibrium from an adsorption equilibrium).

- (3) (p. 7). In partition equilibria, there is relative **independence of K in binary or multiple solute systems** (as is generally experienced in the solvent-solvent extraction of multiple solute components).

However, in **adsorption**, competition between solutes for adsorbent surfaces or specific sites of the adsorbent leads to reduction of the adsorption capacities of individual solutes in a multi-solute system relative to capacities as a single solute.

- (4) (p. 7). **Limiting partition capacities are smaller for compounds exhibiting higher partition coefficients.**

Therefore: Inverse relationship between limiting partition capacity and molecular weight is opposite to what one would expect for adsorption on a solid. Therefore, solutes with high molecular weights tend to have lower-limiting partition capacities. Reduction of solubility in the organic phase with increasing molecular weight of the

solute (which magnifies any incompatibility between solute and organic solvent) is expected for a partition process.

- (5) (p. 8). **Partition coefficients of organic compounds** (in solvent-water systems) **show small inverse dependence on temperature.**

Conversely, **adsorption** of a solute from solution on an adsorbent exhibits higher exothermic heat that results from condensation of the solute on the surface and from (exothermic) interaction of solute with the surface.

Implications for engineers:

In presence of NAPL phase (solvent) in subsurface:

- (1) chemicals will associate as $f(S_w)$;
- (2) $K_{(NAPL/water)}$ independent of chemical concentration
- (3) $K_{(NAPL/water)}$ will not be influenced by presence of other chemicals;
- (4) NAPL capacity inversely related to K
- (5) K will not be affected significantly by temperature

1-2 SORPTION BY SOIL IN AQUEOUS SYSTEMS

1. (p. 9). In water, equilibrium isotherms for sorption of non-ionic organic compounds on soils/sediments are usually linear.

2. (p.10). The high linear range of the isotherm + known dependence of sorption on soil organic matter in aqueous solutions ----> soil sorption of nonionic organic compounds from water is mainly by partitioning in (rather than by adsorption on) soil organic matter.

3. (p. 14) $S_{om} = K_{om} S_w$ [11]

S_{om} = solubility in soil organic matter

S_w = solubility in water.

Example with DDT: $S_{om} = 830$ mg/Kg; compare with solubility in octanol = 42 g/L, which is 50 times its solubility in organic matter. This is to be expected for DDT (nonpolar solid compound) in a polar high-molecular weight amorphous solid material. The high partition coefficient for DDT is a result of its low solubility in water!!

4. (p. 15). Soil organic matter: (1) soil does not display significant adsorption of nonionic organic compounds in water is due to the strong adsorptive competition of water for soil minerals, which results in displacement of organic compounds; and (2) low solubility (i.e., poor compatibility) of organic compounds in water enhances solute partitioning (solubilization) in soil organic-matter phase. e.g., sorption coefficient difference for benzene vs DDT.

5. (p. 15). TABLE 1-2. VERY GOOD!! STUDY

$$\log K_{om} = -0.813 \log (S_w V) - 0.993 \quad r^2 = 0.995 \quad [12]$$

Because variation in V among solutes is small compared to that of S_w , therefore,

$$\log K_{om} = -0.729 \log S_w + 0.001 \quad r^2 = 0.996 \quad [13]$$

6. (p. 17) (1) water insolubility is major determinant of K_{om} ;
- (2) soil organic matter is not nearly as good a solvent as ordinary organic solvents;
 - (3) therefore, $\log K_{om}$ value should be smaller than $\log K_{ow}$;
 - (4) $\log K_{om}$ should be linearly related to $\log K_{ow}$
 - (5) using data in TABLE 1-2: $\log K_{om} = 0.904 \log K_{ow} - 0.779 \quad r^2 = 0.989$ [14]

7. (p. 17) Expressed in terms of soil organic carbon, C (K_{oc}), then
$$K_{oc} = 1.72 K_{om}$$
by assuming that organic matter contains ~ 58% carbon

Stop discussion of chapter 1 (do not do pp. 17-26)

Implications for engineers:

(1) Calculate partitioning of organics in soil to evaluate pump and treat effectiveness:

(a) Use K_{ow} (book value) and % organic matter (measure) to calculate K_{om}

(b) Rank chemicals with regard to K_{om} to evaluate potential effectiveness of pump and treat systems.

(c) Can also use S_w to evaluate K_{om} for pump and treat or for soil flushing/washing

(2) Strategies for soil flushing - increase aqueous solubility of chemicals, since partitioning is primarily due to low S_w of chemicals, not to reaction with non-aqueous (soil or NAPL) phase.

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1. (p. 31) **Adsorption** = process where constituents are concentrated at the interface of two phases (solid-liquid, gaseous-liquid, gaseous-solid)
Absorption = process where a component is transferred from the bulk state of one phase into the bulk state of the other phase. (Dissolved oxygen dissolves in water)
Sorption = describes adsorption or absorption (do not know or specify process)
Sorption occurs when the free energy of the sorption reaction is negative:

$$\Delta G = \Delta H - T\Delta S$$

(enthalpy) (entropy)

Enthalpy term - primarily a function of the difference in bonding between adsorbing surface and the sorbate (solute), and bonding between the solvent (water) and solute.

Entropy term - related to increase or decrease in order of system upon sorption.

NOTE: FOLLOWING INFORMATION TAKEN FROM: "ELEMENTS OF PHYSICAL CHEMISTRY," BY MONCRIEF AND JONES c. 1977. pp. 65-79:

- $\Delta G < 0$ is criterion for spontaneity depends on (two states of function): entropy & enthalpy.
 - $\Delta H < 0$ (exothermic) and $\Delta S > 0$ (increase in disorder) is ok for $\Delta G < 0$
 - $\Delta H > 0$ (endothermic) and $\Delta S > 0$ is ok for $\Delta G < 0$
 - $\Delta H < 0$ and $\Delta S < 0$ (decrease in disorder) is ok if ΔH is large enough to overshadow the $T\Delta S$ term

SUMMARY TABLE

ΔH	ΔS	ΔG	State of system
< 0	> 0	< 0	lower energy; higher disorder
> 0	> 0	< 0	higher energy, higher disorder, $T\Delta S > \Delta H$
< 0	< 0	< 0	lower energy, lower disorder, $\Delta H > T\Delta S$

2. (p. 32) 2-1.1 **Enthalpy Related Adsorption Forces**
Sorption due to strong specific interaction between sorbate and sorbent.
This attraction overcomes solute-solvent interactions (that keep sorbing species in solution)
- (1) London-van der Waals (1-2 kcal/mol); (6) Induction (< 2 kcal/mol)
 - (2) Coulombic-electrostatic; (7) Chemisorption ($\Delta H > 7$ kcal/mol)
 - (3) Charge Transfer (π bonds, hydrogen bonds [2-10 kcal/mol])
 - (4) Ligand Exchange;
 - (5) Dipole-dipole or Orientation Energy (< 2 kcal/mol)
3. (p. 33) 2-1.2 **Entropy Related Adsorption Forces (HYDROPHOBIC SORPTION)**
Hydrophobic sorption is entropy driven.
The enthalpy term may or may not contribute to a negative free energy.
- (1) Hydrophobic sorption (Fig. 2-1, p.34) Very Good
 - (a) Partitioning of nonpolar organics out of the polar water phase onto hydrophobic surface in soil.
 - (b) Large entropy change resulting from removal of solute from solution.
 - (c) Major feature - weak interaction between solute and solvent.
4. (p. 34) 2-2 Isotherms. Sorption of nonpolar organics on soils produces linear isotherms up to 60% to 80% of aqueous concentrations of sorbing species water solubility (Fig. 2-2). Fig. 2-2 is an example of an ISOTHERM.

5. (p. 35) Linear portion of isotherm - described with **Freundlich equation**:

$$C_s = K_f C_w^{1/n}$$

1/n = 1 with many nonpolar species, therefore

$$C_s = K_f C_w$$

and K_f becomes a partition constant,

$$K_f = C_s/C_w = K_d$$

Engineering implications:

- (1) Use K_f (or K_d) in assessment of pump & treat as well as soil flushing;
 - (2) Use K_f (or K_d) in models of transport (VIP and ground water models)
6. (p. 35) Sorption of nonpolar organics - independent of temperature, i.e., lack of variation of K_f with Temperature ----->
- (1) small exothermic and endothermic enthalpies are involved in sorption, explained as due to similar enthalpies of solution in aqueous & organic phases;
 - (2) lack of strong bond formation between sorbing species and sorbent (humus). Nonpolar chemicals form weak van der Waal bonds with water and with humus; difference between the magnitude of the bonds (ΔH) is small upon sorption.
 - (3) this observation is supportive of the concept of partitioning between bulk water phase and bulk organic phase (humus).
 - (4) since the enthalpy term is small, the driving force has to be the entropy term, i.e., hydrophobic forces related to increased entropy of system upon destruction of the cavities (makes water more ordered than usual) in aqueous phase.
 - (5) (p. 36) K_{oc} illustrated in FIG. 2-3. $K_{oc} = K_f/\%$ organic carbon
 - (6) (p. 37) K_{oc} can be considered a compound property for nonpolar organics.
 - (7) (p. 38) Fig. 2-5: Relationship strong between Log K_{oc} and Log K_{ow} .

Engineering implications:

- (1) Get K_d for soil by looking up K_{oc} (or K_{ow} conversion) and measuring % OC
 - (2) Use K_d as discussed above (engineering implications)
7. (p. 38) 2-3.1 Contribution of Mineral Surfaces to Hydrophobic Sorption: when OC < 0.1%.
8. (p. 40) 2-3.2 Effect of modification of polarity of solvent
- (1) Fig. 2-8 Very Good. As % ethanol in water increased, R_f values changed in proportion to solubility of the three compounds in ethanol:water mixture.

Engineering implications:

- (1) Chromatographic effect of chemical transport in soil (predictions)
 - (2) For soil flushing or soil washing, change polarity of flushing solution.
9. 2-3.3 - Effects of Surfactants
- (1) (p. 41) Fig. 2-9 Shows effect of surfactant (sodium lauryl sulfate, LAS) on PCB mobility as related to critical micelle concentration (CMC).
10. (p. 43) Comments/Conclusions
- (1) Sorption process driven by (1) enthalpy or (2) entropy forces;
 - (2) Sorption of nonpolar chemicals - primarily entropy driven;
 - (3) Soils low in organic matter: K_{oc} - K_{ow} and K_{oc} -solubility relationships **not** adequate;
 - (4) K_{oc} - K_{ow} and K_{oc} -solubility good only for hydrophobic chemicals and hydrophobic contribution to sorption;
 - (5) **A basic understanding of water, solvent, and soil chemistry is essential to understanding sorption mechanisms and processes - for engineering applications.**

End chapter 2, p. 44 =====