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SORPTION OF HYDROPHOBIC COMPOUNDS BY SEDIMENTS, SOILS AND SUSPENDED SOLIDS—I

THEORY AND BACKGROUND

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Abstract—This is the first of a two-part series describing the adsorption of hydrophobic pollutants by sediments, soils, and suspended solids. Many pollutants, including a large number of hazardous compounds, are hydrophobic and their environmental behavior varies markedly between sorbed and dissolved states. It is thus necessary to account for sorption reactions in analysis and prediction of the environmental transport and fate of such pollutants. In this first part the energetics of sorption reactions are discussed and models for description of equilibrium relationships are summarized. Factors which affect the sorption of pollutants in natural environmental systems are then considered and evaluated.

INTRODUCTION

It has become evident in recent years that industrial and economic growth has not been without environmental cost. A realization that chemical contamination of the environment is extensive and significant has emerged, largely as a result of increased awareness and improved methods for evaluation. Certain chemicals are known to exhibit carcinogenic, mutagenic or teratogenic properties in small doses, and the accumulation of such agents in various compartments of the environment is cause for alarm. Regulatory response has limited further environmental contamination in certain cases. Nonetheless, the long half-lives and inter-compartmental transfer properties of many compounds, coupled with their tendencies to accumulate in the food chain, make them significant threats long after source abatement.

Certain halogenated hydrocarbons that have been used in a variety of industrial and agricultural applications are of particular environmental concern. Severe restrictions have been placed on the manufacture, sale, and use of such compounds as DDT, Aldrin, Dieldrin, PCB's, PBB's and numerous industrial solvents. It is often precisely those properties of such chemicals which make them useful that contribute to their significance as environmental and public health threats. Such materials are in general hydrophobic, and therefore tend to sorb onto suspended solid materials, establishing a condition of dynamic equilibrium between dissolved and solids-associated states. As the transport and fate of solids, and consequently sorbed pollutants, is often radically different from that of the surrounding water, the extent of such reactions is of paramount importance in assessing pollutant behavior. The kinetics of the association reactions determine the relative importance of sorption in relation to other transfer mechanisms. Finally, the reversibility of the association of chemicals with solids is in large part responsible for determining the ultimate fate of aquatic contaminants.

The sorption of hydrophobic compounds by solid materials has been reported by a number of investigators (Huang and Liao, 1970; Leland *et al.*, 1973; Richardson and Epstein, 1971; Champion and Olsen, 1971; Lotse *et al.*, 1968; Pierce *et al.*, 1974; Haque *et al.*, 1968; Haque and Schmedding, 1976; Picer *et al.*, 1977; Weber *et al.*, 1980). Work by Munson *et al.* (1976) on the transport of chlorinated hydrocarbons in the Upper Chesapeake Bay showed that comparisons of bottom sediment data to suspended solids (dry) data for concentrations of PCB and Chlordane indicated 4–10 times higher concentrations in the suspended material. These studies support the hypothesis that suspended materials are likely to be a major transport medium for certain substances, as determined by the extent to which such substances partition to solid materials. This paper, the first of a series of two, reviews the current level of understanding of sorption processes relative to hydrophobic compounds in aquatic systems. Particular emphasis is given to the details of sorption theory and to the extent to which it can be applied to this situation.

SORPTION FORCES

The term "sorption" is used in the present context to describe any accumulation of dissolved substances by solid particles. The distinction between solid and dissolved states is at times elusive, particularly in the presence of high molecular weight organics of natural

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origin; however, it normally suffices to define these terms operationally (i.e. separable by centrifugation or filtration).

Various attractive forces exist between solute molecules and the molecules of the solid surface or sorbent, all having their origin in the electromagnetic interactions of nuclei and electrons. Traditionally, three loosely defined categories have been distinguished: physical, chemical and electrostatic interactions. In the consideration of hydrophobic solutes, gross electrostatic or Coulombic attractions (i.e. between ions and charged functional groups) need not be considered. The actual bonding forces in both physical and chemical sorption, however, are predominantly electrostatic in nature.

Physical sorption results from the action of van der Waals forces, comprised of London dispersion forces and classical electrostatic forces. The theory developed by London (1930a, b) describes the existence of rapidly fluctuating temporary dipole and quadrupole moments due to the motion of electrons in their orbitals. As a molecule from bulk solution approaches the surface molecules of a solid sorbent, the electron distributions interact to induce additional dipole and quadrupole moments and distort to achieve an optimal energy state. The result is a net attraction due to the dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions. Dipole–dipole interactions are probably the most important, varying inversely with the sixth power of the distance between molecules, while dipole–quadrupole and quadrupole–quadrupole interactions are proportional to the eighth and tenth powers, respectively. Repulsive forces vary with the twelfth power of distance and are therefore negligible except at very small intermolecular distances, where they serve to establish a characteristic distance, referred to as the van der Waals radius.

The strength of such sorptive forces can be gauged by measurements of differential heats of adsorption. Values for van der Waals-type interactions for small molecules are generally on the order of 1 to 2 kcal mol^{-1} (Kiselev, 1965). This relatively small bonding force is often amplified in the case of hydrophobic molecules by a substantial thermodynamic gradient driving the molecules out of solution. Although the sorptive bond is still a van der Waals-type interaction, the combined effect is often referred to as "hydrophobic bonding" (Hamaker and Thompson, 1972).

The energy driving hydrophobic molecules out of solution can be explained in light of the current level of understanding regarding the structure of water. It is thought that H_2O molecules in liquid water exist in one of two types of structural associations. The first type of association is one in which each H_2O molecule is tetrahedrally coordinated to four other H_2O molecules via hydrogen bonds, yielding a structure similar to that of crystalline ice. The second association is an agglomeration of more densely packed but less ordered H_2O molecules. A non-polar molecule can be held in solution by an arrangement of the ice-like crystals around the solute and the reaction is generally exothermic. The favorable enthalpy is countered, however, by an unfavorable entropy of solution resulting from the increased ordering of solvent molecules (Hamaker and Thompson, 1972). Solute molecules can be driven from solution, at concentrations below maximum solubility, if the system can achieve a state that is thermodynamically favorable to precipitation. The chlorinated hydrocarbon pesticides, for example, tend to sorb heavily to organic-rich sediments and soils because pesticide/humin interactions are energetically preferable to pesticide/water or pesticide/pesticide interactions. The overall reaction, however, is predominately entropic in nature.

The second component of physical sorptive forces is that of classical electrostatic interactions. In the consideration of hydrophobic substances, gross electrostatic interactions are usually negligible, but attraction potentials can be developed between polar molecules and ionic or heteropolar solids. The strength of this attraction is dependent upon the strength and characteristics of the surface electric field and the magnitude of the dipole and quadrupole moments of the solute molecules. These interactions are generally not significant in the present context as most hydrophobic compounds are highly non-polar. A slight degree of polarity, however, can radically alter the stability of molecules in solution, thereby exerting considerable control over hydrophobic bonding.

Chemical sorption, or chemisorption, involves electronic interactions between specific sites on the sorbent surface and solute molecules. The resultant bond can have all the characteristics of a "true chemical bond" and is characterized by a large heat of adsorption, typically 15–50 kcal mol^{-1}. A substantial activation energy may be involved in the reaction, allowing it to occur at high temperatures. Chemisorption can often be identified by the type of isotherm that appears to intersect the solid-phase axis, suggesting high partitioning at low solute concentrations (Kipling, 1965).

Normally, it is difficult to assess the relative importance of the various sorptive reactions. Chemisorption can occasionally be distinguished from pure physical adsorption at high tempertures where the latter becomes less significant. However, due to the temperature dependence of solute/solvent interactions, this distinction may not be possible when physical adsorption is complemented by hydrophobic bonding. The heterogeneous nature of natural suspended solids necessarily precludes any thorough evaluation of surface chemistry, and possible sorbent/sorbate chemical interactions remain largely speculative. Actual sorption processes probably involve varying degrees of all types of interactions, but often, one type predominates. While the current level of understanding does not lead to a good general model for sorptive behavior, an understanding of the processes involved is beneficial.

SORPTION MODELS

In practice, sorption studies are conducted by equilibrating known quantities of a solid with solutions of the compound of interest. A plot of the variation of solid-phase concentration—the amount of the compound sorbed per unit mass of solid—vs the solution-phase concentration under equilibrium conditions, is termed an isotherm. Several models have been developed to describe this relationship. A particular model may describe experimental data accurately under one set of conditions, but fail entirely under another. No single model has been found to be generally applicable, a fact that is easily understood in light of the derivative assumptions made for each.

The Langmuir model was developed for adsorption of gases onto solids and makes the following assumptions (Langmuir, 1918):

the energy of adsorption is constant and independent of surface coverage;

adsorption occurs only on localized sites and there is no interaction between absorbate molecules; and

the maximum adsorption possible is that of a complete monolayer.

The relationship can be derived by considering the kinetics of condensation and evaporation of gas molecules at a solid surface (Moore, 1972). If θ represents the fraction of complete monolayer coverage that exists at a given time, then the rate of evaporation from the surface is proportional to θ. Similarly, the rate of condensation of gas-phase molecules onto the surface is proportional to the number of free sites remaining, or $1-\theta$, and to the rate at which molecules contact the surface. The latter term is proportional to P, the absolute pressure of the gas. Equating these two rates for equilibrium conditions yields:

$$k_d\theta = k_a\mathrm{P}(1-\theta) \tag{1}$$

where k_d is the rate constant for evaporation and k_a is the constant for condensation. The fraction of surface covered, θ, is then

$$\theta = \frac{k_a\mathrm{P}}{k_d + k_a\mathrm{P}} = \frac{b\mathrm{P}}{1+b\mathrm{P}}. \tag{2}$$

The adsorption coefficient, $b = k_a/k_d$, is related to the enthalpy of adsorption (ΔH) by

$$b = b_0\exp(-\Delta H/RT) \tag{3}$$

where b_0 is a constant related to the entropy (Weber, 1972; Weber and Van Vliet, 1980). Equation (2) can also be derived using methods of statistical thermodynamics (Hill, 1960).

In solid–liquid systems equation (2) is usually written:

$$q_e = \frac{Q^\circ bC_e}{1+bC_e} \tag{4}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent; Q° is the solid-phase concentration corresponding to all available sites being filled, or the maximum adsorption, and C_e is the liquid-phase concentration at equilibrium. Equation (4) can be written in a variety of linear forms:

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ} \tag{5}$$

$$\frac{1}{q_e} = \frac{1}{Q^\circ} + \frac{1}{bQ^\circ C_e} \tag{6}$$

or,

$$q_e = Q^\circ - \frac{q_e}{\mathrm{b}\mathrm{C}_e} \tag{7}$$

While all are equivalent, one particular form may be more desirable than the others depending on the range and spread of the data to be described (Weber, 1972; Reinbold *et al.*, 1979).

Brunauer *et al.* (1938) extended the Langmuir model to include the adsorption of multiple molecular layers. They assumed that any given layer need not be complete before subsequent layers can form. The first molecules to adhere to the surface do so with an energy comparable to the heat of adsorption for monolayer attachment, while subsequent layers are treated essentially as condensation reactions. If it is assumed that all layers beyond the first have equal energies of adsorption, the BET equation takes the simplified form:

$$q_e = \frac{BC_eQ^\circ}{(C_s - C_e)[1+(B-1)(C_e/C_s)]} \tag{8}$$

where C_s is the saturation concentration of the solute, C_e is the liquid-phase concentration at equilibrium, Q° is the solid-phase concentration corresponding to a complete monolayer, and q_e is the solid-phase equilibrium concentration. B is a constant expressive of the energy of adsorption:

$$B = \frac{d_2c_1}{d_1c_2}\exp(E_1 - E_2)/RT \tag{9}$$

where E_1 is the average heat of adsorption of the first layer, E_2 is the heat of condensation, and d_2c_1/d_1c_2 is the ratio of evaporation–condensation coefficients for the adsorbed layers which is often nearly equal to unity (Bailey and White, 1970). Equation 8 can be linearized to facilitate its application:

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{BQ^\circ} + \frac{B-1}{BQ^\circ}\cdot\frac{C_e}{C_s}. \tag{10}$$

The Gibbs adsorption equation (Gibbs, 1876, 1878) considers the change in surface concentration necessary to achieve a thermodynamic balance between two homogeneous phases. Most non-polar substances tend to reduce the interfacial tension of water by accumulating at the phase boundary and increasing the area of the interface, as this is energetically preferable to other means of achieving equilibrium (Stumm and Morgan, 1981; Weber, 1972). The Gibbs equation has the form:

$$\Gamma_i = -\frac{a_i}{RT}\frac{d\gamma}{da_i} \tag{11}$$

where Γ_i is the surface excess (above that existing in the bulk phase) of component i, a_i is the activity of component i and γ is the surface tension. The Gibbs equation is not readily applicable to sorption reactions in the environment due to the difficulty and uncertainty of the required measurements and to severe violations of the fundamental assumptions (Kipling, 1965; Adamson, 1976). It is cited here because it provides a useful basis for comprehension of sorption processes.

Despite the sound theoretical basis of the Langmuir, BET and Gibbs models, these isotherms often fail to describe sorption data adequately. Freundlich (1926) found that such data were frequently better described by the relationship:

$$q_e = K_F C_e^{1/n} \tag{12}$$

where K_F and n are characteristic constants. Equation (12) linearizes in logarithmic form:

$$\ln q_e = \ln K_F + 1/n \ln C_e. \tag{13}$$

Freundlich attempted to attach rigorous physical significance to the constants K_F and n, but was, for the most part, unsuccessful. The value of K_F can, however, be taken as a relative indicator of sorption capacity, while $1/n$ is indicative of the intensity of the reaction (Weber, 1972).

Kipling (1965) cited the work of Henry (1922) which justified the Freundlich equation as a special case of the Gibbs relationship. If the Gibbs surface excess, Γ, is assumed to equal the amount adsorbed, q_e, for dilute solutions, the Gibbs equation becomes:

$$q_e = -\frac{C_e}{RT}\cdot\frac{d\sigma}{dC_e} = \frac{C_e}{RT}\cdot\frac{\sigma_0-\sigma_1}{Q^\circ}\cdot\frac{dq_e}{dC_e} \tag{14}$$

where σ_0 is the surface free energy of the surface in contact with pure solvent, σ_1 is that of the surface covered with a complete monolayer of solute, and

$$\sigma = \sigma_0(1-\theta) + \sigma_1\theta \tag{15}$$

is the surface free energy for fractional surface coverage. Integration of equation (14) yields:

$$\ln q_e = \frac{RTQ^\circ}{\sigma_0-\sigma_1}\ln C_e + \ln K \tag{16}$$

which reduces to the Freundlich equation if we set

$$\frac{RTQ^\circ}{\sigma_0-\sigma_1} = \frac{1}{n} \tag{17}$$

The primary assumption of this derivation, $\Gamma = q_e$, is valid only for low concentrations, and a possible limitation to the applicability of the Freundlich model is introduced. It should also be kept in mind that the Freundlich model is consistent with an exponential distribution of site energies, characteristic of heterogeneous surfaces, and with immobile adsorption (Weber, 1972; Adamson, 1976).

The simplest isotherm model is that of linear adsorption or constant partitioning:

$$q_e = K_p C_e \tag{18}$$

Where K_p is termed the partition coefficient. This model for description of sorption equilibria has gained widespread acceptance due to its lack of mathematical complexity. When justified, linear partitioning is particularly useful in mathematical modelling of pollutant behavior, as it can be solved implicitly for any of the terms. Caution should be exercised in use of the partition coefficient, however, as the relationship is often not valid, especially over large ranges of concentration. This problem is frequently encountered in modelling work when coefficients are generated in the laboratory and then applied to conditions that fall outside the ranges of the development parameters.

This is not to suggest that linear partitioning is solely a mathematical convenience without basis in theory. All of the previously discussed models reduce either directly or indirectly to linear relationships under special conditions. Considering the Langmuir isotherm [equation (4)], it can be seen that the denominator approaches a value of 1.0 for dilute solutions and $Q^\circ b$ becomes a coefficient of linear partitioning. Conceptually, this corresponds to such low values of surface concentration ($q_e \ll Q^\circ$) that additional adsorption changes the available surface area insignificantly and the reaction is dependent only upon the solution-phase concentration. Similarly, the Freundlich isotherm is linear when $1/n = 1.0$, a condition that is frequently found in sorption studies with soil at low solution concentrations. The previously described relationship between the Gibbs and Freundlich models and the fact that the BET isotherm reduces to the Langmuir model at low concentrations (Weber, 1972) indicate that all of the relationships tend to predict linear sorption at low solution concentrations.

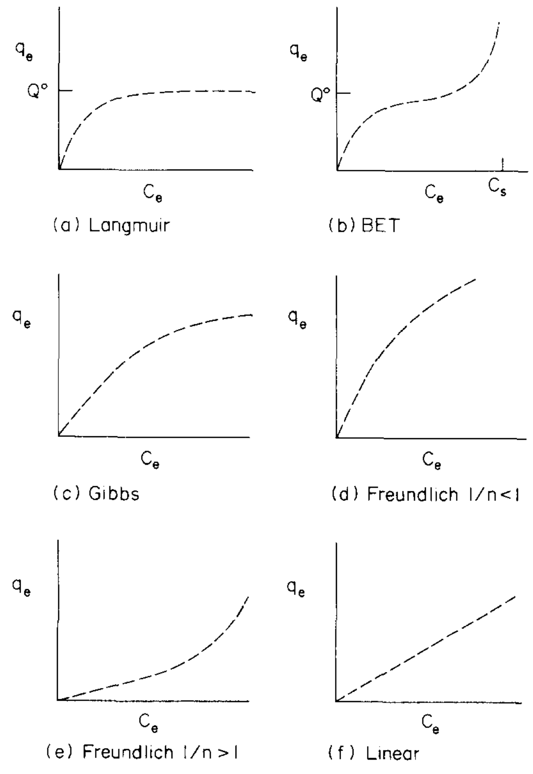
APPLICATION OF SORPTION MODELS

The treatment of sorption data generally begins with two tasks: (1) selection of an appropriate isotherm model, and (2) evaluation of constants for the model selected. The first step is often biased by the intended use of the data and model parameters. For example, mathematical simplicity may be the most important consideration if description of the sorption reaction is only a submodel in a larger system model. In this case, any model that adequately describes the data over the concentration range of interest will suffice. Linear plots of the amount sorbed as a function of the equilibrium solution concentration for the models described above are shown in Fig. 1. A comparison of similar plots for data from a particular system of interest indicates which of the models is most appropriate for that system.

It can be seen from Fig. 1 that at low concentrations all of the models approach linearity and that the choice of a model may be based in part upon the usefulness of the model parameters. For example, the Freundlich K_F term has been used extensively to quantify the extent of sorption. The comparison of different sorbents, solutes or conditions can be aided by evaluation of this term. Similarly, if an indication of ultimate sorptive capacity is desired, the monolayer saturation term, Q°, may be of interest. Figure 2 illustrates graphical methods for evaluating the various isotherm parameters.

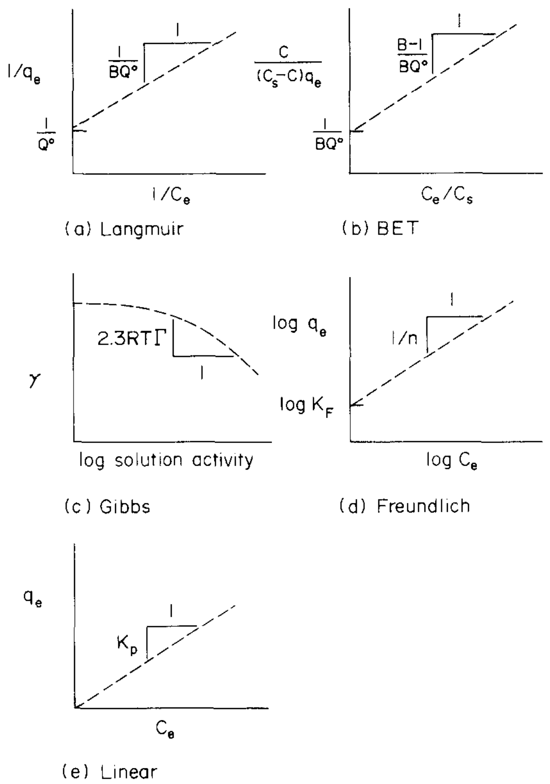
FACTORS INFLUENCING SORPTION

The effects of a variety of factors on sorption processes in soil have been reviewed in great detail (Bailey and White, 1970; Browman and Chesters, 1975; Hamaker and Thompson, 1972). Most of the studies cited involved high levels of pesticides reaching the soil either by direct application or indirectly through the action of natural phenomena. The dearth of literature pertaining to the interactions of organic compounds at residue levels with suspended solids or sediments is due to the relatively recent acknowledgment of the importance of such reactions. A few important concepts can, however, be gleaned from past soils work and applied to the situation of trace levels of hydrophobic compounds.



(a) Langmuir (b) BET
(c) Gibbs (d) Freundlich 1/n<1
(e) Freundlich 1/n>1 (f) Linear

Fig. 1. Graphical representation of isotherm models (after Weber, 1972; Adamson, 1976).



(a) Langmuir (b) BET
(c) Gibbs (d) Freundlich
(e) Linear

Fig. 2. Graphical evaluation of isotherm constants (after Weber, 1972; Stumm and Morgan, 1981).

Demonstration of the overwhelming importance of the organic carbon content of a soil or sediment in the sorption of neutral organic compounds can be credited to the work of Lambert (1966, 1967, 1968) and Lambert *et al.* (1965). Dividing the linear partition coefficient, K_p, by the fractional organic carbon content of the sorbent, f_{oc}, a normalized partition coefficient was defined:

$$K_{oc} = \frac{K_p}{f_{oc}}. \qquad (19)$$

This new term was shown to remain virtually constant for a particular compound, partitioning to soils with a wide range of organic carbon values. In addition to establishing the controlling role of organic matter on sorption reactions, the high degree of correlation found by Lambert indicates that other factors may be of little importance. Attempts to further characterize the role of organic matter has been made by selectively removing various organic fractions and comparing the extent of sorption (Pierce *et al.*, 1974; Shin *et al.*, 1970). These studies concluded that the insoluble or humin fraction of the soil (removable only under extreme oxidizing conditions) is most important.

An inverse relationship between particle size and sorption has been observed (Richardson and Epstein, 1971; Boucher and Lee, 1972; Lotse *et al.*, 1968), but correlations are typically poor. Some investigators (Karickhoff *et al.*, 1979) attribute these observations to the fact that smaller particles have a higher organic carbon content.

Work on delineation of sorbate properties which influence sorption centers almost entirely around what has been termed the hydrophilic–hydrophobic balance, as measured by the degree of partitioning of a compound between water and an immiscible organic solvent (Lambert, 1967; Hance, 1967). Briggs (1973) developed a relationship between the sorption of phenyl urea herbicides by soils and their partitioning into *n*-octanol. The use of this solvent has become widespread and extensive compilations of octanol–water partition coefficients are available (Hansch and Leo, 1979).

Karickhoff *et al.* (1979) developed a relationship which accounts for both the octanol–water partition coefficient of the sorbate and the organic carbon content of the sorbent, using sorption data from hydrophobic solutes and aquatic sediment samples:

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21 \qquad (20)$$

where K_{ow} is the octanol–water partition coefficient. Similar relationships have been found by other investigators although the magnitude of the constants vary somewhat due to differences in experimental techniques and the use of other sorbates and sorbents. Kenaga and Goring (1980) and Lyman *et al.* (1982) provide good reviews of this material.

Because partitioning relationships have been used extensively in a number of fields, considerable effort has been directed at establishing methods to calculate partition coefficients on the basis of chemical structure. Linear free energy relationships assume that changes in free energy brought about by substitution onto a parent molecule are additive. Hansch's π constants, for example, may be considered to be changes in log partition coefficients due to substitution on a parent compound and may be added to known log K_{ow} values to predict the octanol–water partitioning of new compounds:

$$\log K_{ow(R\text{-}X)} = \log K_{ow(R\text{-}H)} + \pi_X \qquad (21)$$

where R–H refers a parent compound, X is a substituent and R–X is the substituted compound (Fujita *et al.*, 1964). Rekker (1977) developed an approach based on a hydrophobic fragment constant, f, that eliminates the need for starting with a known K_{ow} value. In this system, molecules are divided into fragments and the f values for each are summed:

$$\log K_{ow} = \sum_{1}^{n} \alpha_n f_n \qquad (22)$$

where α_n is the number of occurrences of a fragment of type n (Hansch, 1980). This approach is currently being adapted to computer analysis to facilitate the calculation of large numbers of K_{ow} values (Hansch, 1980). An extensive list of reported values for both π constants and hydrophobic fragment constants has been compiled by Hansch and Leo (1979). A number of other linear free energy relationships exist but their use is less common.

Several attempts to correlate aqueous solubility with sorption were reviewed by Bailey and White (1970). While a general trend toward an inverse relationship is frequently found, correlation is poor and conclusions remain largely qualitative. Karickhoff *et al.* (1979) presented a regression equation similar to the K_{oc}–K_{ow} relationship:

$$\log K_{oc} = -0.54\, S_w + 0.44 \qquad (23)$$

where S_w is the aqueous solubility. The relationship is offered as a comparison to equation (20), but Karickhoff *et al.* (1979) concluded that sediment–water partitioning can be predicted within a factor of 2 or 3 using octanol–water partition coefficients, while solubility gives, at best, an order of magnitude estimate. This difference can be explained by considering the several factors outlined below.

Partitioning between the organic matter in natural solids and water is most nearly analogous to liquid–liquid phase equilibria. This concept was proposed by Lambert (1967) and has gained widespread acceptance in recent years (Chiou and Freed, 1979).

The thermodynamics of saturated aqueous solutions differ significantly from those in two-phase systems where neither phase approaches saturation.

Aqueous solubility, suggesting a fixed and identifiable concentration, does not exist as such. Schoor (1975) points out that solubility needs to be treated as a continuous function representative of increasing molecular aggregation.

Methods for measuring water solubility are as numerous and varied as are reported results. The difficulties in performing such studies, combined with the continuous nature of the relationship, suggest that the results will be heavily dependent on the methods employed.

Another property that has been correlated to sorption is the parachor, P, which is defined as:

$$P = \bar{V}^{1/4}$$

where $\bar{V}$ is the molar volume of the solute. The parachor normalizes measured values for molar volumes to account for the effects of surface tension and should therefore be an accurate measure of the relative volume in solution (Hamaker and Thompson, 1972; Dexter, 1976). Lambert (1967) reported good linearity between the log partition coefficients for several herbicides and their parachors, while Briggs (1969) showed a poor correlation for another group of herbicides. Hance (1969) suggested that the parachor should only describe sorption for materials that do not form hydrogen bonds, and proposed the use of parachor-45N, where N is the number of possible hydrogen bonds; however, Briggs (1969) found poor linearity here also. Dexter (1976) found a linear relationship between the parachor and the aqueous activity coefficient which was then used in a Langmuir-type sorption model. The correlation appears to hold only for homologous series of compounds and deviates from linearity at high values of the parachor. This approach offers the advantage, however, that the parachor can be calculated by the additive method of Quayle (1953).

It is generally accepted that at low solute concentrations the assumption of constant partitioning is valid. Several investigators have reported, however, that partition coefficients appear to increase as the concentration of solids is decreased (Cox, 1970; Rice and Sikka, 1973). A recent paper by O'Connor and Connolly (1980) documents the phenomenon for a number of compounds and metals and suggests an empirical relationship of the form:

$$K_p = K_{p\infty} + \frac{\beta}{S_0 + S_\alpha} \tag{25}$$

where $K_{p\infty}$ is the limiting partition coefficient at high solids concentration, S is the concentration of solids, and S_0, α and β are empirical constants that must be evaluated for each sorbate/sorbent combination.

Even in the case of constant partitioning, where the solid-phase concentration is independent of solids concentration, the relative fraction of compound in the aqueous phase is a function of the available solids. This can be seen by expressing q_e as:

$$q_e = \frac{C_T - C_e}{S} \tag{26}$$

where C_T is the total concentration, dissolved and sorbed, of the compound in a volume of water. Substitution into equation (18) yields:

$$\frac{C_e}{C_T} = \frac{1}{K_pS + 1}. \tag{27}$$

A semi-log plot of this relationship is shown in Fig. 3. It can be seen that at low solids concentrations (e.g. $< 10 \text{ mg l}^{-1}$) relatively high partition coefficients are required ($> 10^4$) before a significant fraction of a pollutant will exist in the solid phase.

DESORPTION

Studies of desorption phenomena are scarce and inconclusive. The sorptive reaction has been reported to be both reversible and irreversible (Karickhoff *et al.*, 1979; Smith *et al.*, 1978; Rogers *et al.*, 1980). While the theoretical models all assume a condition of dynamic equilibrium and complete reversibility, this assumption is dubious in the case of hydrophobic compounds and organics-laden solids. The difficulty and poor recovery of some extraction procedures suggest that a portion of the sorbed compound may be bound in an irreversible state. The kinetics of desorption are generally slow and appear to be related somewhat to the "age" of the sorbed compound.

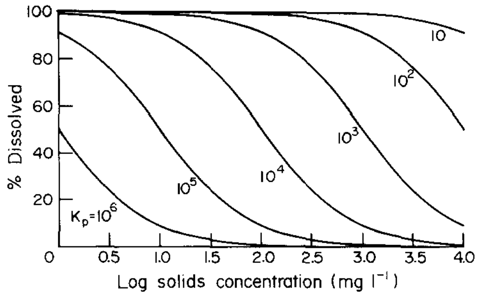


Fig. 3. Effect of partition coefficient and solids concentration on the percentage of compound in the liquid phase (after Wolfe *et al.*, 1977).

KINETICS OF SORPTION

The kinetics of the sorption of hydrophobic compounds have received only scarce attention in the literature, but are generally found to be rapid (Rice and Sikka, 1973; Harding and Phillips, 1978; Lotse *et al.*, 1968; Picer *et al.*, 1977). Laboratory batch-reactor studies typically reach 90% of equilibrium sorption values in less than one hour and often in a few minutes. Such test results may be misleading, however, as the rate-limiting step may be a function of the sampling procedure. It generally suffices to assume that in systems of practical significance kinetics are not constraining and that sorption can be treated as an instantaneous reaction.

CONCLUSIONS

Although only a limited amount of work has been done on the sorption of hydrophobic compounds in aquatic systems, a number of conclusions can be drawn if this work is considered in light of the results from areas of more extensive research.

Hydrophobic bonding, an entropically driven dissolution reaction, is a major sorption mechanism.

A universal sorption model has yet to be found and data must be treated on a case-by-case basis.

Total organic carbon content appears to be the major factor in determining a solid's sorptive potential.

The octanol–water partition coefficient is the best known indicator of the extent to which a compound will sorb.

Sorption reactions of hydrophobic compounds are generally rapid.

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