

Functional Relationship between Sorption in Soil and Chemical Structure

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By utilizing an equilibrium constant which considers soil-organic matter as the sorbing medium, a functional relationship between sorption in soil and chemical structure has been developed for certain classes of chemicals. This relationship is based upon extrathermodynamic linear free energy approximations and uses the parachor as an approximate measure of the molar volume

of the chemical under consideration. Distribution equilibria between soil and water for a number of chemical homologs of two different chemical classes were used to establish the relationship. The result is a natural consequence of the informative chromatographic model for movement and sorption of chemicals applied to the soil.

Sorption of chemicals in soil is an extremely complex phenomenon and any explanation of what is, in fact, occurring should reflect this complexity. Numerous articles concerning sorption characteristics of herbicides have recently appeared in the literature; these have been for the most part descriptive in nature. The authors have expressed an almost unanimous concern for the lack of an existing relationship between soil sorption and chemical structure (Bailey and White, 1964; Hance, 1965; Harris, 1966; Ward and Upchurch, 1965).

In attempting to describe a functional relationship between soil sorption and chemical structure, the use of suitable models for explanatory purposes may decrease the magnitude of the complexity involved. A simple but useful model describing the movement and sorption of certain types of chemicals in the soil has been described by Lambert *et al.* (1965). Their model is based upon the theory of chromatography and considers the soil as a chromatographic column carrying a stationary phase of organic matter. One natural consequence of this informative chromatographic model is that it predicts a relationship between chemical structure and soil sorption phenomena. The applicability of chromatographic principles to soils is not new and its utility for herbicidal behavior has been discussed by Hartley (1964).

Extension of Conceptual Model

If one considers the chromatographic model to be an adequate representation of the phenomenon involved, then certain consequences, in terms of the model, will arise naturally. These consequences can be considered from the point of view of the effect of chemical structure on soil sorption equilibria. One method by which this may be accomplished is the utilization of extrathermodynamic relationships; specifically, those classified as linear free energy relationships.

A theory of the effects of substituents or structural changes on the rates or equilibria of organic chemical reactions was developed by Hammett in 1940. The general form of the correlations he obtained is a linear

relationship between the logarithms of the rate or equilibrium constants for a large number of aromatic side-chain reactions and the variation in reactant structure. More recently, Martin (1949), during the development of the theory of partition chromatography, proposed a relationship between the logarithm of the partition coefficient and a set of parameters, which are characteristic of those functional groupings constituting the molecule under consideration. Certainly there are many assumptions made in deriving the above relationships and, as a consequence, specific restrictions are imposed for their use. However, if the limitations are borne in mind, the relationships are valid and of great practical importance.

Functional Relationship

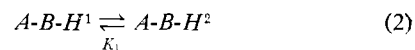
The general theory of extrathermodynamic linear free energy relationships will not be reviewed here. Mathematically this theory is based upon the premise that quantities such as standard free energies are additive functions of molecular structure.

Let us represent a molecule as $A-B-H$, where A , B , and H refer to atoms or functional groupings. The standard free energy, \bar{F}° , may be expressed as

$$\bar{F}^\circ = F_A + F_B + F_H + F_{A,B} + F_{A,H} + F_{B,H} \quad (1)$$

The quantities F_A , F_B , and F_H are independent functions of A , B , and H , respectively. $F_{A,B}$, $F_{A,H}$, and $F_{B,H}$ are terms resulting from the interaction of A with B , A with H , and B with H . These F_i terms are both constitutive and additive functions of molecular structure.

Now let us consider a process: the transfer of molecule $A-B-H$ from liquid phase 1 to liquid phase 2. The distribution equilibria may be described as



where the superscripts refer to phases 1 and 2. The equilibrium constant, K_1 , for the reaction is

$$K_1 = \frac{(A-B-H^2)}{(A-B-H^1)} \quad (3)$$

The change in standard free energy for the reaction

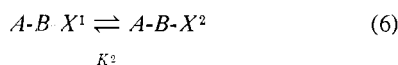
$$\Delta\bar{F}^\circ = \bar{F}^\circ_{A-B-H^2} - \bar{F}^\circ_{A-B-H^1} \quad (4)$$

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is related to the equilibrium constant, K_1 , by the equation

$$\Delta\bar{F}^\circ = -RT \ln K_1 \quad (5)$$

If next we consider the same distribution equilibria for another molecule, $A-B-X$, differing from $A-B-H$ only by the introduction of a substituent X for H , we write



where

$$K_2 = \frac{(A-B \cdot X^2)}{(A-B \cdot X^1)} \quad (7)$$

The ratio of K_2 to K_1 , K_2/K_1 , may be expressed as

$$K_2/K_1 = \frac{(A-B \cdot X^2)(A-B \cdot H^1)}{(A-B \cdot X^1)(A-B \cdot H^2)} \quad (8)$$

Using the standard free energy notation, Equation 8 may be expressed as

$$\Delta\Delta\bar{F}^\circ = \bar{F}^\circ_{A-B \cdot X^2} + \bar{F}^\circ_{A-B \cdot H^1} - \bar{F}^\circ_{A-B \cdot X^1} - \bar{F}^\circ_{A-B \cdot H^2} \quad (9)$$

or using the notations introduced in Equation 1,

$$\begin{aligned} \Delta\Delta\bar{F}^\circ = & F_{A^2} + F_{B^2} + F_{X^2} + F_{(A,B)^2} + F_{(A,X)^2} + F_{(B,X)^2} + \\ & F_{A^1} + F_{B^1} + F_{H^1} + F_{(A,B)^1} + F_{(A,H)^1} + F_{(B,H)^1} - \\ & F_{A^1} - F_{B^1} - F_{X^1} - F_{(A,B)^1} - F_{(A,X)^1} - F_{(B,X)^1} - \\ & F_{A^2} - F_{B^2} - F_{H^2} - F_{(A,B)^2} - F_{(A,H)^2} - F_{(B,H)^2} \quad (10) \end{aligned}$$

Interaction terms involving the solvent have not been included. These terms vanish in the first approximation for reasons discussed in a later section. Combining terms one obtains

$$\begin{aligned} \Delta\Delta\bar{F}^\circ = & F_{X^2} + F_{(A,X)^2} + F_{(B,X)^2} + F_{H^1} + F_{(A,H)^1} + \\ & F_{(B,H)^1} - F_{X^1} - F_{(A,X)^1} - F_{(B,X)^1} - F_{H^2} - F_{(A,H)^2} - \\ & F_{(B,H)^2} \quad (11) \end{aligned}$$

If one assumes that the interaction terms, $F_{(i,j)q}$, are factorable (This need not be argued here. Suffice it to say that this arises from the assumption that the structural changes being considered are small. Other theoretical considerations when dealing with solute-solvent interactions show this postulate to be of general validity.) so that $F_{(A,X)^2} = F_{A^2} + F_{X^2}$ and $F_{(B,X)^2} = F_{B^2} + F_{X^2}$, etc., then by combining terms one obtains

$$\Delta\Delta\bar{F}^\circ = aF_{X^2} + aF_{H^1} - aF_{X^1} - aF_{H^2} \quad (12)$$

where a is a constant. This may be written as

$$\Delta\Delta\bar{F}^\circ = a[\Delta F_{(X-H)^2} - \Delta F_{(X-H)^1}] \quad (13)$$

where $\Delta F_{(X-H)^2} = F_{X^2} - F_{H^2}$ and $\Delta F_{(X-H)^1} = F_{X^1} - F_{H^1}$. Expressing Equation 13 in terms of the equilibrium constant one obtains

$$\ln K_2/K_1 \propto \Delta F_{(X-H)^2} - \Delta F_{(X-H)^1} \quad (14)$$

A qualitative interpretation of Equation 14 would be that the logarithm of the ratio of the distribution

coefficients, $\ln K_2/K_1$, for molecules $A-B-H$ and $A-B-X$ between phases 1 and 2, is proportional to the differences in the free energies required to transport atoms (or groups) H and X between the two phases. At this point it might be wise to emphasize that the original postulate—i.e., that the free energy of a substance in solution is the sum of additive and constitutive term contributions from each of its molecular groups—is only an approximation.

The approximate function expressed by Equation 14 will be helpful in the following development in that it allows one to focus attention on individual atoms or functional groups constituting the molecule. In 1925, Langmuir voiced the opinion that a major factor contributing to the solubility of a solute in a solvent was the energy necessary to make a hole in the solvent. This idea was pursued by several men and used successfully in the development of a theory of physical toxicity by McGowan in 1952. Recent experimental verification of McGowan's hypothesis was made by Deno and Berkheimer (1960) in an investigation of activity coefficients of hydrocarbons.

This volume energy concept may be applied to the processes expressed by Equation 9 and the corresponding free energy change given by Equation 13. If the transfer of molecules $A-B-H$ and $A-B-X$ between phases 1 and 2 is made under conditions where the concentration of solute in each phase remains unchanged, and if only London dispersion forces are operative, entropy terms vanish and the free energy of transfer may be expressed as

$$\Delta\Delta\bar{F} = \Delta E_{X^2, H^2} - \Delta E_{X^1, H^1} \quad (15)$$

where $\Delta E_{X^2, H^2}$ is the difference in energy required to form a hole in solvent 2 to accommodate X or H . Similarly $\Delta E_{X^1, H^1}$ is the energy difference in solvent 1. Interaction terms for a given group, X or H , with the solvent may be thought of as a measure of London dispersion forces. For a given solute (or group) in a given two-phase system these values are nearly the same and therefore tend to cancel. The experimental verification of McGowan's (1952) work by Deno and Berkheimer in 1960 is added substantiation that this is generally valid for solute-solvent interactions. One restriction should be noted—i.e., when there is appreciable hydrogen bonding of the solute to one of the solvents. In this case a constant term is required in Equation 15. If one is interested in the magnitude of the solute-solvent interaction terms, this constant must be evaluated separately. For the development which follows, this aspect may be disregarded, as it would result only in changing the graphical intercept of the final equations.

Consider again Equation 15, as an approximation, the energy required to form a hole in the solvent is proportional to the volume of the hole, V_s , multiplied by the internal pressure of the liquid phase, U^l . The product, $V_s U^l$, is termed the volume expansion energy as opposed to the cavity formation energy, a more exact energy expression. Substituting this proportionality into Equation 15 and converting $\Delta\Delta\bar{F}^\circ$ to the appropriate equilibrium expression, one obtains

$$\ln K_2/K_1 = a'(V_X - V_H)U^2 - a'(V_X - V_H)U' \quad (16)$$

and by combining terms

$$\ln K_2/K_1 = a'[(V_X - V_H) \Delta U] \quad (17)$$

where ΔU is the difference in internal pressures of the two solvent phases.

One convenient measure of V_s is the parachor, P , a constitutive and additive function of molecular structure, which is defined for a liquid as

$$P = \frac{M\gamma^{1/4}}{\rho - \rho^\circ} \quad (18)$$

where M is the molecular weight; γ the surface tension; ρ the density of the liquid; ρ° is density of the vapor. The vapor density ρ° is usually neglected in comparison with ρ so that

$$P = \frac{M\gamma^{1/4}}{\rho} \text{ or } P = V_m \gamma^{1/4} \quad (19)$$

where V_m is the molar volume. Comparison of parachors of various substances is then essentially a comparison of molecular volumes modified to eliminate the influence of internal pressures. A table of recommended group and bond contributions useful in calculating P was tabulated by Quayle in 1953. In addition, he cataloged the parachors of a wide variety of organic compounds. The substitution of P_i for V_i in Equation 17 yields

$$\ln K_2/K_1 = a[(P_X - P_H) \Delta U] \text{ or } \Delta \ln K = a \Delta P \Delta U \quad (20)$$

For operational convenience Equation 20 may be divided into two separate energy functions,

$$\ln K_2 = aP_X \Delta U \quad (21)$$

and

$$\ln K_1 = aP_H \Delta U$$

These equations are defined as referring to a process in which the group X or H is transferred between the two appropriate phases. They are similar in concept to the use in electrochemistry of half reactions and corresponding half cell, E° , potentials. In the same sense they may be used operationally in determining group contributions to complete equilibria expressions.

Application of Derived Equations

The fact that Equation 21 expresses a relationship between equilibrium concentrations of a solute between two phases and the molar volume of that solute is in itself sufficient grounds to attempt an application to soil sorption equilibria. The choice of K_e , an equilibrium constant, to use in these equations, requires some explanation. By way of example, let us restrict our consideration to soil-applied herbicides, and in particular, the "uncharged" organic chemicals. It is this class of compounds which has proved so amenable to the chromatographic model developed by Lambert *et al.* in 1965. In this model description of the interaction of chemicals with soil, the character of the

equilibrium constant, K_e , has been altered from the classical constant, in that the sorbing medium is now considered to be the soil-organic matter rather than the total mass of soil. This aspect was incorporated explicitly into the equilibrium coefficient which becomes, for all practical purposes, a true constant independent of soil type, within the framework of the model.

The use of K_f , the constant from the Freundlich equation, to correlate with chemical structure is not justified from theoretical considerations. If one assumes that Henry's law is obeyed in sufficiently dilute solution (infinite dilution in the limit), it would be desirable to use the limiting slope of the isotherm. However, at these lower concentrations, if $n \neq 1$, the Freundlich equation breaks down, since the limiting slope is infinite or zero. Certainly when $n = 1$ the use of K_f in Equation 21 requires no explanation. A much better value for K_e might be obtained from thermodynamic considerations by use of a power series to express the equilibrium between the concentration of solute sorbed, x/m , and the concentration of solute in solution, C_e . An expression of the type

$$\frac{x}{m} = \alpha C_e + \beta C_e^2 + \gamma C_e^3 + \dots \quad (22)$$

should be highly applicable. α , β , and γ are the adjustable coefficients used to fit the data, x is the quantity of chemical sorbed, and m is the mass of sorbing medium.

If an additional restriction is imposed—i.e., that C_e be no greater than 1 μ mole per liter—the third term of the series will in all probability vanish. In fact the series will for most practical purposes converge under these conditions without the second term, β probably being a small number. Equation 22 is useful in that under the boundary conditions specified (concentration limit), the proportionately constant α may be taken as a measure of K_e . In any event, the data obtained will provide the justification for using or rejecting the equation.

The application of Equation 22 will of course require more effort than the use of the Freundlich equation, and under certain conditions, K_f is a sufficiently good approximation of the required K_e for use in Equation 21. How good an approximation depends upon both K_f and the value of n , since K_e is a function of both K_f and $\frac{1}{n}$ —i.e., the slope for the Freundlich case is

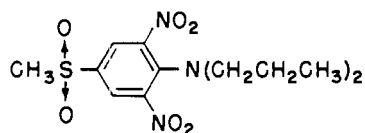
$$\frac{d(x/m)}{dC_e} = \frac{K_f}{n} C_e^{1/n-1} \quad (23)$$

The Freundlich isotherm has been discussed here because of its current widespread use with herbicide-soil sorption equilibria. The point to be made is, however, that its use should be discouraged in favor of an equation as represented by Equation 22. Once computational methods have been established for use of Equation 22, it becomes a matter of routine to evaluate the required K_e .

Results

Only two independent studies are accessible which will allow a test of Equation 21 for soil sorption equilibria. One such study has been conducted at Modesto specifically for this purpose. The second study conducted for other purposes contains enough data which are amenable to the aforementioned treatment to provide an independent test of the proposed relationship. The data are in a paper by Hance (1965) in which a number of Freundlich isotherms are plotted for a series of urea derivatives on a variety of soils. Hance found no quantitative correlation between soil sorption and water solubility or soil sorption and chemical structure.

Soil sorption isotherms of seven analogs of SD 11831 [aniline, 4-(methylsulfonyl)-2,6-dinitro-*N,N*-di-propyl-] have been investigated at Modesto.



SD 11831

Plots of x/m vs. C (concentrations expressed on a molar basis) were linear on our standard Ripperdan (1% organic matter) and Sacramento (5% o.m.) soils. A plot of K_e vs. P for these compounds is depicted in Figure 1. The observed linearity confirms the validity of the proposed relationship. The agreement between K_e values obtained from Ripperdan (1% o.m.) and Sacramento (5% o.m.) soils is given in Table I. This is added substantiation for the relationship between soil organic matter content and the extent of soil sorption developed by Lambert *et al.* in 1965.

Data from the paper by Hance were also subjected to the above treatment by converting the isotherm data to the corresponding K_e values. The K_e values for each compound were averaged for the six soils

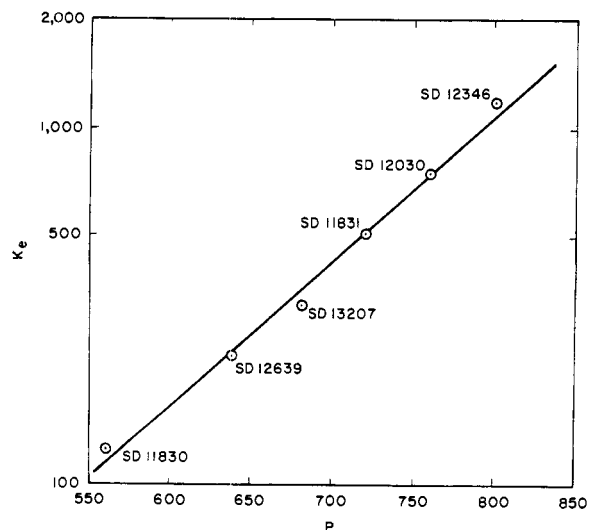
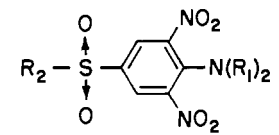


Figure 1. Plot of K_e vs. parachor for analogs of SD 11831

Table I. Comparison of K_e Values for SD 11831 Analogs Obtained from Different Soils



SD	R ₁	R ₂	K_e Values	
			Ripperdan, ^a 1% o.m.	Sacramento, ^b 5% o.m.
11830	CH ₃	CH ₃	125	145
12639	C ₂ H ₅	CH ₃	230	193
11831	C ₃ H ₇	CH ₃	500	520
13207	C ₃ H ₅	C ₂ H ₅	320	269
12030	C ₃ H ₇	C ₂ H ₅	750	702
12346	C ₃ H ₇	C ₃ H ₇	1170	
12400	CH ₃	iso-C ₃ H ₇	222	

^a From multipoint isotherms (K_e values plotted in Figure 1).

^b By replicated single point determinations.

used. These average values for the seven substituted ureas are plotted in Figure 2. Only the tertiary amides were compared because of hydrogen bonding restrictions previously discussed. It is surprising how well the data fit, since the range of K_e values spanned for any single compound on all six soils was in general a factor of about 2 times. This variation might be attributed to the difficulty in obtaining a representative soil sample since very small samples, 0.1 to 2 grams, were used to obtain the isotherms. In any event, the plot reaffirms the results obtained from our own study.

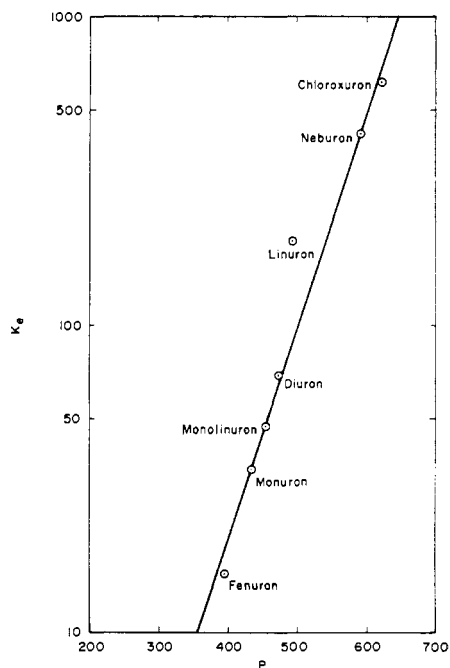
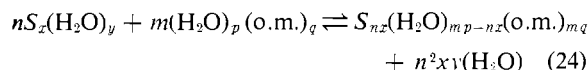


Figure 2. Plot of K_e vs. parachor for substituted phenylurea herbicides

The differences in the slope between Figures 1 and 2 are construed at this time as evidence of the two families of compounds sorbing with different energies on the soil organic matter. This is only speculation, and more work must be done before the cause of the differences is established.

A certain degree of caution must be exercised in interpreting the results obtained, especially because of complications arising from the fact that both adsorption and absorption phenomena are occurring, and the probability in this type of study of the formation of mixed solute-water-organic matter complexes.

Determinations of herbicide-soil sorption isotherms are normally carried out using high ratios of solvent (water) to sorbent (soil) in the presence of very low concentrations of solute. Under these conditions where the mole fraction of water is extremely high, the water may be an effective competitor for sites on the organic matter. If this situation exists, then the sorption phenomena should be more suitably described as a replacement reaction. Mechanistically this may be formulated as



S represents the solute, H_2O the water, and o.m. the soil-organic matter.

There may be secondary effects which when operative might produce some curvature in the plots of Figures 1 and 2. Within experimental error and for all practical purposes these effects may be neglected.

Significance and Conclusions

The rationale behind the use of parachor in Equation 21 stems from its being an approximate measure of the molar volume. This was based upon Langmuir's (1925) energy considerations for solubility. The functional relationship developed here in conjunction with the equations relating biological activity to K_e (Lambert *et al.*, 1965) offers an explanation for some of the observations made by other investigators in the past. More precisely, it accounts for the inverse correlation between water solubility and dosage of herbicides observed by Freed and Burschel (1957) and the strong inverse correlation between adsorption and solubility found by Leopold *et al.* (1960).

The significance of this correlation is that for certain classes of compounds the distribution coefficients, which describe sorption equilibria, are predictable functions of molecular structure. It means that for these com-

pounds we can predict where in the soil the chemical will reside under the influence of certain environmental conditions. The importance of this type of prediction is predicated upon the fact that the sorption of pesticide in the soil mediates its biological activity and that the loci of chemical in the soil will determine what factors are capable of operating upon it to effect its disappearance.

In practice these concepts may be utilized with supplementary information of a physicochemical and/or biological nature to account for and in some cases predict the fate and biological activity of pesticides added to the soil (Lambert *et al.*, 1965; Lambert, 1966).

This type of treatment represents a step towards establishing a quantitative relationship between soil sorption equilibria and chemical structure. In so doing, it emphasizes the importance of utilizing the partition or distribution coefficient, defined with respect to organic matter, as the most representative index of soil sorption equilibria. As is always the case when a new relationship is established, more questions may be posed which require additional study to answer. The relationship established here does, however, provide a theoretical justification for our conceptual model, and perhaps a deeper insight into the fundamental processes contributing to soil sorption equilibria.

Literature Cited

- Bailey, G. W., White, J. A., *J. Agr. Food Chem.* **12**, 324 (1964).
 Deno, N. C., Berkheimer, H. E., *J. Chem. Eng. Data* **5**, 1 (1960).
 Freed, V. H., Burschel, P., *Z. Pflanzenkrankh. Pflanzenschutz* **64**, 477 (1957).
 Hammett, L. P., "Physical Organic Chemistry," p. 184, McGraw-Hill, New York, 1940.
 Hance, R. J., *Weed Res.* **5**, 98 (1965).
 Harris, C. I., *Weeds* **14**, 6 (1966).
 Hartley, G. S., "Physiology and Biochemistry of Herbicides," L. J. Audus, Ed., p. 111, Academic Press, London, 1964.
 Lambert, S. M., *Weeds* **14**, 273 (1966).
 Lambert, S. M., Porter, P. E., Schieferstein, R. H., *Weeds* **13**, 185 (1965).
 Langmuir, I., *Colloid Symp. Monograph* **3**, 48 (1925).
 Leopold, A. C., van Schaik, P., Neal, M., *Weeds* **8**, 48 (1960).
 Martin, A. J. P., *Biochem. Soc. Symp.* **3**, 4 (1949).
 McGowan, J. C., *J. Appl. Chem.* **2**, 323 (1952).
 Quayle, O. R., *Chem. Rev.* **53**, 439 (1953).
 Ward, T. M., Upchurch, R. P., *J. Agr. Food Chem.* **13**, 334 (1965).

Received for review November 7, 1966. Accepted April 24, 1967. Division of Agricultural and Food Chemistry, 152nd Meeting, ACS, New York, N.Y., September 1966.