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Partition Equilibria of Nonionic Organic Compounds between Soil Organic Matter and Water†

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■ Equilibrium isotherms for the simultaneous uptake of binary nonionic organic compounds from water on soil indicated no competitive effect between the two solutes. This observation supports the hypothesis that partition to the soil organic phase is the primary process for sorption of nonionic organic compounds from water on soil. The partition process between soil organic matter and water was analyzed by using the conventional solution concept for solutes in water and the Flory–Huggins treatment for solutes in the polymeric humic phase. Sorption determined for 12 aromatic compounds on a Woodburn soil shows that the extent of solute insolubility in water (S) is the primary factor affecting the soil organic matter–water partition coefficient (K_{om}) and that the effect of solute incompatibility with soil organic matter is significant but secondary. This explains the commonly observed correlations of log K_{om} vs. log S and log K_{om} vs. log K_{ow} (octanol–water).

Introduction

Earlier publications (*1*, *2*) provided evidence that sorption of nonionic organic compounds from water on soil consists primarily of partition into the soil organic phase; adsorption by the soil mineral fraction is relatively unimportant in wet soils presumably because of the strong dipole interaction between soil minerals and water, which excludes neutral organic solutes from this portion of the soil. We here report further support for the partition hypothesis in soil–water systems and present a novel analysis of partition equilibria between soil organic phase and water, taking into account the solute solubility in polymeric humic substances.

Partitioning of organic solutes between the soil organic phase and water may be treated in a manner similar to that between an organic solvent phase and water (*3*, *4*). To analyze the relative effects on partition coefficient of solute solubility in water, compatibility with soil organic phase, and alteration of water solubility by soil organic components dissolved in water, a reference "ideal line" (*3*) relating sorption coefficient with water solubility is needed. We assume that the effect of soil–water mutual saturation on the solute's water solubility is insignificant with topsoil since the fraction of water-soluble organic components (which may have a potential effect on solute solubility) is usually negligible. We consider the major components of soil humus to be amorphous polymeric (macromolecular) substances and therefore adapt the Flory–Huggins theory (*5*, *6*) to account for the solute activity in an amorphous polymer. The partition process with soil organic matter is conceived to be analogous to that involved with synthetic resins used in ion-exclusion, salting-out, and solubilization chromatography for separating nonionic species (*7–10*).

The relation between partition coefficient and water solubility for slightly water-soluble organic solutes in an organic solvent–water mixture, in which the solvent has small solubility in water, is given by (*3*)

$$\log K = -\log S - \log \bar{V}_0^* - \log \gamma_0^* + \log (\gamma_w^*/\gamma_w) \quad (1)$$

where K is the solute partition coefficient, S is the molar water solubility of the liquid or supercooled liquid solute, $\bar{V}_0^*$ is the molar volume of water-saturated organic phase, γ_0^* is the solute activity coefficient (Raoult's law convention) in water-saturated solvent phase, γ_w^* is the solute activity coefficient in solvent-saturated water, and γ_w is

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the solute activity coefficient in water. The ideal line for the solutes partitioned between an organic solvent (such as octanol) and water is thus

$$\log K^\circ = -\log S - \log \bar{V}_0^* \quad (2)$$

where K° represents the partition coefficient when solutes form ideal solutions in the (water-saturated) solvent phase and when the solute solubility in water is not affected by the solvent dissolved in water.

When the organic phase is polymer, as are soil humic substances, γ_0^* in eq 1 (defined on a mole-fraction basis) must be modified to account for the large disparity in molecular volumes of solute and polymer, an effect that introduces large negative deviations from Raoult's law without associated heat effects (*5, 6*). The Flory–Huggins theory (*5, 6, 11, 12*) treats the activity of solutes at dilute concentrations in an amorphous polymer as

$$\ln a = \ln \phi + \phi_p(1 - \bar{V}/\bar{V}_p) + \chi\phi_p^2 \quad (3)$$

where a is the activity of solute, ϕ is the volume fraction of solute, ϕ_p is the volume fraction of polymer, $\bar{V}$ is the molar volume of solute, $\bar{V}_p$ is the average molar volume of polymeric substances, and χ is the Flory–Huggins interaction parameter, a sum of excess enthalpic (χ_H) and excess entropic (χ_S) contributions of the solute–polymer interaction (*13, 14*). When water is sorbed to the polymer phase, as for water-saturated soil organic matter, the properties of a, ϕ, ϕ_p, $\bar{V}_p$, and χ are those corrected for the effect of water sorbed. Thus, for instance, ϕ_p is the volume fraction of soil organic matter and sorbed water (i.e., $\phi_p = 1 - \phi$) and $\bar{V}_p$ is the average molar volume of water-saturated soil organic matter ($\bar{V}_p = \bar{V}_p^*$).

To obtain the solute activity coefficient (γ_0^*) at given mole fraction in water-saturated soil organic phase, $\ln a$ in eq 3 may be set equal to $\ln x\gamma_0^*$, where x is the mole fraction of solute in water-saturated soil organic phase. At dilute concentrations of solute in this phase, x and ϕ can be approximated as

$$x = n/(n + n_p) \simeq n/n_p \quad (4)$$

and

$$\phi = n\bar{V}/(n\bar{V} + n_p\bar{V}_p) \simeq n\bar{V}/(n_p\bar{V}_p) \quad (5)$$

where n is the moles of solute and n_p is the moles of soil humus and sorbed water. Substituting eq 4 and 5 into eq 3 gives

$$\ln \gamma_0^* = \ln \bar{V} - \ln \bar{V}_p^* + \phi_p(1 - \bar{V}/\bar{V}_p^*) + \chi\phi_p^2 \quad (6)$$

The solute partition coefficient between soil organic phase and bulk water can then be derived by substituting eq 6 into eq 1 with $\bar{V}_p^* = \bar{V}_0^*$ and $\phi_p \simeq 1$ along with the assumption of $\gamma_w^*/\gamma_w \simeq 1$ and $\bar{V}/\bar{V}_p^* \ll 1$, giving

$$\log K_{om} = -\log S\bar{V} - \log \rho - (1 + \chi)/2.303 \quad (7)$$

where K_{om} is the solute partition coefficient between soil organic phase and water and ρ is the density of the organic matter introduced to express K_{om} in a more usual weight basis.

According to Hildebrand et al. (*13*) and Scott (*14*), if the contribution to the incompatibility of a solute in a polymer, other than that of size difference, is given by the regular solution theory, the component χ_H of χ can be reasonably correlated by the solubility parameters of solute and polymer. In this case

$$\chi = \chi_S + (\bar{V}/RT)(\delta - \delta_p)^2 \quad (8)$$

where χ_S is approximately the reciprocal of the coordination number of the polymer subunits, δ is the solubility parameter of solute, and δ_p is the apparent (total) solubility parameter of water-saturated polymer. The value of χ_S depends presumably on the characteristics of the polymer network (crosslinking and chain length). Scott (*14*) treated χ_S as an empirical constant, assumed to be about 0.25 for high polymers. The ideal line for compounds with negligible heats of interaction ($\chi = \chi_S$) in the polymer phase would thus be

$$\log K_{om}^\circ = -\log S\bar{V} - \log \rho - (1 + \chi_S)/2.303 \quad (9)$$

where K_{om}° is the partition coefficient when $\chi = \chi_S$ and ρ is assumed for soil organic matter to be 1.2 by comparison with values for similar polymeric materials (*15*). With use of eq 9 as the ideal line and the experimental data of $\log K_{om}$, the incompatibility of a compound with (water-saturated) soil organic matter is $(\chi - \chi_S)/2.303 = \log (K_{om}^\circ/K_{om})$. If $(\chi - \chi_S)/2.303$ is small compared to $\log S\bar{V}$ for a group of solutes partitioned to the organic matter phase of a soil, the relation between $\log K_{om}$ and $\log S\bar{V}$ should be linear.

This study investigates the sorption of some aromatic compounds (benzene derivatives and PCBs) from both single-solute and binary-solute aqueous solutions on a Woodburn soil and discusses the relation of $\log K_{om}$ vs. $\log S\bar{V}$, $\log K_{om}$ vs. $\log S$, and $\log K_{om}$ vs. $\log K_{ow}$ (octanol–water) for the selected compounds.

Experimental Section

All sorption experiments were conducted with a Woodburn silt loam soil, which has the following compositions: 1.9% organic matter, 68% silt, 21% clay, and 9% sand, with a cation-exchange capacity of 14 mequiv/100 g of soil. Test compounds were reagent grades or analytical standards from Analabs, Aldrich, and Mallinckrodt and used as received except for some chlorinated biphenyls (PCBs) that were recrystallized in methanol to remove impurities.

Stock aqueous solutions were prepared by saturating each chemical with water at approximately 50 °C and then allowing the suspensions to stand at 20 °C. Excess chemicals in suspension were removed by centrifugation and saturated aqueous phases separated. A series of more dilute solutions were prepared for equilibration with appropriate amounts of soil. Soil–solution mixtures were equilibrated at 20 °C in 30-mL screw-capped centrifuge tubes (equipped with Teflon-lined lids) for 24 h on a mechanical shaker. Samples were centrifuged at 20 °C for 1 h in a controlled-temperature centrifuge to spin down soil particulates. To avoid vapor losses in transferring aqueous solutions to the sample tubes, a series of tubes with weighed amounts of soils were prepared and solutions quickly introduced to the tubes and capped. Reweighing established the volume of the solution in each tube.

With benzene, ethylbenzene, and chlorobenzene, vapor loss from the equilibrated aqueous phases was avoided by sampling through the septum in the caps using a gas-tight syringe. Aqueous samples of benzene and ethylbenzene were injected directly into a gas chromatograph while chlorobenzene solutions were extracted with suitable amounts of hexane prior to analysis with the gas chromatograph. In each case, small corrections were made for the amounts of chemicals in the air space of the original sample tubes, based on the known Henry's law constants and the air volumes. Other chemicals were sampled with pipets and the solutions extracted with hexane for subsequent analyses.

In the study of the simultaneous sorption of 1,3-dichlorobenzene and 1,2,4-trichlorobenzene by soil, the

Table I. Water Solubilities (S), Molar Volumes ($\bar{V}$), Octanol-Water Partition Coefficients (K_{ow}), and Soil Organic Matter-Water Distribution Coefficients (K_{om}) of Selected Organic Solutes

compound	$\log S$,[a] mol/L	V,[b] L/mol	$\log S\bar{V}$	$\log K_{om}$	$\log K_{ow}$[c]
benzene	−1.64	0.0894	−2.69	1.26	2.13
anisole	−1.85	0.109	−2.82	1.30	2.11
chlorobenzene	−2.36	0.102	−3.35	1.68	2.84
ethylbenzene	−2.84	0.123	−3.75	1.98	3.15
1,2-dichlorobenzene	−2.98	0.113	−3.98	2.27	3.38
1,3-dichlorobenzene	−3.04	0.114	−3.98	2.23	3.38
1,4-dichlorobenzene	(−3.03)	0.118	−3.96	2.20	3.39
1,2,4-trichlorobenzene	−3.57	0.125	−4.47	2.70	4.02
2-PCB	(−4.57)	0.174	−5.33	3.23	4.51
2,2′-PCB	(−5.08)	0.189	−5.57	3.68	4.80
2,4′-PCB	(−5.28)	0.189	−5.97	3.89	5.10
2,4,4′-PCB	(−5.98)	0.204	−6.67	4.38	5.62

[a] The listed solubilities are the 20-25 °C values cited in ref 3 except for anisole from ref 20 and PCBs (at 20 °C) from this work. The numbers in parentheses are the supercooled liquid solute solubilities estimated according to the method described in ref 3. For 2-, 2,2′-, 2,4′-, and 2,4,4′-PCB, the calculations were based on their solid solubilities of 3760, 717, 637, and 115 μg/L at 20 °C, respectively, and an assumption of 13.5 cal/(mol K) for their entropies of fusion. [b] The molar volumes of PCBs are estimated by using the densities of liquid Aroclor mixtures that have approximately the same chlorine atoms as the individual PCBs. [c] The K_{ow} values of PCBs (except for 2-PCB) are the experimental data from this work, and the values for the remaining compounds are from ref 3 and 21.

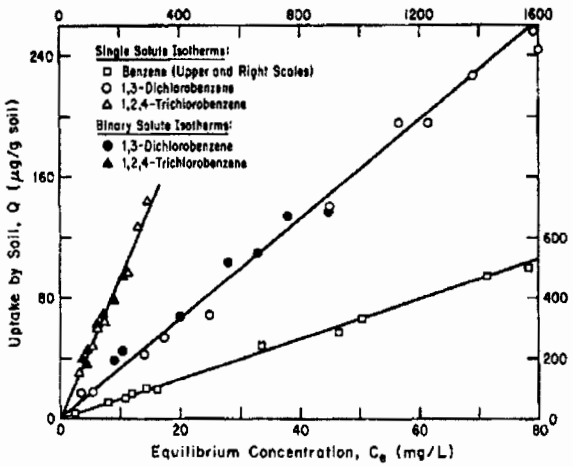

Figure 1. Typical soil–water equilibrium isotherms for benzene, 1,3-dichlorobenzene, and 1,2,4-trichlorobenzene as single solutes and as binary solutes on a Woodburn silt loam soil at 20 °C.

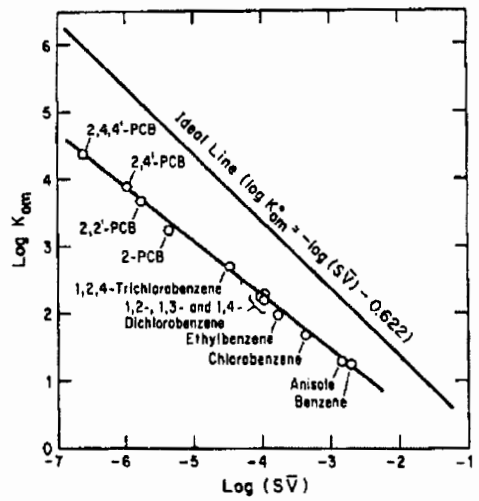

Figure 2. Plot of experimental log K_{om} values vs. log $S\bar{V}$ values for the selected organic compounds in comparison with the ideal line for the soil organic matter–water system.

concentrations of the two compounds were selected such that they would provide comparable sorption when observed independently.

The benzene and ethylbenzene solutions were analyzed by a Tracor 550 gas chromatograph with a Chromosorb 105 column and hydrogen flame detector. Anisole solutions were analyzed by UV absorption using a Cary 11 spectrophotometer. The remaining compounds were analyzed with the Tracor 550 gas chromatograph with a Carbowax 20 M column and EC detector. The amount sorbed was based on the difference in aqueous concentrations before and after equilibration. The amount of chemicals retained by the glass wall was found insignificant compared to the amount sorbed by soil, and hence no correction was made.

Results and Discussion

Typical isotherms from water at 20 °C for benzene, 1,3-dichlorobenzene, and 1,2,4-trichlorobenzene as single components and for the last two in combination on a Woodburn silt loam soil are shown in Figure 1. No indication of isotherm curvature at equilibrium concentrations extending to 60–90% of saturation was found. This characteristic complies with the criteria for solute partition in the soil organic matter phase (*1, 2, 4*). The idea that sorption from water is mainly a partition process was further tested by comparing the single-solute and binary-solute isotherms of 1,3-dichlorobenzene and 1,2,4-trichlorobenzene. Competition would indicate adsorption (*16–19*); independent sorption indicates partitioning. Figure 1 shows no apparent competitive effect.

Table I summarizes sorption data for 12 aromatic compounds on the same soil along with related physical properties. The K_{om} values are obtained from the slopes of the isotherms divided by the organic matter content of the soil. While these data are for a single soil, many investigators (*1, 4, 22–29*) have shown that the sorptive characteristics of the organic components of soils of widely differing types and sources are comparable. The results in Table I can therefore be considered reasonably representative of many soils. Figure 2 is a plot of log K_{om} vs. log $S\bar{V}$ along with the ideal line from eq 9. The regression equation of data from the 12 organic compounds is

$$\log K_{om} = -0.813 \log (S\bar{V}) - 0.993 \qquad (10)$$

with a correlation coefficient $r^2 = 0.995$, where S is in moles per liter and $\bar{V}$ in liters per mole. Similar to the partition of organic solutes in octanol–water systems (in which log

$K_{ow} = -0.862 \log S + 0.710$) (*3, 4*), the experimental log K_{om} values show a systematic deviation from the ideal line, making the slope of the experimental line significantly different from −1. However, while the effect of log $S\bar{V}$ is more important than the effect of solute incompatability with soil organic phase, i.e., $(\chi - \chi_S)/2.303$, the latter is greater than the corresponding effect (log γ_0^*, eq 1) for the same compounds with the octanol phase (*3, 4*). The finding that soil organic matter is inferior to octanol as partition phase for relatively nonpolar organic compounds is quite reasonable as the soil organic matter is generally more polar than octanol. This difference in polarity is illustrated by the observation that soil humus can sorb a significant amount of water (*30*), whereas octanol holds only about 5% water by weight (*31*).

Using eq 8 to account for the deviations from the ideal line (log K_{om}° − log K_{om}) for the compounds for which solubility parameters are available (*32*) (benzene $\delta = 9.2$; chlorobenzene, 9.5; ethylbenzene, 8.8; 1,2-dichlorobenzene, 10.0), δ_p is calculated to be 12.7, 13.2, 12.3, and 13.6 for the (water-saturated) humic substances of the studied soil. The average value ($\delta_p = 13.0$) appears to fall into a reasonable range for soil humus that contains certain polar groups and water in its network, indicating that its polarity is between acetal resin ($\delta_p = 11.1$) and polyacrylonitrile ($\delta_p = 15.4$) and perhaps close to nylon 66 ($\delta_p = 13.6$) (*33*). The calculated δ_p value for the organic matter of the studied soil is appreciably higher than $\delta = 10.3$ for octanol, although the δ value for the octanol phase of the octanol–water mixture would be somewhat greater because of water saturation. The calculated δ_p could be inaccurate as eq 3, 6, and 8 are derived with certain assumptions and approximations.

Since variability of $\bar{V}$ is small compared to that of S, the correlation between log K_{om} and log S should be essentially linear, as reported previously (*1, 4, 22–28*). Omitting the molar volume term, the present study leads to

$$\log K_{om} = -0.729 \log S + 0.001 \qquad (11)$$

with $r^2 = 0.996$, where S is in moles per liter. In eq 10 and 11, the S values for solid solutes are the estimated solubilities of the corresponding supercooled liquids. The reason for this adjustment is discussed later.

Because water insolubility is the major factor affecting the values of K_{om} and the values of K_{ow} (octanol–water) for slightly water-soluble organic solutes (*3*), a practically linear relationship should also exist between log K_{om} and log K_{ow}, as observed for various compounds in different soils (*22–29*). In this study, the regression gives

$$\log K_{om} = 0.904 \log K_{ow} - 0.779 \qquad (12)$$

with $n = 12$ and $r^2 = 0.989$. The coefficient of log K_{ow} for a selected group of compounds should approximate the ratio of the change of log K_{om} with log S to that of log K_{ow} with log S. The ratio of −0.729 in eq 11 to −0.799 in log K_{ow} vs. log S for the 12 compounds in Table I yields 0.912, in good agreement with eq 12.

Since the effect of melting point contributes to part of the solute insolubility without affecting the partition coefficient (*3, 34*), we have converted the water solubilities of the solid solutes to the estimated solubilities of the corresponding supercooled liquids by standard thermodynamic methods (*3, 13*). This procedure normalizes all solute solubilities in terms of their liquid forms. Consistent with the partition criteria, 1,4-dichlorobenzene as a supercooled liquid and 1,2- and 1,3-dichlorobenzenes as liquids, now having about equal solubilities, give about the same values in K_{ow} (*21*) and in K_{om}. Similarly, anthracene and phenanthrene as supercooled liquids have about the same water solubilities (*3*) and K_{ow} (*21*) and K_{om} (*22*) values, despite a large difference in their solubilities as solids (*3*). In general, the Flory–Huggins treatment for solute solubility in a polymer phase and the melting-point correction for solid solubilities lead to an improved understanding of the correlations of log K_{om} vs. log $S\bar{V}$, log K_{om} vs. log S, and log K_{om} vs. log K_{ow}. From the partition standpoint, one can expect the K_{om} values and hence the correlation equations with log K_{om} for given compounds in different soils to be affected by the composition of the soil organic matter. A characterization of structural variations of humic substances in soils (sediments) is an important step toward defining the range of variability of K_{om} values.

Finally, the partition concept for soil–water systems appears to parallel the theory for reversed-phase high-pressure liquid chromatography (HPLC). Both processes involve partition of the solute into the polymeric (organic) phase. The mineral fraction of soil and the column support interact preferentially with the polar solvent (water) and are thus relatively inert to nonionic organic compounds. Just as the composition of the stationary phase in reverse-phase HPLC affects the retention, K_{om} is affected by the network and polarity of soil humus as it varies with oxidation and ambient conditions. Thus, although the water solubility of an organic solute appears to be the primary factor determining K_{om}, it would be of interest to investigate how humic components vary in different soils and how their capacity to remove solutes from water depends on these chemical and physical differences, including the effect of water sorbed to humic components.

Registry No. H_2O, 7732-18-5; 2-PCB, 2051-60-7; 2,2′-PCB, 13029-08-8; 2,4′-PCB, 34883-43-7; 2,4,4′-PCB, 7012-37-5; benzene, 71-43-2; anisole, 100-66-3; chlorobenzene, 108-90-7; ethylbenzene, 100-41-4; 1,2-dichlorobenzene, 95-50-1; 1,3-dichlorobenzene, 541-73-1; 1,4-dichlorobenzene, 106-46-7; 1,2,4-trichlorobenzene, 120-82-1; 1-octanol, 111-87-5.

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