



ENVIRONMENTAL RESEARCH BRIEF

Assessing the Environmental Partitioning of Organic Acid Compounds

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Background

The ultimate disposition of organic compounds in the environment is influenced tremendously by their tendency to partition, or "adsorb" to sediment particles or other distinct environmental components or phases. To date, the majority of sorption research for organic chemicals has focused on describing partitioning processes of neutral compounds, such as the polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and dioxins. Many environmentally relevant organic compounds, however, contain acid or base functional groups. Compounds containing acid functional groups include the chlorinated phenoxyalkyl acid herbicides, such as 2,4-D and 2,4,5-T; chloro- and nitrophenols, such as pentachlorophenol (PCP); and sulfonated compounds, such as azo and anthraquinone acid dyes, and linear alkylbenzenesulfonate (LAS) surfactants. Organic bases of significance include the nitrogen heterocycles, such as quinoline, and aromatic amines, such as benzidine.

This Research Brief focuses on the partitioning of organic acid compounds in octanol-water and in sediment-water systems. The main emphasis is to characterize the adsorption processes of these compounds "mechanistically," to permit the development of quantitative structure-activity relationships. In light of the differences in adsorption reactions among neutral, cationic, and anionic organic compounds, a brief theoretical description is given as to why these compounds partition as they do in the environment. For example, why do certain environmental components, such as fish lipid, or the organic material in soils and sediments preferentially adsorb neutral compounds over charged species? An explanation is given based on thermodynamic considerations, and various assumptions and requirements necessary to quantify these partitioning processes are examined.

Equilibrium Partitioning

If no kinetic limitations exist, the tendency to partition, expressed as an equilibrium adsorption coefficient (K_d), is directly related to the standard free energy of adsorption, ΔG°_{ads} as expressed by Equation 1. (See [1,2] for a more thorough discussion).

$$\Delta G^{\circ}_{ads} = -RT \ln K_d \quad (1)$$

To characterize the adsorption of organic compounds to environmental matrices, such as soils, sediments, and biota, this "standard free energy" of adsorption must be factored into adsorption components (i.e., soil organic carbon). Adsorption to each of these components, in turn, results from additive effects of various adsorption interactions or "energies." According to Stern [see 1,2], in the most basic form these energies can be separated into an intrinsic chemical energy term (ΔG°_{chem}) and an electrostatic energy term (ΔG°_{el}).

$$\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{chem} + \Delta G^{\circ}_{el} \quad (2)$$

For neutral organic compounds, the total energy of adsorption contains no electrostatic component, and hence, is equal to the intrinsic chemical adsorption energy (ΔG°_{chem}). For moderately large (molecular weight > 100) nonpolar compounds, this adsorption energy is dominated by hydrophobic forces. Hence partitioning occurs "out" of hydrophilic phases such as water to more hydrophobic phases. Water solubility (corrected for crystal energy of solids), octanol-water partitioning, connectivity indices, chromatographic retention times, and estimated molecular surface areas, all have been used to index chemical activity (or free energy changes) of hydrophobic compounds for estimating partitioning to media such as soil organic carbon and fish lipid.

Because the intrinsic chemical adsorption energy (ΔG°_{chem}) for organic compounds, as a rule, results from hydrophobic interactions, this term for both cationic and anionic organic

compounds is less than for neutral compounds of similar structure. For these charged species, however, the primary change in the overall adsorption energy may result from electrostatic contributions to adsorption (ΔG_{el}^0). This electrostatic contribution can be positive or negative and is equal to the product of the compound's valence (z), Faraday's constant (F), and the surface potential (ψ). Most natural soils and sediments contain mineral and organic surfaces that possess negatively charged functional groups. Therefore, the overall sign of ΔG_{el}^0 is ultimately determined by the charge of the adsorbing ion.

For adsorption of cationic organic compounds ($z = +1$), the overall sign of ΔG_{el}^0 is negative, and electrostatic interactions can promote adsorption beyond what is predicted for a similar neutral compound based purely on hydrophobic interactions. Examples of this in the literature include the adsorption of benzidine (4,4-diaminobiphenyl, $pK_a = 4.3$) [3] and quinoline ($pK_a = 4.94$) [4] onto sediments or aquifer material. The adsorption of these compounds to natural surfaces is highly pH-dependent because of their relatively low pK_a values. At pH values where the cationic form of these compounds predominates, adsorption can be two orders of magnitude greater than the hydrophobic adsorption of the corresponding neutral species. This type of reaction is generally referred to as ligand (or cation) exchange, and modeling this process relies on understanding the adsorption behavior of other exchangeable ions, such as Ca^{+2} and Mg^{+2} . Also, adsorption can occur to various subcomponents of soils and sediments, such as the organic matrix and various mineral components. To effectively describe these processes, model algorithms must be somewhat complex. Modeling the adsorption of organic cations may best be accomplished by incorporating adsorption algorithms into "electrostatic" or ligand exchange adsorption models, similar to those used to estimate metals adsorption.

For the adsorption of anionic organic compounds ($z = -1$), the overall sign on ΔG_{el}^0 is positive, and electrostatic interactions act to attenuate adsorption. Hence, adsorption to natural sediments by the anionic form of an organic acid is generally less than adsorption of the corresponding neutral species. Because no specific electrostatic interactions occur to promote adsorption, the partitioning process must result from the existence of a significant chemical adsorption energy term. This situation results in adsorption occurring predominantly through hydrophobic interactions, attenuated by electrostatic forces. Indeed, in limited cases [5,6], the adsorption of anionic organic compounds has been normalized to the organic carbon content of the sediments and soils. In another study [7], adsorption of LAS surfactants was shown to increase with surfactant alkyl chain length through the surfactant series investigated, indicating that hydrophobicity contributes to the total energy of adsorption.

In quantitatively assessing these partitioning reactions, separating the hydrophobic component of partitioning from the electrostatic component is essentially impossible. As with neutral organic compounds, however, model systems can be used to assess and possibly quantitatively describe sorption processes. Model systems include some of the same "systems" or parameters used to assess partitioning of neutral compounds, such as solubility or octanol-water distribution. Indeed, many of the same factors that influence

the transfer of organic acids between octanol and water (or affect the apparent water solubility) influence the transfer of these compounds between the components of the more heterogeneous system of sediment-water [8-10]. These similar factors include the degree of dissociation and the hydrophobicity and electrostatic influences of both sorbent and sorbate.

As a result of these similarities, the distribution of several organic acids between octanol and water phases has been examined as a function of aqueous phase salt concentration (for KCl, NaCl, LiCl, $MgCl_2$, and $CaCl_2$) and aqueous phase pH [9]. Compounds that have moderately low (< 5) pK_a values were chosen. From these experiments, equilibrium partition coefficients of the neutral and charged forms, as well as several pK_a values have been calculated. The sediment-water distribution of selected organic acids also has been investigated as a function of aqueous phase ionic composition and pH [10]. Experimental results and model development for each system is briefly reviewed.

Octanol-Water Partitioning

The distribution of organic acids between water and octanol in the presence of monovalent inorganic cations can be described by Reactions 1 through 6 of Figure 1. The reactions in Figure 1 are formulated in terms of KCl as the monovalent salt, although NaCl and LiCl also have been used. The mass action equations for these reactions, along with the material balance and electroneutrality constraints, comprise the chemical equilibrium model.

Reactions of HA	Expression
1. $[HA]_w = [H^+]_w + [A^-]_w$	K_a
2. $[HA]_w = [HA]_o$	K_{ow}
Reactions in KCl, NaCl, and LiCl salt systems.	
3. $[K^+]_w + [Cl^-]_w = [K^+]_o + [Cl^-]_o$	K_{ix}
4. $[K^+]_w + [Cl^-]_w = [K^+Cl^-]_o$	K_{ipx}
5. $[K^+]_w + [A^-]_w = [K^+]_o + [A^-]_o$	K_i
6. $[K^+]_w + [A^-]_w = [K^+A^-]_o$	K_{ip}
7. $[K^+]_w + [OH^-]_w = [K^+]_o + [OH^-]_o$	
8. $[K^+]_w + [OH^-]_w = [K^+OH^-]_o$	

Figure 1. Equilibrium reactions of monovalent organic acids in octanol-water. Adapted from reference [8]. HA represents a neutral organic molecule and A⁻ represents the corresponding monovalent organic anion. Terms subscripted with "w" or "o" represent aqueous phase or octanol phase concentrations, respectively.

Reaction 1 describes acid dissociation in the aqueous phase. Reaction 2 describes transfer of the neutral species (HA) to the octanol phase. This reaction is the basis of linear free energy relationships relating K_{oc} (the sediment or soil equilibrium partition coefficient, normalized for organic carbon content) and K_{ow} (the octanol-water partition coefficient) for sorption of nonpolar organic compounds

[11,12]. For any ionizable compound, this mechanism is important when a significant fraction of the total compound exists in the neutral form. Reactions 3 and 4 represent transfer of the free and ion-paired inorganic species, respectively, to the octanol phase. For both KCl and NaCl, an aqueous phase concentration of 0.2 M (with no organic compounds present) will result in approximately 40 μ M total salt partitioning into the octanol phase. Reactions 5 and 6 describe the transfer of the free and ion-paired organic species, respectively, and the inorganic counter-ion to the octanol phase. The transfer of the organic ion, as a free species or as an ion-pair, is highly dependent upon the counter-ion. Also, as the aqueous phase inorganic salt concentration is increased, the transfer of the organic ion as an ion-pair is favored.

To illustrate these effects, the overall distribution ratio (D), of total compound in the octanol phase to total in the aqueous phase, can be calculated:

$$D = \frac{([HA]_o + [A^-]_o + [M^+ A^-]_o)}{([HA]_w + [A^-]_w)} \quad (3)$$

where M^+ represents the monovalent electrolyte K^+ , Na^+ , or Li^+ . For experiments performed at sufficiently high pH (e.g., 12), $[HA]$ is an insignificant species in either phase, and the overall distribution results from Reactions 5 and 6 of Figure 1. Using the calculated partition coefficients K_{ix} and K_{ipx} for the inorganic species KCl, NaCl, or LiCl, and the measured coefficients K_i and K_{ip} for the organic compounds pentachlorophenol (PCP), 4-chloro- α -(4-chlorophenyl)-benzeneacetic acid (DDA), and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), we can obtain the overall distribution of these compounds (Figure 2) as a function of aqueous phase salt concentration. For comparison, the concentration of the organic species $[A^-]_w$ was fixed at 10 μ M, and the pH value was set at 12. For the salts NaCl and KCl, little difference in the calculated distribution is seen, whereas partitioning into the octanol obviously is favored for the LiCl system. Also, the importance of the hydrophobicity of these compounds is apparent. The magnitude of partitioning into the octanol for the organic anions follows the sequence PCP > DDA > 2,4,5-T for all three salt systems. This is the same ordering as the octanol-water distribution coefficients of the corresponding neutral species (K_{ow}). Indeed, for ten organic compounds investigated, including various carboxylic acids and phenols, the calculated partition coefficients for formation of the ion-pair in the octanol phase (K_{ip}) correlates extremely well to K_{ow} values [9].

Results of four experiments in which pH was varied at constant ionic strength ($[K^+]_w = 0.1$ M) are presented in Figure 3. The curves were calculated using the partition coefficients given in Figure 3 for the organic compounds and calculated values for the coefficients K_{ix} and K_{ipx} for KCl. At low pH values (approximately pH 1 to 2), the neutral species is dominant in both phases, and the value of $\log D$ is independent of pH. At intermediate pH values (approximately 4 to 6), the neutral species is dominant in the octanol phase and the anionic species becomes dominant in the aqueous phase, and the distribution ratio becomes pH dependent. At high pH (above pH 9), the anion predominates in both phases, and the distribution ratio is

again independent of pH, but dependent on ionic strength, as previously discussed.

The significance of each component of this equilibrium system can be more clearly seen in a \log [concentration] versus pH diagram as presented in Figure 4 for 4,6-dinitro-o-cresol (DNOC). All lines in this figure are calculated from the six equilibrium constants for DNOC and KCl, the total mass of DNOC and KCl in the system, and the volumes of each phase. The difference between the concentration of DNOC in the octanol at low pH and the concentration in the water at high pH is due to the difference in the volumes of the two phases.

Sediment-Water Partitioning

As in octanol-water partitioning, the distribution of organic acids between sediment and water is highly dependent upon the degree of chemical dissociation. To assess the effects of pH (and hence, dissociation) on sediment-water distribution, initial experiments have been performed using a pH-stat. The pH-stat can be used to titrate and maintain a sediment slurry to a given or set pH value. Over the course of an experiment, a slurry can be sampled and the pH then can be lowered to a new set-point sequentially, resulting in a "titration curve." Considerable changes in sediment characteristics result from such a titration. This approach, however, allows factoring of the overall chemical distribution into discrete coefficients for the neutral species (K_d) and the anionic species (K_{di}). These constants may be defined operationally as

$$K_d = \frac{[HA]_{sed}}{[HA]_w} \quad (4)$$

$$K_{di} = \frac{[A^-]_{sed}}{[A^-]_w} \quad (5)$$

with

$$K_a = \frac{\{H^+\} [A^-]_w}{[HA]_w} \quad (6)$$

where $[HA]_{sed}$ (mol/kg) and $[HA]_w$ (M) are the neutral species concentrations in sediment and aqueous phase, respectively, and $[A^-]_{sed}$ and $[A^-]_w$ are the anionic species sediment and aqueous phase concentrations, respectively. Because only total concentration in each phase can be determined analytically, mass balance equations for each phase and for the total system are needed,

$$[HA]_{aq} = [HA]_w + [A^-]_w \quad (7)$$

$$[HA]_s = [HA]_{sed} + [A^-]_{sed} \quad (8)$$

$$[HA]_t = [HA]_{aq} + (m/v)[HA]_s \quad (9)$$

where, (m/v) is the sediment mass (kg) to aqueous volume (L) ratio. Combination of Equations 4 through 9 results in an expression for the fraction of total compound in the aqueous phase,

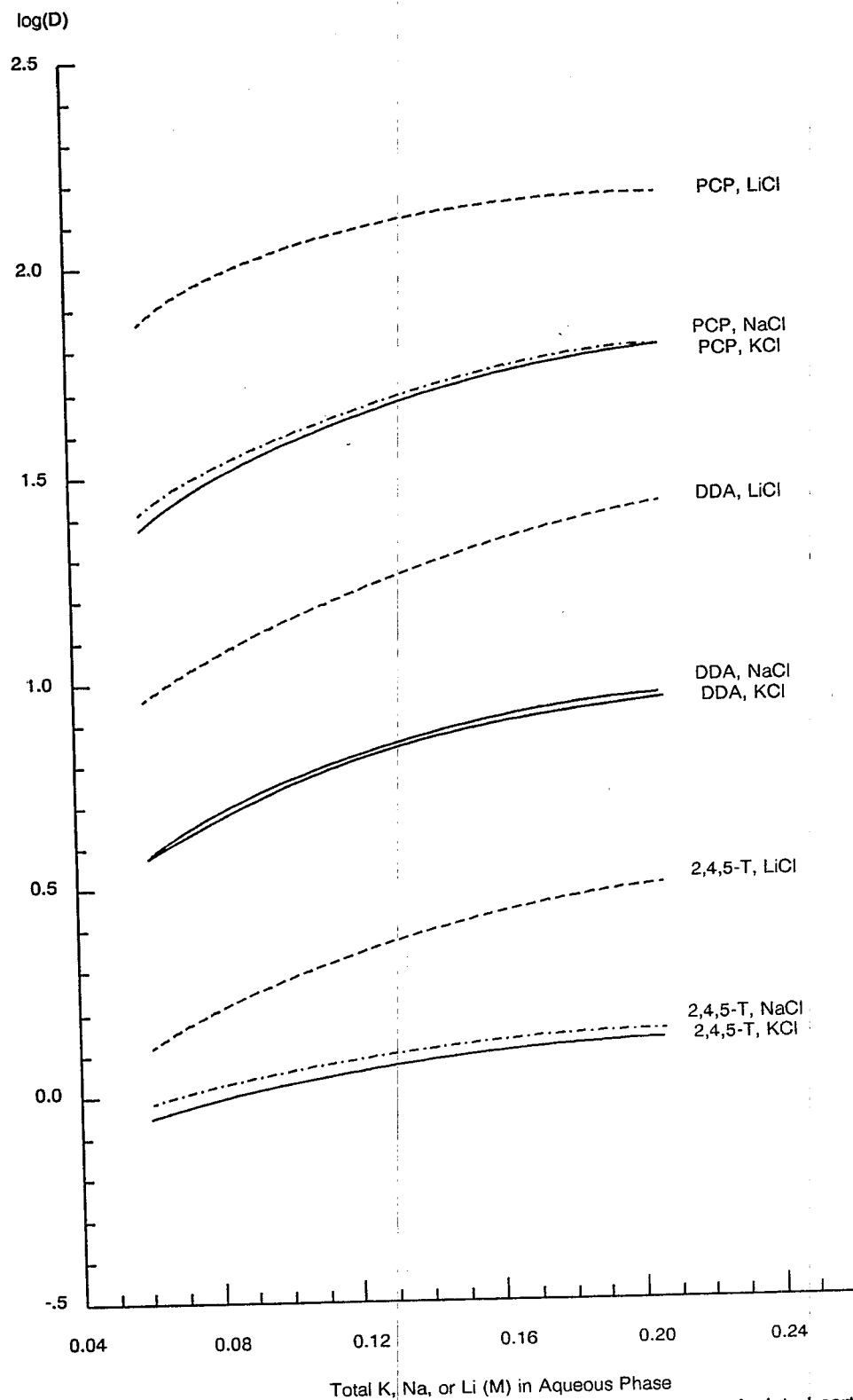


Figure 2. The octanol-water distribution of 2,4,5-T, DDA, and PCP, using the calculated partition coefficients from experimental data, and setting $[A]_w$ at 20 μ M and the pH at 12.

$$f_{aq} = \frac{[HA]_w + [A^-]_w}{[HA]_t} \quad (10)$$

$$= \frac{(K_a + \{H^+\})}{(K_a + \{H^+\}) + (K_d \{H^+\} + K_{di} K_a) (m/v)}$$

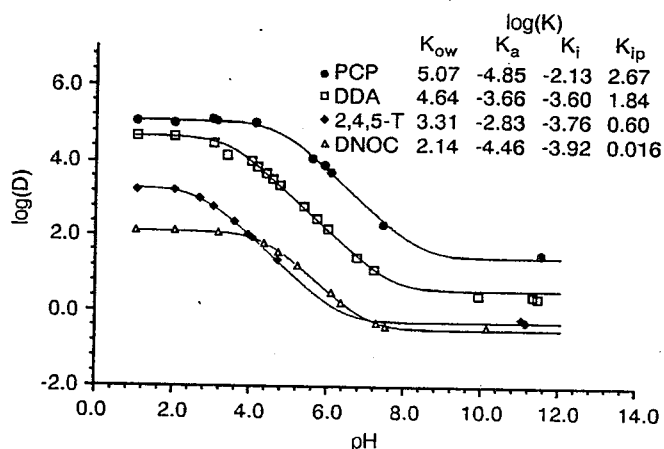


Figure 3. The octanol-water distribution of four compounds as a function of aqueous phase pH. Symbols are data points, and lines are calculated by minimizing residuals on K_{ow} and K_a . In experiments, the aqueous phase contained 0.1 M KCl, and HCl or KOH for pH adjustment. The total mass of compound per tube in each experiment was constant.

Results of initial studies on several organic acid compounds, using a silty sediment from the Ohio River (EPA sediment 11) suggests a definite pH dependence on K_{di} [10]. In accord with electrostatic considerations described previously, some type of pH dependence on the adsorption of the anion may seem unequivocal, resulting from changes in the surface charge or degree of protonation of the organic carbon matrix. For the compounds studied on EPA sediment 11 to date, K_{di} can be expressed as

$$\log K_{di} = \sigma_i(pH) + \log K_i \quad (11)$$

where, the average pH dependence or slope (σ_i) is equal to 0.30, and K_i is the "intrinsic" chemical adsorption term (given in Table 1 for each compound). Only one sediment system was examined, however, and clearly more evidence is needed to confirm this general pH dependence. In total, 5 parameters are used in Equations 10 and 11. One constant, pK_a , is intrinsic to the adsorbate; two constants, K_d and K_i , describe the interactions between adsorbate and adsorbent; one constant, σ_i , is contained in K_{di} (along with K_i) and is intrinsic to the adsorbent; and pH (or $\{H^+\}$) is the independent variable.

The experimental data for four compounds are shown in Figure 5, along with model results using the constants given in Table 1. For PCP, DDA and 2-(2,4,5-trichlorophenoxy)-

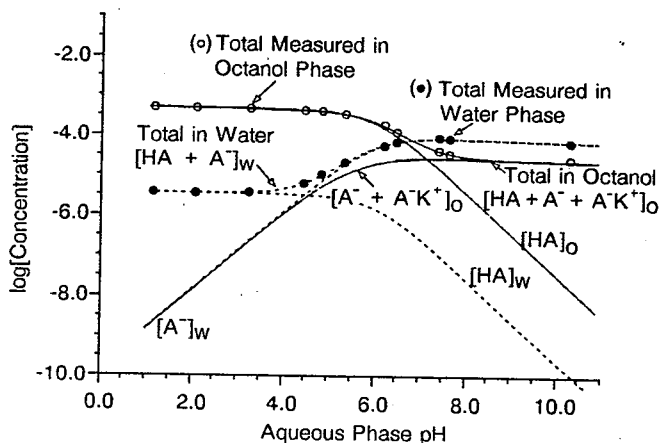


Figure 4. pC - pH diagram of DNOC species partitioning between octanol and water as a function of pH. Symbols are data points and lines are model fit. The volumes of each aqueous phase = 10 ml, volume of octanol = 2.5 ml, total mass of DNOC in each tube = 1.25×10^{-6} moles. The aqueous phase contains 0.1 M KCl, and HCl or KOH for pH adjustment.

Table 1. Constants Used in Modeling the Adsorption of Organic Acid Compounds to Sediment 11

Compound	(m/v) ^a	pK_a ^b	$\log K_d$	$\log K_i$
PCP	0.05	4.85	3.0	3.33
DDA	0.08	3.66	2.45	2.31
DNOC	0.10	4.46	1.93	2.83
Silvex	0.10	3.07	1.87	2.03

^aSediment mass to water volume ratio (kg/L)

^bReference [9].

propionic acid (silvex), organic carbon-normalized partition coefficients for the neutral species (K_{oc}) are, within a factor of two, equal to the K_{ow} . The K_{oc} for DNOC is significantly greater than its K_{ow} , likely resulting from polar interactions with the sediment by the nitro-groups on DNOC. A similar trend exists for the anionic species.

Summary

Partitioning in octanol-water and sediment-water systems by organic compounds that contain a single, relatively strong ($2 < pK_a < 5$) acidic functional group has been examined. Clearly, a significant conclusion of this work is that, at pH values found in most natural environments (i.e., 5 to 9), partitioning can occur by both the neutral and ionic forms of these and similar compounds. Therefore, to determine a *priori* chemical distribution in the environment, partitioning must be factored into measurable or predictable quantities for each adsorbing species, as has been attempted here. The adsorption of neutral organic compounds is the simplest case, wherein the adsorption energy is largely determined by hydrophobic interactions. Octanol-water distribution (K_{ow}), in turn, has been used as a measure of chemical hydrophobicity. Octanol-water distribution for organic anions is more complex and is a function of both chemical hydrophobicity and inorganic ion composition. For

the partitioning to sediments, an "ionic" or electrostatic effect also is observed for organic ions. This effect is most obvious as a result of varying the pH of sediment systems, and may result from changes in surface properties (i.e., charge). These and other effects that determine the adsorption of organic anions to natural materials must be examined further.

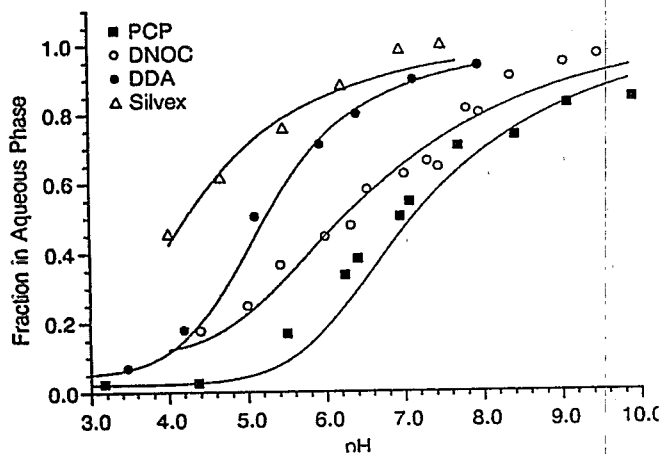


Figure 5. The pH-dependent adsorption of four organic acid compounds to EPA sediment 11 (organic carbon = 1.77%), and the predicted partitioning using Equations 10 and 11, and the values of K_d , K_i , and K_a given in Table 1, with α_i equal to -0.3.

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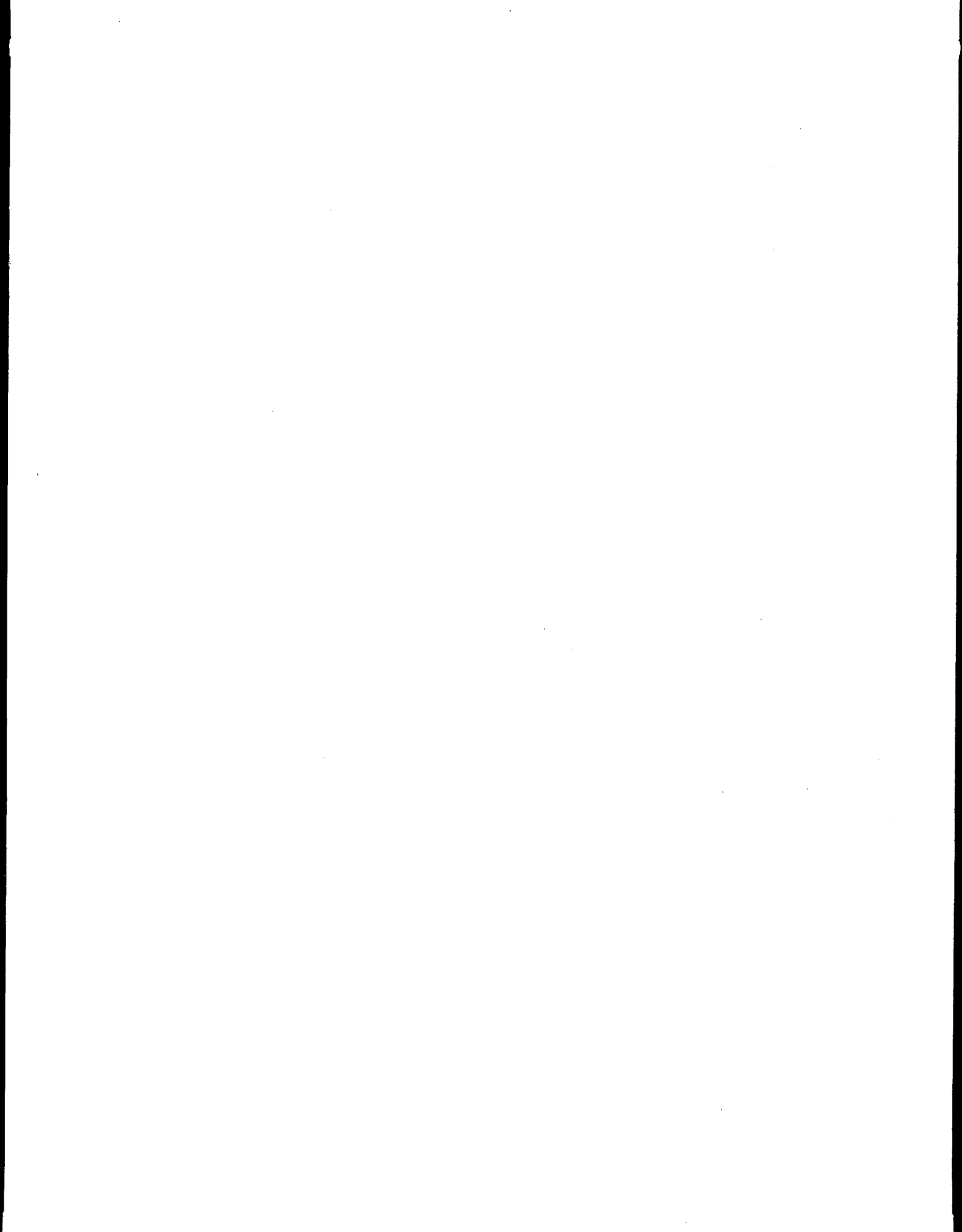
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