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Acknowledgments

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Partitioning of Organic Compounds in Octanol-Water Systems[†]

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■ When plots of the log of the octanol-water partition coefficients (K_{ow}) vs. log of water solubilities (S) of a wide variety of liquid and solid solutes are modified by converting the solid solubilities to the estimated solubilities of the corresponding supercooled liquids, the differences between the correlations for different classes of compounds are significantly reduced. Nevertheless, the experimental points deviate significantly below the "ideal" line that is calculated on the assumption of Raoult's law in the octanol phase and zero effect of dissolved octanol on water solubility; the downward deviations increase systematically with reducing S (or increasing K_{ow}), with the result that the slope of the correlation line has a significantly lower magnitude than the ideal value of -1. The deviations are caused by liquid solute incompatibility in the (water-saturated) octanol phase (as measured by the activity coefficient) and by the (lesser) effect of dissolved octanol on water solubility, both of which increase systematically with decreasing S .

Introduction

Octanol-water partition coefficients (K_{ow}) and water solubilities (S) have been widely used to study both bio-concentration (1-6) and sorption by soil (7-10) of organic

compounds from water. A better understanding of the concepts defining the relation between K_{ow} and S should extend the usefulness of these parameters in interpreting the behavior of organic compounds in the environment.

Chiou et al. (1) reported a linear correlation of $\log K_{ow}$ vs. $\log S$ that covered a range of some 6 orders of magnitude in K_{ow} and exhibited a slope that was significantly different from -1. Mackay (11) suggested that a slope of -1 should be found for liquids and would also be found for solids after appropriate correction of their solubilities for the chemical potential differences between the solids and their supercooled liquids. Chiou and Freed (12) noted that this analysis did not take into account the effect on partition of the mutual solubilities of octanol and water. We here consider these effects in some detail and present new data on the effect of dissolved octanol on the water solubilities of DDT and hexachlorobenzene (HCB). We also consider specifically the effect on K_{ow} of the activity coefficient of the solute in octanol-saturated water, an effect that was not considered explicitly by either Mackay (11) or Chiou and Freed (12). Finally, we present some new solubility and partition data, examine some estimated and experimental literature data for consistency, and consider the overall correlation including solid solutes.

Theoretical Considerations

We first consider partitioning of a liquid solute between two partially miscible solvent phases; we shall later make

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appropriate approximations for the octanol–water system and the standard estimates of partition coefficients for solids.

The condition of equality of chemical potential of a solute in both phases, together with the choice of pure (liquid) solute as the standard state (which leads to the Raoult's law convention for activity coefficients), leads to the result that at equilibrium

$$x_o \gamma_o^* = x_w \gamma_w^* \quad (1)$$

where x_o and x_w are the respective solute mole fractions and γ_o^* and γ_w^* the respective activity coefficients in the organic (later octanol) and water phases at equilibrium (not necessarily equal to those in the pure solvents). To derive the partition coefficients in customary concentration ratios, one makes the approximation that at dilute solution each mole fraction is equal to the product of the molar concentration C and the molar volume V^* of each phase (13). Substitution into eq 1 gives

$$C_o \bar{V}_o^* \gamma_o^* = C_w \bar{V}_w^* \gamma_w^* \quad (2)$$

where C_o and C_w are the molar concentrations of the solute and \bar{V}_o^* and \bar{V}_w^* the respective molar volumes (L/mol) of the organic and water phases, corrected for the solvent–water mutual saturation.

The solute partition coefficient is commonly defined as $K_{ow} = C_o/C_w$, which can now be expressed as

$$K_{ow} = \frac{C_o}{C_w} = \frac{\gamma_w^*}{\gamma_o^*} \frac{\bar{V}_w^*}{\bar{V}_o^*} \quad (3)$$

For dilute solutions this partition coefficient differs from the coefficient based on mole fractions by a factor equal to the ratio of the solvent molar volumes. This equation differs from similar expressions by Mackay and co-workers (11, 14) and by Yalkowsky and Valvani (15) in that the properties refer to the equilibrium phases rather than to pure solvents. In organic–water partition mixtures in which the solubility of the organic solvent in water is small, as for octanol with a solubility of 4.5×10^{-3} M (16, 17), \bar{V}_w^* is essentially the same as the molar volume of water \bar{V}_w .

For a liquid solute of limited solubility in equilibrium with water, we can write (by analogy with eq 1)

$$x_s^o \gamma_s = x_w^o \gamma_w \quad (4)$$

where x_s^o and γ_s are the mole fraction and the activity coefficient of the solute in the solute-rich phase and x_w^o and γ_w are the similar quantities in the water-rich phase. We make the approximation that x_s^o and γ_s are close to 1 (for low solubility of water in the liquid solute), in which case $x_w^o \gamma_w = 1$. Again setting $x_w^o = C_w^o \bar{V}_w = S \bar{V}_w$, one finds that $S = 1/(\gamma_w \bar{V}_w)$, where S and γ_w refer to molar solute solubility and activity coefficient in water.

In the octanol–water system, the relation between K_{ow} and S is simply the relation between $(\gamma_w^* \bar{V}_w)/(\gamma_o^* \bar{V}_o^*)$ and $1/(\gamma_w \bar{V}_w)$. It can be expressed as

$$K_{ow} = \frac{1}{S \bar{V}_o^* \gamma_o^*} \frac{\gamma_w^*}{\gamma_w} \quad (5)$$

or as

$$\log K_{ow} = -\log S - \log \bar{V}_o^* - \log \gamma_o^* + \log (\gamma_w^*/\gamma_w) \quad (6)$$

We now consider a plot of $\log K_{ow}$ against $\log S$ for different solutes. If the solute forms an ideal solution in the water-saturated octanol phase and if the solute solubility is the same in water and in octanol-saturated water (we shall soon consider the opposite hypotheses), then the last two terms in eq 6 drop out, and what remains is a

linear plot of $\log K_{ow}$ vs. $\log S$, with slope of -1 and intercept of $-\log \bar{V}_o^*$ (at $\log S = 0$). The intercept in this case is essentially constant for all solutes in dilute solution; the range of the ideal line is determined by the accuracy of the dilute solution approximation. If we set K_{ow}^o as the partition coefficient from the ideal line that corresponds to a given value of S , then we can write

$$\log K_{ow} = \log K_{ow}^o - \log \gamma_o^* + \log (\gamma_o^*/\gamma_w) \quad (7)$$

Equation 7 designates the last two terms as sources of discrepancies between K_{ow} and K_{ow}^o . Their effects on K_{ow} are secondary to the major effect of water solubility but are nevertheless significant, and both usually produce a downward deviation from the ideal line. In order to decrease the magnitude of the slope of the correlation line ($\log K_{ow}$ vs. $\log S$), the downward deviations from these factors must increase systematically with decreasing water solubility. Both expectations are reasonable. To the extent that there is incompatibility between octanol and paraffin hydrocarbons (positive $\log \gamma_o^*$), one would expect the effect to increase with increasing molecular weight. In a homologous series we would again expect the incompatibility to increase with increasing molecular weight (and decreasing solubility) as the solutes become more hydrocarbon-like. We would also expect the presence of dissolved water (2.3 M (18)) to increase the incompatibility. Similarly, we would expect the effect of dissolved octanol on water solubility to be most pronounced for the least soluble solutes. Therefore, the frequent observation of slopes that are significantly (but not markedly) less steep than the ideal line is quite reasonable, given a sufficiently wide range of solubilities. For liquids of appreciable solubility, where there is negligible effect of dissolved octanol on water solubility, the downward deviation from the ideal line is simply a measure of $\log \gamma_o^*$.

The foregoing analysis also applies to supercooled liquids, and thence to solids by use of standard thermodynamic methods for estimating the solubility of a supercooled liquid from that of the corresponding solid. The well-known result is that $S = (1/\gamma_w \bar{V}_w)/(f_s/f_l)$, where f_s and f_l are the fugacities at equilibrium temperature T of the solid and of its supercooled liquid. The fugacity ratio is given by the formula (19)

$$\log (f_s/f_l) = \frac{-\Delta \bar{H}_f}{2.303R} \left(\frac{T_m - T}{TT_m} \right) \quad (8)$$

where T_m and T are the melting and equilibrium temperatures (K), $\Delta \bar{H}_f$ is the heat of fusion, and R is the gas constant. The value of f_s/f_l gives the ideal solubility (in mole fraction) of the solid at T , and differences between the experimental and ideal solubilities measure the extent of nonideality of solution of the supercooled liquid.

As noted by Mackay (11), the effect of melting point on solubility will always cause a downward deviation of a plotted point from the ideal line, because the effect is to reduce water solubility without affecting the partition coefficient (since it affects both solvents equally). It is better, therefore, not to include solids in the correlation without a correction for the melting-point effect. One can carry out this estimation in the absence of accurate heats of fusion, for example, for solids with low melting points by using the estimation methods of Walden (20), Tsonopoulos and Prausnitz (21), Yalkowsky (22), Yalkowsky et al. (23), and Mackay and Shiu (24), which estimate the entropy of fusion ($\Delta \bar{H}_f/T_m$) for many simple aromatic compounds at about 13.5 ± 3 eu. We shall see how this correction improves the correlation and makes for a steeper (but not ideal) slope.

We now describe our experiments and the characteristics of the $\log K_{ow} - \log S$ correlations for various organic solutes.

Experimental Section

To determine the solubilities of *o*- and *m*-toluidine, *N*-methylaniline, *N,N*-dimethylaniline, *o*- and *m*-chloroaniline, *o*-, *m*-, and *p*-dichlorobenzene, and 1,2,4-trichlorobenzene, we equilibrated excess chemical with organic-free distilled water in screw-capped bottles in a reciprocal shaker for 24 h. The solution was allowed to sit for 2 days before first samples were taken for analysis. For solutes with appreciable volatility (dichlorobenzenes and trichlorobenzene), samples were taken by syringe through a drilled hole in the cap fitted with a Teflon-faced silicon septum. The saturated solution was diluted with water in a similarly capped volumetric flask, and aqueous samples were taken via a syringe and injected directly onto a porous polymer Chromosorb 101 column in a Varian 3700 gas chromatograph equipped with a ^{63}Ni EC detector. Sample analysis was continued daily (for dichlorobenzenes) until steady concentrations were observed. For other relatively nonvolatile solutes, no preventive measures were taken against evaporative losses, and the concentrations were analyzed by UV. The solubility of DDT in water was established by equilibrating the solute in a Teflon-lined, capped, 25-mL Corex centrifuge tube for 24 h. The samples were centrifuged at 3500 rpm (1560g) for 1 h to settle down the excess DDT and then allowed to stand at least 2 h before aliquots of the supernatant solution were removed for analysis. The solubility of HCB in water was determined earlier according to the method of Haque and Schmedding (25).

The solubilities of DDT in octanol and in water-saturated octanol were carried out with the same procedure as was used for DDT in water. In the latter study, DDT was added to the octanol containing excess water. After the solubility in water-saturated octanol was determined, adjusted amounts of DDT were added to mixtures of octanol and water (2 mL/20 mL) in 25-mL centrifuge tubes to give concentrations in the octanol phase in the range of 50–90% saturation. The samples were equilibrated, centrifuged, and maintained as described. The octanol phase was then removed and stored in a separate container for subsequent analysis. To get accurate measurements of the aqueous-phase concentration, one must remove the octanol residue on the surface of the water, and the octanol film on the portion of the wall which was previously in contact with octanol must be carefully cleaned off (normally by wiping with tissue paper). To assist in complete elimination of excess octanol from the water phase, we recentrifuged the samples in the same tubes. By this method, the excess octanol normally appeared as visible droplets and could be removed easily with a suction pipet. The process was continued until no more droplets are formed on centrifugation. Aqueous samples were then withdrawn for analysis. The solubility of DDT in octanol-saturated water (S_w^*) was computed from the determined concentrations in octanol-saturated water (C_w) and water-saturated octanol (C_o) as $S_w^* = (C_w/C_o)S_o^*$, where S_o^* is the solubility of the solute in water-saturated octanol. This procedure gives more accurate results than equilibration of (octanol-saturated) water with solid DDT because excess octanol droplets are more easily detected than small DDT crystals in the water.

The solubility of hexachlorobenzene (HCB) in octanol was determined by the same procedure as for DDT. The solubilities in water-saturated octanol and in octanol-saturated water were obtained by analyzing the equilib-

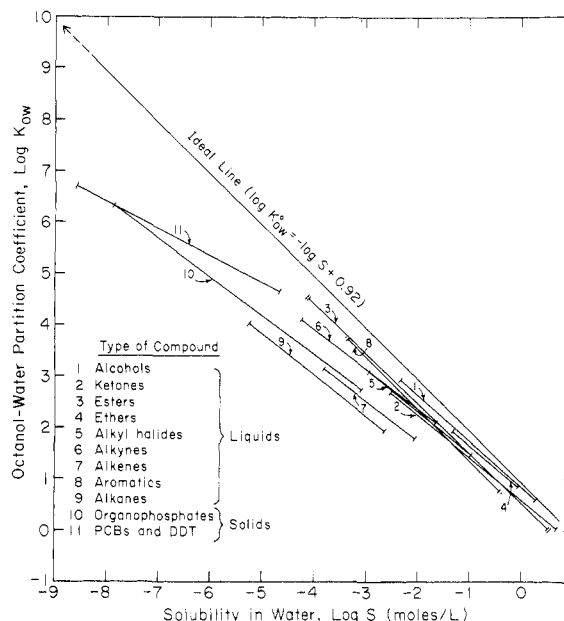


Figure 1. Relationship between octanol-water partition coefficient and water solubility for various classes of liquids and solid organic compounds in comparison with the ideal line. Data for liquids are from Hansch et al. (26) and those for solids from Chiou et al. (1) and Tulp and Hutzinger (27).

rium concentrations of the two mutually saturated solvent phases of the octanol-water mixture containing excess amounts of HCB. The mixture was equilibrated and the two solution phases were separated according to the methods described.

The method for measuring octanol-water partition coefficients has earlier been described (1). Two-milliliter aliquots of octanol stock solution of the solute (normally at 1000 ppm) were equilibrated with 20 mL of organic-free water in a Teflon-lined, capped, 25-mL centrifuge tube. The mixture was equilibrated and centrifuged, and the phases were separated according to the procedure described. For GC analysis, octanol samples were diluted with hexane and aqueous samples extracted with hexane.

Results and Discussion

The values of \bar{V}_o^* and \bar{V}_w^* in K_{ow} can be calculated from the mutual solubilities of octanol and water and used to define the ideal line. With the solubility of water in octanol at 2.3 M (or mole fraction of 0.27) at room temperature (18), $\bar{V}_o^* = 0.12$ L/mol (instead of $\bar{V}_o = 0.157$ L/mol for pure octanol) on the assumption of volume additivity. This gives the intercept as 0.92 for the ideal line. The small solubility of octanol in water has negligible effect on its molar volume; hence, $\bar{V}_w^* = \bar{V}_w = 0.018$ L/mol.

The relationship between $\log K_{ow}$ and $\log S$ for various classes of organic compounds is shown in Figure 1, along with the ideal line for the octanol-water system. Table I gives the regression equations for each group. In evaluating these results, we first assume γ_w/γ_w^* to be 1 (its magnitude will be analyzed later for DDT and HCB); K_{ow}^o/K_{ow} then becomes equal to γ_o^* for liquids. The data for organic liquids (classes 1–9) are those of Hansch et al. (26), in which most partition coefficients are calculated values. Imprecise as some of these data may be, they nevertheless illustrate the behavior of organic liquids in octanol-water systems. Alcohols and ethers approach ideal solution behavior in the octanol phase because their structure and polarity make them compatible with octanol. Over the range of the reported water solubilities, the deviations from the ideal line of ketones, esters, alkyl halides,

Table I. Correlations of Octanol-Water Partition Coefficients (K_{ow}) with Aqueous Solubilities (S) for Organic Chemicals at Room Temperature for $\log K_{ow} = a \log S + b$

| type of compd | a^d | b^e | no. of compds | r |
|-------------------------------|--------|--------|---------------|-------|
| liquid organics ^a | | | | |
| alcohols | -0.898 | 0.832 | 41 | 0.967 |
| ketones | -0.813 | 0.586 | 13 | 0.980 |
| esters | -0.987 | 0.513 | 18 | 0.990 |
| ethers | -0.846 | 0.791 | 12 | 0.938 |
| alkyl halides | -0.819 | 0.681 | 20 | 0.928 |
| alkynes | -0.773 | 0.806 | 7 | 0.953 |
| alkenes | -0.773 | 0.192 | 12 | 0.985 |
| aromatics | -1.004 | 0.340 | 16 | 0.975 |
| alkanes | -0.808 | -0.201 | 16 | 0.953 |
| all compds | -0.747 | 0.730 | 156 | 0.935 |
| solid organics | | | | |
| organophosphates ^b | -0.747 | 0.472 | 10 | 0.969 |
| PCBs and DDT ^{b,c} | -0.518 | 2.222 | 7 | 0.997 |

^a Data from Hansch et al. (26). ^b Data from Chiou et al. (1). ^c Data from Tulp and Hutzinger (27). ^d Slope. ^e Intercept.

alkynes, and aromatics are fairly comparable with those of alcohols and ethers.

Alkanes and alkenes, by contrast, deviate downward from the ideal line by some 2 orders of magnitude in the partition coefficients, which would require γ_o^* values of about 100. The fact that these unusually high values are inconsistent with the observed miscibility of octane with water-saturated octanol suggests that the data are not accurate. Indeed, the experimental K_{ow} values of some alkanes and alkenes reported recently by Leo et al. (28) are about 1 order of magnitude greater than the calculated values. With this adjustment, the alkane and alkene regression lines would probably shift upward by as much as 1 order of magnitude, which would put them in close proximity to other regression lines. In general, large positive values of γ_o^* , or large downward deviations from the ideal line, should be regarded with caution for octanol-miscible liquids.

We now consider solids. The correlation lines for two solid groups, organophosphates and PCBs/DDT, are included in Figure 1 to illustrate the melting-point effect. Most organophosphates have relatively low melting points ($\leq 70^\circ\text{C}$) (29); the reasonable assumption that their heats of fusion are smaller than 6 kcal/mol leads to the prediction that their values of $\log(f_1/f_s)$ should be less than 0.5. This correlation shifts the data points toward the extrapolated regression lines for other organic liquids. Because the melting-point corrections in $\log S$ are relatively

small, the liquid organophosphates, malathion and parathion, follow reasonably closely the same regression line as the other (solid) organophosphates; this suggests that the observed deviation from the ideal line is largely due to the polarity difference between these solutes and (water-saturated) octanol. In the PCBs/DDT series, 2-chlorobiphenyl and 3-chlorobiphenyl do not depart appreciably from the extended regression lines of aromatics and other liquids, again because 3-chlorobiphenyl is a liquid at 25°C and 2-chlorobiphenyl has a low melting point (34°C).

Inclusion of solid solutes into a group of homologous liquid solutes normally increases the scatter in the linear plot, again because of the melting-point effect. For instance, solid naphthalene, phenanthrene, anthracene, and pyrene have K_{ow} values (10) substantially lower than one predicts from their (solid) water solubilities and the regression line for liquid aromatics. The correlations are greatly improved, however, when the solid solubilities are converted to the solubilities of their supercooled liquids by incorporating the melting-point correction. This is illustrated in Table II, where the calculated values of γ_o^* for both solid and liquid aromatics appear to show relatively small but systematic changes with liquid and supercooled liquid solubilities.

Solid DDT, with $\log S = -7.81$ (36) at 25°C and $\log K_{ow} = 6.36$ at 20°C , deviates downward from the ideal line by about 2.37 logarithm units. With $\Delta\bar{H}_f = 6.70$ kcal/mol (37) and $mp = 108.5^\circ\text{C}$, the melting-point correction shifts $\log S$ upward by 1.07 units, and thus reduces the downward deviation of DDT to about 1.30. Similarly, the poor fit of solid HCB ($\log S = -7.76$ at 25°C (36) and $\log K_{ow} = 5.50$ at 20°C) to the liquid aromatic regression line results mainly from the melting-point effect. With $\Delta\bar{H}_f = 7.35$ kcal/mol (38) and $mp = 229^\circ\text{C}$, it gives $\log(f_1/f_s)$ at 2.19 for HCB at 25°C , which reduces its deviation to 0.99 units. Thus, DDT and HCB as estimated supercooled liquids fall reasonably close to the extended regression line for aromatic liquids.

As noted earlier, any effects of dissolved octanol on water solubility (as reflected in $\log \gamma_w^*/\gamma_w$ from eq 6) would be expected to be most pronounced with solutes of very low water solubility, such as DDT and HCB, and to cause a downward deviation (because it is negative) from the ideal line in addition to the effect of $\log \gamma_o^*$. Given the estimated total downward deviation for DDT and HCB supercooled liquids as 1.30 and 0.99, respectively (which are equal in magnitude to the last two terms in eq 6), we can estimate separately the effect of $\log \gamma_o^*$, then estimate the effect of $\log \gamma_w^*/\gamma_w$ by difference, and finally compare the estimated effect of $\log \gamma_w^*/\gamma_w$ (resulting from octanol solubility in water) with experimental solubility values.

Table II. $\log(f_1/f_s)$ and $\log \gamma_o^*$ of Some Aromatic Hydrocarbons at 25°C

| compd | mp, $^\circ\text{C}$ | $\Delta\bar{H}_f$, kcal/mol | $\log(f_1/f_s)$ | $\log S$ | $\log K_{ow}$ | $\log \gamma_o^h$ |
|---------------------|----------------------|------------------------------|-----------------|--------------------|-------------------|-------------------|
| benzene | liquid | | | -1.64 ^d | 2.13 ^h | 0.43 |
| toluene | liquid | | | -2.25 ^d | 2.69 ^h | 0.48 |
| propylbenzene | liquid | | | -3.30 ^e | 3.68 ^h | 0.53 |
| 1,4-dichlorobenzene | 53 | 4.35 ^a | 0.27 | -3.31 ^f | 3.39 ^h | 0.57 |
| naphthalene | 80 | 4.61 ^b | 0.53 | -3.61 ^g | 3.36 ⁱ | 0.64 |
| biphenyl | 71 | 4.43 ^a | 0.43 | -4.31 ^g | 4.09 ^h | 0.71 |
| 2-methylnaphthalene | 34 | 2.85 ^b | 0.061 | -3.75 ^g | 4.11 ⁱ | 0.50 |
| phenanthrene | 101 | 4.45 ^b | 0.66 | -5.14 ^g | 4.57 ⁱ | 0.83 |
| anthracene | 216 | 6.89 ^b | 1.97 | -6.60 ^j | 4.54 ⁱ | 1.01 |
| pyrene | 156 | 4.20 ^c | 0.94 | -6.18 ^g | 5.18 ⁱ | 0.98 |

^a Reference 21. ^b Reference 30. ^c Reference 31. ^d Reference 32. ^e Reference 33. ^f Reference 34. ^g Reference 24. ^h Reference 18. ⁱ Reference 10. ^j Reference 35. ^h $\log \gamma_o^* \cong \log K_{ow}^\circ - \log K_{ow}$, where $\log K_{ow}^\circ$ is the "ideal" partition coefficient based on supercooled liquid solubility: $\log S + \log(f_1/f_s)$. This equation does not include the small effect of dissolved octanol in the water phase.

Table III. DDT Equilibrium Concentrations at 50–90% Saturation in the Octanol-Rich and Water-Rich Phases of the Octanol-Water Mixture at ~24 °C

| sample no. | C_w , $\mu\text{g/L}$ | C_o , g/L | $\log (C_o/C_w)$ |
|------------|-------------------------|-------------|------------------|
| 1 | 12.8 | 29.1 | 6.36 |
| 2 | 11.8 | 29.0 | 6.39 |
| 3 | 11.5 | 25.1 | 6.34 |
| 4 | 10.6 | 25.1 | 6.37 |
| 5 | 13.2 | 23.7 | 6.25 |
| 6 | 10.8 | 22.5 | 6.32 |
| 7 | 12.4 | 21.3 | 6.24 |
| 8 | 12.2 | 21.2 | 6.24 |
| 9 | 5.87 | 16.5 | 6.45 |
| 10 | 8.03 | 16.2 | 6.31 |

We estimate γ_o^* for DDT and HCB by comparing the calculated ideal solubilities with experimental solubilities in water-saturated octanol. The ideal solubilities of DDT and HCB at 25 °C calculated from their heats of fusion and melting points are 0.70 mol/L (0.084 mole fraction) and 0.054 mol/L (0.0065 mole fraction), respectively, and the observed solubilities in water-saturated octanol are 0.0899 mol/L for DDT at 24 °C (in pure octanol, 0.117 mol/L) and 0.0101 mol/L for HCB at 24.5 °C (in pure octanol, 0.0124 mol/L at 23 °C). These results give $\log \gamma_o^* = 0.89$ and $\log (\gamma_w/\gamma_w^*) = 0.41$ for DDT; the respective values for HCB are 0.73 and 0.26. The calculations suggest that the presence of octanol in water promotes DDT water solubility by about 160% ($\gamma_w/\gamma_w^* = 2.6$) and HCB solubility by 80% ($\gamma_w/\gamma_w^* = 1.8$). With the solubility in pure water of 5.5 $\mu\text{g/L}$ for DDT and 5.0 $\mu\text{g/L}$ for HCB at 25 °C (36) (which are in agreement with our experimental values of 5.0 and 4.9 $\mu\text{g/L}$ at 20 °C, respectively), the solubilities of these two compounds in octanol-saturated water are estimated as 14 and 9.1 $\mu\text{g/L}$ at 25 °C.

The foregoing analysis is further supported by the observed solubilities of DDT and HCB in octanol-saturated water. In the DDT experiment (Table III), the concentration over a range of 50–90% saturation in the octanol-saturated water (C_w) in 10 individual samples were found to compare closely with the corresponding concentrations in the water-saturated octanol phase (C_o). The partition coefficients obtained directly from the respective $\log (C_o/C_w)$ values gives an average of 6.33 ± 0.07 , which agrees with the observed value of 6.36 in a separate determination at 20 °C. The extrapolated DDT solubility in octanol-saturated water (S_w^*) using the equation $S_w^* = (C_w/C_o)S_o^*$ with $S_o^* = 31.9$ g/L gives an average of 15.3 ± 2.4 $\mu\text{g/L}$, which is in keeping with the earlier estimated value of 14 $\mu\text{g/L}$. In the HCB study with 10 individual samples in which excess HCB was added to the octanol-water mixtures, the average saturated concentration in the water-rich phase is 9.32 ± 0.51 $\mu\text{g/L}$ (Table IV). This value and the average $\log (S_o^*/S_w^*)$ of 5.49 ± 0.03 are in agreement with the predicted S_w^* of 9.1 $\mu\text{g/L}$ and our measured $\log K_{ow}$ of 5.50. The results for supercooled DDT and HCB suggest that there is a monotonic increase with decreasing water solubility of the enhancing effect of dissolved octanol on solute water solubility. Part of the difference in γ_o^* between solutes of high and low water solubilities in Table II may be related to the neglect of this effect.

We now consider the correlation between experimental K_{ow} and S for a number of common aromatic liquids and supercooled liquids (i.e., of solids with a melting-point correction for S). The estimated water solubilities at 25 °C are in parentheses in Table V. The solubilities of the liquids are at 25 °C except for chloroanilines and toluidines

Table IV. HCB Saturation Concentrations in the Octanol-Rich and Water-Rich Phases of the Octanol-Water Mixture at ~24.5 °C

| sample no. | S_w^* , $\mu\text{g/L}$ | S_o^* , g/L | $\log S_o^*/S_w^*$ |
|------------|---------------------------|---------------|--------------------|
| 1 | 10.0 | 2.88 | 5.46 |
| 2 | 9.54 | 2.87 | 5.48 |
| 3 | 8.40 | 2.93 | 5.54 |
| 4 | 8.80 | 2.90 | 5.52 |
| 5 | 9.63 | 2.98 | 5.49 |
| 6 | 9.57 | 2.99 | 5.50 |
| 7 | 8.83 | 2.81 | 5.50 |
| 8 | 9.17 | 2.78 | 5.48 |
| 9 | 9.84 | 2.85 | 5.46 |
| 10 | 9.46 | 2.80 | 5.47 |

Table V. Octanol-Water Partition Coefficients and Liquid and Supercooled Liquid Solubilities of Aromatic Compounds

| compd | $\log S_o^a$ mol/L | ref | $\log K_{ow}$ | ref |
|-----------------------------|-----------------------|-----|---------------|-----|
| aniline | -0.405 | 39 | 0.90 | 18 |
| <i>o</i> -toluidine | -0.817 | | 1.29 | 18 |
| <i>m</i> -toluidine | -0.853 | | 1.40 | 18 |
| <i>N</i> -methylaniline | -1.28 | | 1.66 | 18 |
| <i>N,N</i> -dimethylaniline | -2.04 | | 2.31 | 18 |
| <i>o</i> -chloroaniline | -1.53 | | 1.90 | 18 |
| <i>m</i> -chloroaniline | -1.37 | | 1.88 | 18 |
| benzene | -1.64 | 32 | 2.13 | 18 |
| toluene | -2.25 | 32 | 2.69 | 18 |
| ethylbenzene | -2.84 | 32 | 3.15 | 18 |
| propylbenzene | -3.30 | 33 | 3.68 | 18 |
| isopropylbenzene | -3.38 | 32 | 3.66 | 18 |
| 1,3,5-trimethylbenzene | -3.09 | 21 | 3.42 | 40 |
| <i>tert</i> -butylbenzene | -3.60 | 21 | 4.11 | 40 |
| fluorobenzene | -1.80 | 41 | 2.27 | 18 |
| chlorobenzene | -2.36 | 41 | 2.84 | 18 |
| bromobenzene | -2.55 | 41 | 2.99 | 18 |
| iodobenzene | -2.78 | 42 | 3.25 | 18 |
| <i>o</i> -xylene | -2.72 | 43 | 2.77 | 18 |
| <i>m</i> -xylene | -2.73 | 44 | 3.20 | 18 |
| <i>p</i> -xylene | -2.73 | 43 | 3.15 | 18 |
| diphenylmethane | -4.07 | 21 | 4.14 | 40 |
| <i>o</i> -dichlorobenzene | -2.98 | | 3.38 | 18 |
| <i>m</i> -dichlorobenzene | -3.04 | | 3.38 | 18 |
| <i>p</i> -dichlorobenzene | (-3.03) | | 3.39 | 18 |
| 1,2,4-trichlorobenzene | -3.57 | | 4.02 | |
| biphenyl | (-3.88) | 44 | 4.09 | 18 |
| 2-chlorobiphenyl | (-4.57) | 36 | 4.54 | 27 |
| 3-chlorobiphenyl | -5.16 | 36 | 4.95 | 27 |
| naphthalene | (-3.08) | 24 | 3.36 | 10 |
| 2-methylnaphthalene | (-3.69) | 24 | 4.11 | 10 |
| phenanthrene | (-4.48) | 24 | 4.57 | 10 |
| anthracene | (-4.63) | 35 | 4.54 | 10 |
| pyrene | (-5.24) | 24 | 5.18 | 10 |
| hexachlorobenzene | (-5.57) | 36 | 5.50 | |
| <i>p,p'</i> -DDT | (-6.74) | 36 | 6.36 | |

^a Values enclosed with parentheses are supercooled liquid solubilities, calculated on the basis of their solid solubilities given in the cited references with correction of solid melting according to eq 8. The melting effect of 2-PCB (mp = 34 °C) was estimated by using $\Delta \bar{H}_f/T_m = 13.5$.

(20 °C) and monohalobenzenes (30 °C). The K_{ow} values are those reported for room temperature (normally at 20–25 °C). A plot of $\log K_{ow}$ vs. $\log S$ is presented in Figure 2. The regression equation is

$$\log K_{ow} = -0.862 \log S + 0.710 \quad (9)$$

for 36 compounds with a slope of -0.862 (which is significantly different from -1 at the 0.0001 level) and an intercept of 0.710 (i.e., $\log K_{ow}$ at $\log S = 0$). The correlation extends over 6 orders of magnitude in S (mol/L) and 5

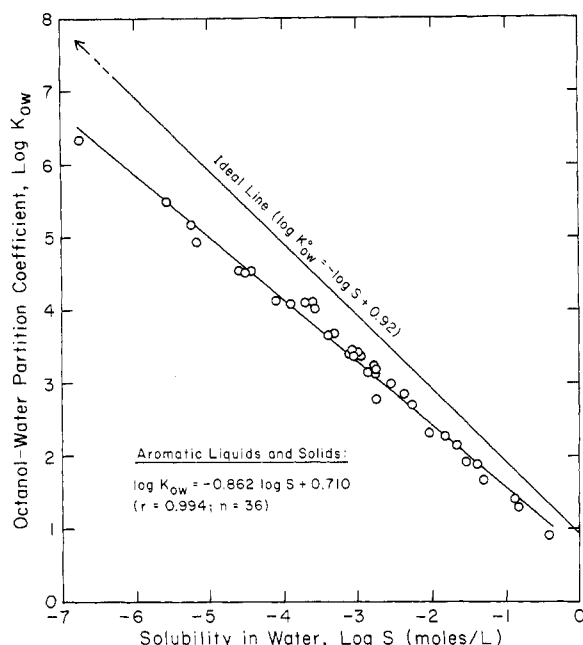


Figure 2. Correlation of octanol-water partition coefficient with water solubility for selected aromatic liquids and solids at 25 °C. The solubilities of solid compounds in the plot are those of their supercooled liquids at 25 °C.

orders of magnitude in K_{ow} with a correlation coefficient $r = 0.994$.

As expected, differences in the correlation curves for different classes of compounds are reduced by application of the melting-point correction. For example, the $\log K_{ow}$ values for low molecular weight alcohols are only about 0.2–0.4 units higher than estimated from the equation for aromatics (eq 9). Hexachloro-1,3-butadiene with $\log K_{ow} = 4.90$ and $\log S = -5.01$ at 20 °C (this work) and other alkyl halides (26) are also well represented by this equation. Similarly, the experimental $\log K_{ow}$ values of pentane, cyclopentane, cyclohexane, and cyclohexene (28) now agree closely with the values estimated from their water solubilities (26) and eq 9. Lindane gives $\log K_{ow} = 3.72$ at 25 °C (45) (3.70 at 20 °C, this work) and $S = 7.8$ mg/L at 25 °C (36) with $mp = 113$ °C and $\Delta H_f = 5.80$ kcal/mol (37). This $\log K_{ow}$ is reasonably close to that estimated (3.86) by eq 9 from the supercooled lindane (\log) solubility of -3.56 . These findings suggest that many liquid and supercooled liquid organic solutes of similar $\log S$ show comparable $\log K_{ow}$ values in the octanol-water system, regardless of homologous series. This characteristic is presumably related to the structure of octanol molecules that enables it to accommodate a diverse group of organic compounds relatively indiscriminately through its hydrophilic OH and/or its lipophilic alkyl chain, and therefore to exhibit relatively low (and hence nearly constant) values for γ_o^* .

To sum up, we now have an understanding of the individual factors that determine the prediction of octanol-water partition coefficients for liquids. In decreasing order, they are water solubility, compatibility with water-saturated octanol, and the effect of dissolved octanol on water solubility. For solids, we have to consider the effect of melting point on water solubility, and we cannot be sure that the corresponding supercooled liquids are miscible with octanol; prediction of partition coefficients from solubilities may be expected to be less accurate for high-melting solids than for liquids. For liquids, however, one should expect quite good predictability of partition coefficients, which should also extend to many organic

solvents in which all of the solutes are miscible.

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Prediction Method for Adsorption Capacities of Commercial Activated Carbons in Removal of Organic Vapors

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■ Adsorption isotherms for vapors of 13 organic solvents on 7 commercial granular activated carbons were studied. The isotherms were analyzed by the Dubinin-Polanyi equation, and relationships between the parameters of the Dubinin-Polanyi equation, W_0 and κ_s , and properties of the activated carbons were investigated. It was found that W_0 was approximately equal to 0.055 mL plus the micropore volume, $v_{3.2}$ (smaller than 3.2 nm in diameter), and κ_s of benzene could be approximated to $2.8 \times 10^{-9} \text{ mol}^2/\text{J}^2$ for various types of commercial activated carbons. From the above results, a prediction method for adsorption capacities of organic vapors on commercial activated carbons was introduced, and the method was confirmed for various conditions.

Emission of organic vapors from industrial and commercial sources is a cause of photochemical smog and nuisance odors. This certainly needs to be controlled. Recovery of organic vapors can contribute to the conservation of petroleum resources. There are several methods such as condensation, absorption, adsorption, contact oxidation, and incineration for removal and/or recovery of organic vapors. The adsorption method using granular activated carbon possesses many advantages for removal and recovery of organic vapors in low concentrations.

Although there are many theories (1-5) concerning adsorption of vapor on activated carbon, the Dubinin-Polanyi equation (1, 2) is a simple and practically useful equation for estimation of adsorption capacity for the organic vapor from waste gas on activated carbon. Dubinin (1, 2) reported that the adsorbed amount in liquid volume per unit weight of microporous adsorbent, W , could be shown by the following equation from Polanyi's adsorption potential theory:

$$\ln (W/W_0) = -\kappa A^2 \quad A = RT \ln (P_0/P) \quad (1)$$

Here, W_0 is an apparent limiting amount of adsorption for each adsorbent, κ is a parameter for each system of adsorbent and adsorbate, A is an adsorption potential, R is the gas constant, and T is the absolute temperature of adsorption. P_0 and P are saturated vapor pressure and adsorbed vapor pressure, respectively. Since eq 1 for a standard adsorbate was replaced by eq 2, eq 1 could be

$$\ln (W/W_0) = -\kappa_s A_s^2 \quad (2)$$

rewritten as eq 3 for any adsorbates on an adsorbent.

$$\ln (W/W_0) = -(\kappa_s/\beta^2) A^2 \quad \kappa_s/\kappa = A^2/A_s^2 = \beta^2 \quad (3)$$

Consequently, the logarithmic adsorbed amount ($\ln W$) could be given by eq 4. Dubinin (2) also reported that

$$\ln W = \ln W_0 - (\kappa_s/\beta^2) \{RT \ln (P_0/P)\}^2 \quad (4)$$

the affinity coefficient β for adsorption on activated carbon could be approximated by the ratio of molar volumes (V/V_s) or parachors (P/P_s) of an adsorbate to the standard adsorbate, regardless of the activated carbon. Reucroft et al. (6) reported that β could be approximated by the ratio of polarities (α/α_s) for polar organic adsorbates better than parachors. Therefore, it was thought that the adsorption capacity for a vapor could be calculated from κ_s and W_0 of the standard vapor and P and P_0 of the adsorbed vapor. However, it has not clearly been confirmed that the values of β do not change with the kinds of activated carbon. Relationships between the properties of activated carbon and the values of W_0 and κ_s have not been shown either.

In this study, adsorption isotherms for various systems of granular activated carbon and organic solvent were investigated. The applicability of the Dubinin-Polanyi equation, eq 1, for various commercial activated carbons was tested. The relationships between the observed values of the parameters, W_0 , κ_s , and β , and the properties of the organic adsorbate and activated carbon are discussed. Further, a practical method of predicting the adsorption capacities for single-solvent vapor under any conditions of temperature and concentration of vapor was introduced by the application of the Dubinin-Polanyi equation.

Materials and Methods

Seven kinds of commercial granular activated carbons, which had been made from coconut shell, coal, or oil pitch by the steam activation method, were used in this study. Their properties are shown in Table I. Their pore-size distributions were calculated from the adsorption isotherms of nitrogen, and the curves are shown in Figure 1 as relations between pore diameter, d , and cumulative volume of pores smaller than d , v_d . Carbon F had been made for use in liquid-phase adsorption, but the other carbons had been made for use in gas-phase adsorption.