

**DETERMINATION OF OCTANOL-WATER PARTITIONING COEFFICIENTS ( $K_{OW}$ ) OF 61 ORGANOPHOSPHORUS AND CARBAMATE INSECTICIDES AND THEIR RELATIONSHIP TO RESPECTIVE WATER SOLUBILITY (S) VALUES**

KEY WORDS: Melting Point Correction, Pesticide, Temperature

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**ABSTRACT**

Octanol-water partitioning coefficients ( $K_{OW}$ ) were determined for 61 organophosphorus and carbamate insecticides and related compounds at 20°C. In some instances, variations in reported  $K_{OW}$  values (including present data) were as great as 180-fold. Despite considerable care in determining  $K_{OW}$  values, there remained a number of compounds whose  $K_{OW}$  - solubility data points fell some distance off the  $\log K_{OW} / \log S$  regression line, examples being fenamiphos and azinphos-methyl. Such deviations may be ascribed to several factors including incorrect estimates of the Heats of Fusion values used in the melting point corrections, and the apparent erratic behaviour of the activity coefficients in water-saturated octanol with respect to the activity coefficients in octanol-saturated water. The regression for  $\log K_{OW}$  vs  $\log S$  (corrected for melting points) for 58 compounds was:

$$\log Kow = -0.833 \log S(\text{corr.}) + 0.323 \quad r = -0.975$$

**INTRODUCTION**

Both octanol-water partitioning coefficients ( $K_{OW}$ ) and water solubilities (S) have been increasingly used to predict soil sorption and bioconcentration of nonionic pesticides from aqueous systems (4,5,11,13,14,15,19). Solubility values have also been used to predict the effectiveness of compounds, of known toxicity, as soil

insecticides (9). A theoretical inverse relationship exists between  $K_{OW}$  values and their respective water solubility values, the details of which have been developed and thoroughly discussed by several researchers (5,6,17,25,26). Chiou *et al.*(6) have recently shown that compounds which are solids, or that depart from ideal behaviour will cause deviations from this inverse relationship. They and others (17,25) have demonstrated that  $K_{OW}$  -S correlations were greatly improved by expressing the solubilities of solids as that of their respective super-cooled liquids by incorporating a melting point correction based on their ideal solubility.

Measurement of  $K_{OW}$  values has traditionally involved the thorough mixing of a chemical in a 1-octanol/water mixture, allowing the phases to separate, and subsequently analyzing the concentrations of compound present in each phase. Karickhoff and Brown (12) have recently published a protocol for  $K_{OW}$  and solubility determinations, and Armstrong *et al.* (2) have written proposed guidelines for measuring several physicochemical parameters including  $K_{OW}$  values. Additionally, methods have been developed involving correlating  $\log K_{OW}$  values with  $\log$  retention times of the solute on high performance thin-layer plates (20), or with  $\log$  retention times obtained by high performance liquid chromatography (HPLC) (18,23). Both approaches have advantages and disadvantages. The traditional method is more time-consuming than the HPLC method, but it has the advantage of directly determining  $K_{OW}$  values. The HPLC method is an indirect method in which a calibration curve must be established using already-known  $\log K_{OW}$  values of several compounds and their respective  $\log$  retention times on the HPLC column. The HPLC method is most useful for compounds which degrade rapidly in water, but would be relatively stable in the eluting solvent over the short analysis period. In this case, direct determination would have produced anomalously high  $K_{OW}$  values.

$K_{OW}$  values, like water solubility values, are essentially benchmark values upon which many important predictions of chemical behaviour in the environment are based. With the increased popularity of computer modeling it is essential to regard  $K_{OW}$  and Solubility in the same light as other physical constants, for without accurate values, computer models are misleading and useless. A literature survey has shown

considerable discrepancies among reported  $K_{OW}$  values, in some cases by several orders of magnitude (19). We have already determined the water solubility of about 60 insecticides (3,28) and in this report will determine their corresponding  $K_{OW}$  values. The regression of  $\log K_{OW}$  on  $\log S$  values would be useful as a predictive tool as well as serving as a cross-check of the  $K_{OW}$  - Solubility values obtained.

### **MATERIALS AND METHODS**

Compound Purity. The purity of the insecticidal compounds has been published elsewhere (3,28). Solids of doubtful purity were re-crystallized three times from methanol (-20°C). Reagent-grade 1-octanol was extracted with 0.1N NaOH, washed with distilled water, and subsequently distilled. Reagent water was double distilled over  $KMnO_4$ .

Octanol-Water Partitioning Studies. Approximately 800 mL aliquots of purified octanol and distilled water reagents were thoroughly mixed in a 2 L separatory funnel to mutually saturate the two phases and subsequently stored there until required. Triplicate 10 mL aliquots of a standard solution ( $1000-2500 \mu\text{g mL}^{-1}$ ) of each insecticide, in water-saturated octanol, was pipetted into 60 mL separatory funnels, and 30 mL of octanol-saturated water was added. The funnels were carefully shaken for 30 sec. (avoiding emulsions) and allowed to sit for at least five hours. The aqueous layer was then drained into a 50 mL stainless steel centrifuge tube (with cap) and centrifuged for 45 min. ( $43,500 \times g$ ,  $20 \pm 0^\circ\text{C}$ ). Aliquots were carefully withdrawn from the centrifuge tubes (avoiding any small octanol droplets on the surface) for gas-liquid chromatograph (GLC) analysis. Usually three successive equilibration - extraction cycles were sufficient to produce constant  $K_{OW}$  values. For the more water-soluble compounds having  $K_{OW}$  values less than 100, the volume ratio of octanol/water was increased to minimize the amount of solute removed with each extraction. For compounds with  $K_{OW} > 10^5$ , the volume ratio was decreased to provide more solute in the water phase for sample concentration and analysis. The amount of solute remaining in the octanol phase was analyzed following the last extraction. In a few

instances where there was a possibility of aqueous decomposition of the compound, the equilibration time was shortened to <1 hour so that all three equilibration-extraction cycles could be completed within a day.

Analytical. Automated GLC's equipped with alkali-flame ionization detectors were used for analyses, as reported previously (3). The Pyrex glass GLC columns, 0.46 m x 2 mm I.D., were packed with either 100/120 mesh chromosorb W HP, coated with 2% OV-275 and treated with 0.1% H<sub>3</sub>PO<sub>4</sub>, or 100/120 mesh chromosorb W HP, coated with 10% QF-1. Operating temperatures varied from 100 to 215°C, depending on the compound. All compounds, excepting phosmet, leptophos and temephos, were injected (in triplicate) as aqueous methanol mixtures (reagent-water being octanol-saturated). Because of their low concentrations in the water phase combined with insufficient sensitivity on the GLC, leptophos and temephos samples were concentrated by three successive extractions into chloroform. The chloroform volume was then reduced to about 1 mL by flash evaporation and was replaced by a volume of hexane. This evaporation process was repeated twice more, with the final hexane volume being less than the original sample volume. Phosmet samples were also prepared by this procedure because it was unstable in water and methanol. Because 1-octanol did not chromatograph well, and in fact tended to interfere with normal GLC column performance, the initial solute concentration in the octanol phase was made relatively high (1000 -2500 µg mL<sup>-1</sup>, but below saturation) and substantially diluted (500-2500 fold) for analysis.

Calculations. At least three successive equilibration-extraction cycles were performed to obtain constant K<sub>OW</sub> values. Consequently solute analysis of the aqueous phase was obtained after each cycle. K<sub>OW</sub> values reported in Table 1 are the average of triplicate determinations based on the concentrations in the water and octanol phases following the last (usually the third) equilibration. K<sub>OW</sub> values for the preceding cycles were also computed so as to determine K<sub>OW</sub> constancy.

## THEORETICAL

Chiou *et al.* (6) have recently developed a theoretical relationship between  $K_{OW}$  and Solubility values in which they expressed  $K_{OW}$  as a concentration ratio

$$K_{OW} = \frac{C_o}{C_w} = \frac{Y_o^*}{Y_o} \frac{\bar{V}_w}{\bar{V}_o} = \frac{Y_w^*}{Y_o^*} \frac{\bar{V}_w}{\bar{V}_o^*} \quad (1)$$

where subscripts o, and w refer to octanol and water phases, respectively,

$C_o, C_w$  = molar solute concentrations in the two phases,

$Y_o, Y_w$  = respective activity coefficients in the two phases,

$\bar{V}_o, \bar{V}_w$  = respective molar volumes ( $L \text{ mol}^{-1}$ ) of solute in the two phases

Superscript asterisks denote that the activity coefficients and molar volumes have been corrected for octanol-water mutual saturation effects (i.e. solubility of octanol in water =  $4.5 \times 10^{-3} \text{ M}$ , for water in octanol = 1.75 M). Since the solubility of octanol in water is quite small,  $\bar{V}_w^* \approx \bar{V}_w$ . For a liquid solute of limited solubility (S) in water,

$$S_{\text{liquid}} = 1 / (Y_w \bar{V}_w) \quad (2)$$

The relationship between  $K_{OW}$  and S can be expressed as (combining Eq. 1 and 2)

$$K_{OW} = \frac{1}{S \bar{V}_o^* Y_o^*} \frac{Y_w^*}{Y_w} \quad (3)$$

which in logarithmic form becomes

$$\log K_{OW} = -\log S - \log \bar{V}_o^* - \log Y_o^* + \log (Y_w^* / Y_w) \quad (4)$$

If the solute were to form an ideal solution in the water-saturated octanol phase and if the solute solubility was the same in water as in octanol-saturated water, Eq. 4 becomes

$$\log K_{OW}^0 = -\log S - \log \bar{V}_o^* \quad (5)$$

where  $K_{OW}^0$  is the partition coefficient in the ideal system. Because of the substantial solubility of water in octanol, the molar volume of water-saturated octanol,  $\bar{V}_o^*$ , is less than  $0.157 \text{ L mol}^{-1}$  for  $\bar{V}_o$  (in pure octanol). Water solubility in octanol has been reported to be 2.3 M (6,10) but we found it to be approximately 1.75 M (20°C)

(1.63 mL water + 50.0 mL octanol). Upon adding water to octanol there was less than a 1% volume contraction. Using an octanol density of 827.0 g mL<sup>-1</sup> (20°C) and 998.23 g mL<sup>-1</sup> (20°C) for water, the total volume occupied by one liter of octanol + 1.75 moles of water was 1.0326 L. Assuming volume additivity, the adjusted octanol concentration was 6.15 M (0.3175 mol / 0.05163 L).  $\bar{V}_O^*$  becomes 1/(6.15 + 1.75) = 0.1266 L mol<sup>-1</sup> and in Eq. 5,  $\log \bar{V}_O^* = -0.897$ , the intercept of the ideal line shown in Fig. 1.

Chiou *et al.* (6) stated that the last two terms of Eq. 4 represent the sources of discrepancies between measured  $K_{OW}$  values and the "ideal  $K_{OW}$ ",  $K_{OW}^o$ . These two terms tend to produce a downward deviation from the ideal line, which must systematically increase with decreasing water solubility since the measured regression line has a lesser slope than the ideal line. Mackay (16) has shown that the effect of melting point of a compound on solubility also results in a downward deviation of the regression line from the ideal line (Eq. 5), because the effect reduces water solubility with-out affecting the  $K_{OW}$  (in which both solvents are equally affected). In order to simultaneously plot both liquid and solid solubility values vs  $K_{OW}$ , a melting point correction must be made for the solid solubility. The solubility of a solid is given by

$$S_{solid} = (1/\gamma_w \bar{V}_w) / (f_l / f_s) \quad (6)$$

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

$$\log (f_l / f_s) = \frac{\Delta \bar{H}_f}{2.303R} \frac{(T_m - T)}{(T T_m)} \quad (7)$$

where T and  $T_m$ , respectively, are the equilibrium temperature and melting point (°K),  $\Delta \bar{H}_f$  is the heat of fusion, and R is the universal gas constant (1.98717 cal. ° K<sup>-1</sup> mol<sup>-1</sup>). Since there are no accurate heats of fusion values ( $\Delta \bar{H}_f$ ) available for most pesticides, an estimate of 13.5 ±3 e.u. (17,25) for the entropy of fusion ( $\Delta \bar{H}_f / T_m$ ) has been found to be reasonably accurate for most low melting point compounds. The melting point correction is made using the following expression (6)

$$\text{Log } S_{SCL} = \log S_{solid} + \log (f_l / f_s) \quad (8)$$

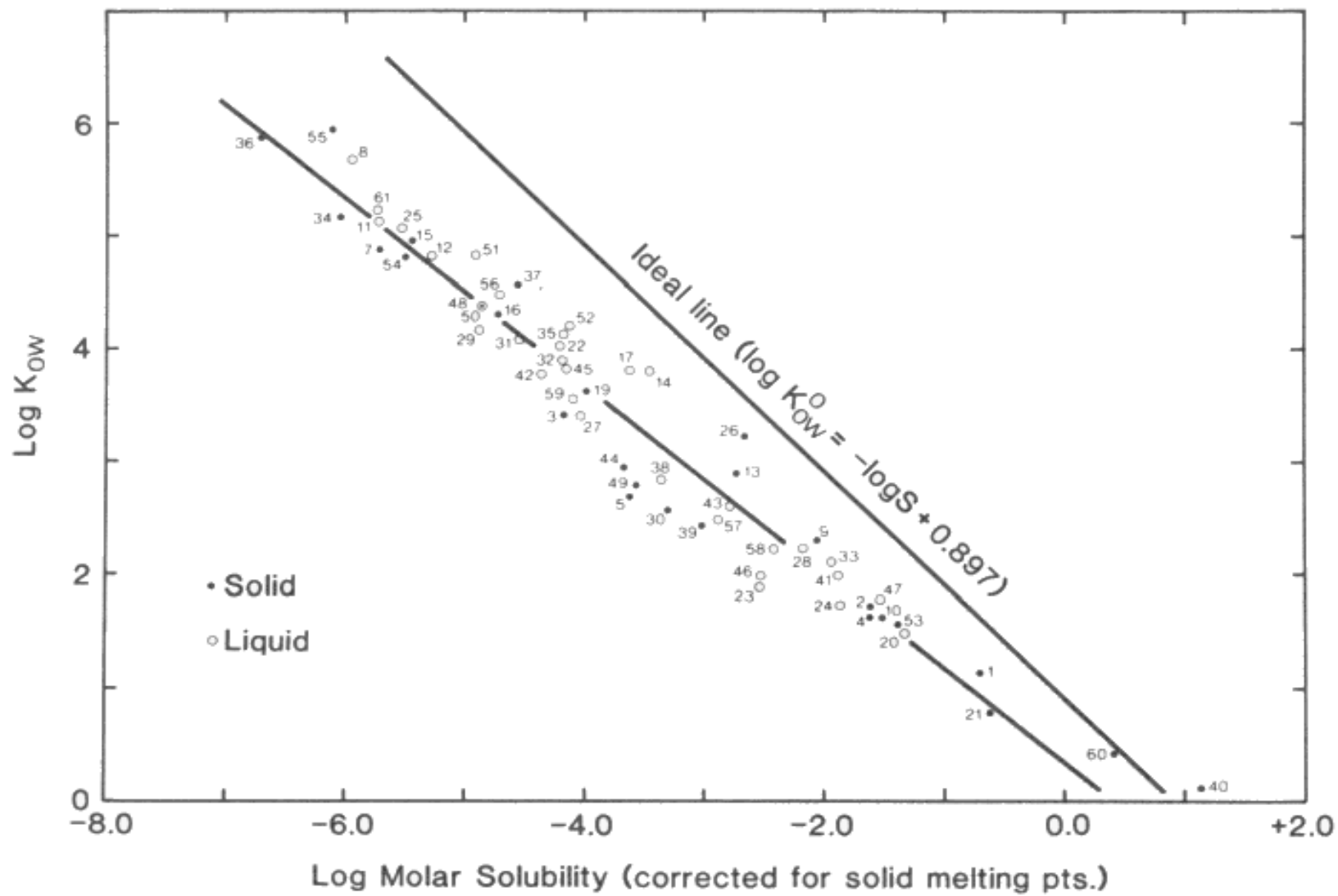


Fig. 1. Logarithmic Plot of K<sub>ow</sub> vs Molar Solubility of Compounds from Table 1.

**TABLE 1. WATER SOLUBILITY AND OCTANOL-WATER PARTITIONING COEFFICIENTS FOR INSECTICIDES AND THEIR RELATED ANALOGS**

No.	Compound	Mol.Wt.	M.Pt. (°C)	Log S (molar)	Log (fl / fs)	Corrected Log S (molar)	K <sub>OW</sub>	Log K <sub>OW</sub>	
								Measured	Literature
1	Aldicarb	190.26	99.0	-1.501	0.795	-0.706	1.359 E01	1.133	1.57 <sup>4</sup> , 0.85 <sup>7</sup> , 0.70 <sup>19</sup>
2	Aminocarb	208.26	93.5	-2.357	0.740	-1.617	5.415 E01	1.734	
3	Azinphos-ethyl	345.37	53.0	-4.517	0.332	-4.185	2.531 E03	3.403	
4	Azinphos-ethyl O-analog	329.31	56.5	-1.993 <sup>b</sup>	0.367	-1.626	4.236 E01	1.627	
5	Azinphos-methyl	317.31	73.5	-4.181	0.539	-3.642	4.914 E02	2.691	
6	Azinphos-methyl O-analog	301.25	77.5	c	0.579		5.991 E00	0.777	
7	Bromophos	365.99	53.5	-6.086	0.337	-5.749	7.649 E04	4.884	
8	Bromophos-ethyl	394.04		-5.954			4.743 E05	5.676	
9	Carbaryl	201.22	142.0	-3.287	1.228	-2.059	2.037 E02	2.309	2.32 <sup>4</sup> , 2.36 <sup>15</sup> , 2.81 <sup>19</sup>
10	Carbofuran	221.25	151.0	-2.840	1.319	-1.521	4.245 E01	1.628	1.60 <sup>15</sup> , 2.32 <sup>19</sup>
11	Carbophenothion	342.85		-5.736			1.320 E05	5.121	
12	Carbophenothion-methyl	314.80		-5.286			6.659 E04	4.823	
13	Chlordimeform	196.68	32.0	-2.862	0.121	-2.741	7.837 E02	2.894	
14	Chlorfenvinphos	359.57		-3.462			6.393 E03	3.806	3.10 <sup>4</sup>
15	Chlorpyrifos	350.58	42.7	-5.682	0.229	-5.453	9.143 E04	4.961	5.11 <sup>5</sup> , 4.99 <sup>15</sup> , 4.82 <sup>19</sup>
16	Chlorpyrifos-methyl	322.53	46.0	-5.003	0.262	-4.741	2.010 E04	4.303	4.31 <sup>5</sup> , 4.17 <sup>15</sup>
17	Diazinon	304.34		-3.646			6.402 E03	3.806	3.11 <sup>4</sup> , 3.02 <sup>19</sup>
18	Diazinon-O-analog	288.28		c			1.180 E02	2.072	
19	Dicapthon	297.64	51.5	-4.306	0.317	-3.989	4.171 E03	3.620	3.58 <sup>5</sup>
20	Dichlorvos	220.98		-1.344 <sup>a</sup>			2.955 E01	1.471	1.40 <sup>15</sup>
21	Dimethoate	229.24	51.5	-0.962 <sup>a</sup>	0.317	-0.645	5.959 E00	0.775	0.79 <sup>4</sup> , -0.29 <sup>15</sup>
22	Disulfoton	274.39		-4.226			1.054 E04	4.023	
23	Disulfoton sulfone	306.39		-2.540			7.422 E01	1.871	
24	Disulfoton sulfoxide	290.39		>-1.861			5.286 E01	1.732	
25	Ethion	384.45		-5.543			1.184 E05	5.073	
26	Fenamiphos	303.36	49.2	-2.965	0.294	-2.671	1.686 E03	3.227	3.18 <sup>4</sup>
27	Fenitrothion	277.23		-4.041			2.493 E03	3.397	3.38 <sup>5</sup> , 3.36 <sup>19</sup>

28	Fensulfothion	308.34		-2.188			169.3 E02	2.229	
29	Fensulfothion sulfide	292.34		-4.898			1.443 E04	4.159	
30	Fensulfothion sulfone	324.34	44.0	-3.580	0.242	-3.338	3.611 E02	2.558	
31	Fenthion	278.32		-4.569			1.233 E04	4.091	
32	Fonofos	246.32		-4.196			7.792 E03	3.892	
33	Fonofos-O-analog	230.26		>-1.947			1.282 E02	2.108	
34	Iodofenphos	412.99	76.0	-6.616	0.564	-6.052	1.444 E05	5.160	
35	Isofenphos	345.39		-4.194			1.323 E04	4.121	
36	Leptophos	344.55	70.4	-7.215	0.507	-6.708	7.597 E05	5.881	6.31 <sup>5</sup> , 4.32 <sup>11</sup> , 3.62 <sup>19</sup>
37	Leptophos-O-analog	328.49	61.5	-4.985	0.418	-4.567	3.784 E04	4.578	
38	Malathion	330.35		-3.364			6.887 E02	2.838	2.89 <sup>5</sup>
39	Methidathion	302.31	39.5	-3.208	0.196	-3.012	2.621 E02	2.419	
40	Methomyl	162.20	78.5	+0.553 <sup>a</sup>	0.589	1.142	1.351 E00	0.131	0.30 <sup>15</sup>
41	Paraoxon	275.19		-1.879			9.552 E01	1.980	
42	Parathion	291.25		-4.371			5.772 E03	3.761	3.93 <sup>4</sup> , 3.815, 3.40 <sup>7</sup>
43	Parathion-amino	245.27		-2.793			3.968 E02	2.599	
44	Parathion-methyl	263.20	35.5	-3.844	0.156	-3.688	8.749 E02	2.942	1.91 <sup>15</sup> , 3.32 <sup>19</sup>
45	Phorate	260.36		-4.163			6.692 E03	3.826	4.26 <sup>4</sup> , 2.92 <sup>19</sup> , 3.33 <sup>7</sup>
46	Phorate sulfone	292.36		-2.531			9.659 E01	1.985	
47	Phorate sulfoxide	276.36		>-1.538			5.959 E01	1.775	
48	Phosalone	367.80	48.0	-5.151	0.282	-4.869	2.375 E04	4.376	4.30 <sup>5</sup>
49	Phosmet	317.30	71.9	-4.114	0.523	-3.591	6.069 E02	2.783	2.83 <sup>5</sup>
50	Phoxim	298.30		-4.862			2.435 E04	4.386	
51	Pirimiphos-ethyl	302.41		-4.924			7.027 E04	4.847	
52	Pirimiphos-methyl	274.35		-4.133			1.580 E04	4.199	
53	Propoxur	209.24	85.5	-2.051	0.659	-1.392	3.671 E01	1.552	1.52 <sup>15</sup> , 1.45 <sup>19</sup>
54	Ronnel	321.54	41.0	-5.729	0.211	-5.518	6.429 E04	4.808	4.88 <sup>5</sup>
55	Temephos	466.50	30.0	-6.237	0.101	-6.136	9.010 E0 5	5.955	
56	Terbufos	288.41		-4.720			3.000 E04	4.477	3.68 <sup>7</sup>
57	Terbufos Sulfone	320.41		-2.895			3.023 E02	2.480	
58	Terbufos sulfoxide	304.41		-2.442			1.631 E02	2.213	
59	Triazophos	313.30		-4.103			3.555 E03	3.551	
60	Trichlorfon	257.43	83.5	-0.223 <sup>a</sup>	0.639	+0.416	2.695 E00	0.431	0.477 <sup>15</sup>
61	Trichloronat	333.59		-5.750			1.709 E05	5.233	

a - solubility value from Worthing (24); <sup>b</sup> - solubility value obtained at 10°C; <sup>c</sup> - not available, see text

where  $S_{\text{solid}}$  = measured solubility of solid

$S_{\text{SCL}}$  = calculated solubility of corresponding supercooled liquid (corrected solubility).

### **STATISTICAL ANALYSES**

The plot of  $\log K_{\text{OW}}$  vs  $\log S$  should, in the ideal case, give a straight line with slope of -1 and intercept of  $-\log \bar{V}_O^*$  (Eq. 5). In reality, deviations from this ideal relationship occur partly because the differing structural characteristics of these compounds (various hydrophilic groups of varying polarities) produce  $\gamma_w^*$  values which tend to change erratically with respect to  $\gamma_w^*$  values (Eq. 4) (C.T. Chiou, personal communication), For predictive purposes, (recognizing these inherent limitations) a Y on X linear regression pro-gram was used for predicting a  $\log K_{\text{OW}}$  estimate from a  $\log S$  (corrected) value, and the reverse regression was computed for predicting a  $\log S$  (corrected) value from a given  $\log K_{\text{OW}}$  value (Table 2).  $\log S$  (corrected) indicates that the solubilities of solids were corrected to those of their corresponding supercooled liquids as per Eq. 7 and 8. The 95% confidence intervals on any single predicted  $\log K_{\text{OW}}$  value based on a specific  $\log S$  (corrected) value are given by Steel and Torrie (22, Eq. 9.19, P.175), using N-2 degrees of freedom for the student-t value. It is important to note that, for the present data in logarithmic notation, these confidence intervals are symmetrical only about the predicted log value. These confidence intervals become asymmetric about the predicted value when antilogs are taken.

### **RESULTS AND DISCUSSION**

A summary of the regression data for 58 of the compounds in Fig. 1 is shown in Table 2. Solubility values were not obtainable for azinphos-methyl O-analog (#6, Table 1) because of its high solubility (estimated near  $16 \text{ g L}^{-1}$ ), and lack of sufficient product. Rapid decomposition prevented obtaining an accurate solubility value for diazinon O-analog (#18). The values for methomyl (#40) were not included in the regression analysis because the  $\log K_{\text{OW}}$  -  $\log S$  data point fell considerably above both the regression line and the ideal line (Fig. 1).

**TABLE 2**  
REGRESSION DATA FOR LOG K<sub>OW</sub> vs LOG S(Corr.)  
FOR COMPOUNDS FROM TABLE 1

Regression Model	No. of Cpds.	Slope	Log Intercept.	Corr. Coeff.
Log K <sub>OW</sub> /Log S	58	-0.833	0.323	-0.975
Log S/Log K <sub>OW</sub>	58	-1.141	0.201	-0.9
Log K <sub>OW</sub> /Log S	26	-0.799	0.418	-0.976
	solids			
Log S/Log K <sub>OW</sub>	26	-1.192	0.334	-0.9
	solids			
Log K <sub>OW</sub> /Log S	32	-0.885	0.163	-0.9
	liquids			
Log S/Log K <sub>OW</sub>	32	-1.077	0.0016	-0.977
	liquids			

Consequently the reliability of its reported solubility value, 58 g L<sup>-1</sup> at 25°C (24), was unknown. The literature solubility values for four other compounds (24), aldicarb (#1), dichlorvos (#20), dimethoate (#21) and trichlorfon (#60) (not determined because of their high solubility) were included in the regression analysis since their data points fell below the ideal line (Fig. 1). The regression line shown in Fig. 1 is for log K<sub>OW</sub> vs log S (corrected).

The regression coefficients for the log K<sub>OW</sub> vs log S regression (Table 2) are quite different from the slope and log intercept values of -0.747 and 0.472, respectively, reported by Chiou *et al.* (6) for 10 organophosphorus compounds ( $r = -0.969$ ). Some of Briggs' data (Table 3) gave slope and log intercept values of -0.731 and 0.651, respectively ( $r = -0.903$ ), using his log S values, corrected for melting points of the solids. The captan data point of Briggs' data falls far below the regression line, and if it is excluded, the slope and log intercept become -0.819 and 0.566, respectively, with  $r = -0.956$ . This slope value is close to our value of -0.833. We found captan to be too unstable in distilled water to obtain a reliable solubility estimate, which might account for Briggs' value being approximately 1.5 log units low (assuming a

**TABLE 3**  
PARTITIONING AND SOLUBILITY DATA FOR 11 COMPOUNDS REPORTED BY  
BRIGGS<sup>3</sup> WITH ADDED MELTING POINT CORRECTIONS

Compound	Log K <sub>OW</sub>	Log S (molar)	Log (f <sub>l</sub> / f <sub>s</sub> ) <sup>a</sup>	Log S (corrected) <sup>b</sup>
Aldicarb	1.57	-1.50	0.795	-0.71
Captan	2.54	-5.78	1.46	-4.32
Carbaryl	2.32	-3.70	-1.228	-2.47
Chlorfenvinphos	3.10	-3.39	-	-
Diazinon	3.11	-3.88	-	-
Dimethoate	0.79	-0.96	0.317	-0.64
Fenamiphos	3.18	-2.64	0.294	-2.35
Folpet	3.63	-5.47	1.58	-3.89
Oxamyl	-0.47	0.11	0.90	1.01
Parathion	3.93	-4.08	-	-
Phorate	4.26	-3.72	-	-

a = calculated using Eq. 7;

b = calculated using Eq. 8

correct K<sub>OW</sub> value). Any error in K<sub>OW</sub> measurement due to captan instability in the water phase would have actually shifted the data point closer to the regression line since K<sub>OW</sub> would have increased in magnitude.

Because of the potential for significant breakdown, shortened equilibration periods (<1 hr/extraction cycle, but still sufficient for equilibrium to be reached (2,12)) were used in the K<sub>OW</sub> determinations of diazinon, diazinon O-analog, dichlorvos, phorate, phosmet and terbufos. As noted earlier, phosmet had to be prepared for GLC analysis in hexane since it was unstable in methanol. All other compounds studied, which have exhibited varying degrees of instability in water, have been more stable in methanol, or in aqueous methanol mixtures.

Although the melting point correction (Eq. 7, 8) of the log S values did considerably improve the log K<sub>OW</sub> - log S correlation for 58 compounds (without correction, log K<sub>OW</sub> /log S coefficients were: slope = -0.854, log intercept = 0.085, r = -0.958), the regression coefficients

(Table 2) were somewhat different if solids and liquids were regressed separately. Additionally, the correlation coefficients were slightly higher for solids and liquids regressed separately, then when combined together, indicating that either the melting point corrections were not entirely accurate, or that some other inherent factor distinguished the two groups of compounds.

Of the 61 compounds studied, literature values for  $K_{OW}$  could be found for only 24 compounds, and of these, 9 compounds had  $K_{OW}$  values (including present data) which varied by more than 5-fold (Table 1). Based on Worthing's solubility value (24) of  $6000 \text{ mg L}^{-1}$  for aldicarb, Briggs'  $\log K_{OW}$  value of 1.57 is about 0.65 log units above our regression line and, in fact, almost places the data point on the ideal line, which is rather unlikely. The average of our value with the other two literature values (0.93) almost places the value on our regression line. Recently Briggs has quoted a lower  $\log K_{OW}$  value (27) of 1.08 for aldicarb, very close to our 1.133 value.

Our  $\log K_{OW}$  value for carbofuran agrees closely with one of the literature citations, which almost falls on the regression line. The 2.32 value (19) seems somewhat questionable as it almost falls on the ideal line, about 0.75 log units above the regression line. Briggs'  $\log K_{OW}$  value of 3.10 for chlorfenvinphos fits our regression line much better than our value of 3.806, despite our lower reported solubility ( $124 \mu\text{g mL}^{-1}$ ). We repeated the  $K_{OW}$  determination several times with two different sources of material, but found similar results. Perhaps the fact that our product purity was only 92%, or the presence of the two isomers played a role in our apparent aberrant value. Likewise our  $\log K_{OW}$  value for diazinon (3.806) was considerably farther than the two cited values (3.11, 3.02) from the regression line. To further aggravate the situation, our solubility value of  $68.8 \mu\text{g mL}^{-1}$  was considerably greater than the  $40 \text{ g mL}^{-1}$  (24) which has been quoted for this compound since 1953 (9). Again, repeated  $K_{OW}$  determinations of diazinon samples from different sources (purity 99.2%) did not resolve this problem.

There was more than a 180-fold variation in reported  $K_{OW}$  values for leptophos, and in excess of a 500-fold variation in reported solubility values (3). Such discrepancies are likely because of difficulty in accurately determining the very low solubility of leptophos, combined with its very low partitioning tendencies into the aqueous from the octanol phase. Our

leptophos data point, using a recently determined solubility value of  $0.021 \mu\text{g mL}^{-1}$  ( $\log S$  (corr.) = -6.708,  $\log K_{\text{OW}} = 5.881$ ) was somewhat different from the data point of Chiou *et al.* (5) ( $\log S$  (corr.) = -7.36,  $\log K_{\text{OW}} = 6.31$ ). Our solubility value was about 4.5 fold greater than theirs, whereas their  $K_{\text{OW}}$  value was about 2.7 fold greater than our value. The other two citations (11,19) for  $\log K_{\text{OW}}$  values were 2-3 magnitudes less than either of our values, and would appear to be suspect.

There were some significant differences in  $K_{\text{OW}}$  procedures between our work and that of Chiou *et al.* (5,6). We equilibrated the octanol-water phases in separatory funnels and carefully withdrew the lower water phase into capped, stainless steel centrifuge tubes for centrifugation at  $43,500 \times g$  for 45 min. They equilibrated their octanol-water phases in Teflon-lined, capped centrifuge tubes, and centrifuged at  $37,000 \times g$  for 20 min. Following centrifugation they carefully withdrew the octanol layer from the top of the centrifuge tubes before sampling the lower water phase whereas we have found with our technique that following centrifugation of the water phase, the few tiny octanol droplets that remain on the surface tend to remain around the circumference of the tube and don't normally interfere with pipet sampling from the center of the tube, It would appear easier with the separatory funnel technique to perform successive water-octanol equilibrations in order to remove any water-soluble impurities that might affect the partitioning process (12). We have found that repeated centrifugation of the water phase has not reduced the solute concentration, perhaps because of the greater centrifugal forces and longer centrifugation period.

Although our  $K_{\text{OW}}$  for methomyl was 2- to 10-fold less than the other literature citations, the quoted solubility of 58% (24) placed the data point above the ideal line (Fig. 1). Dr. Chiou (personal communication) has pointed out that Eq. 4 applies only for solutes of limited water solubility. For high water solubility compounds such as methomyl, the molar volume of the aqueous phase in equilibrium with excess solute will be greater than  $\bar{V}_w = 0.0181, \text{ mol}^{-1}$ . In addition, the activity coefficient of the compound in water,  $\gamma_w$ , at the saturation point will be quite different from that in the aqueous phase of the partition mixture. The  $\log (\gamma_w^* / \gamma_w)$  for methomyl may be positive, making it stay above the ideal line.

There was a 25-fold range in reported  $K_{OW}$  values for methyl parathion, with our value falling about 0.4 log units below the regression line. The log value of 3.32 (19) seems closest to the regression line, despite our repeated determinations using re-crystallized product. For phorate and terbufos, there was greater than a 20-fold and 180-fold range, respectively, in reported  $K_{OW}$  values, with our data points being closest to the regression line in each case. It must be emphasized that these relative comparisons amongst reported log  $K_{OW}$  values are just that, and the fact that the data points fall on or near the regression line don't invalidate the reported values. This discussion is intended to point out the sort of variability that exists among laboratories, be it due to differences in experimental technique (a reflection of both the technique and the experimenter's abilities), compound and reagent purity, or other unaccounted-for factors such as those discussed in the Theoretical section.

In this study we have accounted for only the temperature and melting point effects upon the data, and have not considered other possible factors noted in Eq. 4. The assumption was also made in the melting point correction for solid solubilities (Eq. 7) that  $\Delta\bar{H}_f/T_m = 13.5$  e.u., which may not hold for some of the compounds, especially those with high melting points ( $>100^\circ\text{C}$ ). Perhaps one of these factors might help explain the apparently aberrant values obtained for fenamiphos (#26). Both our work and that of Briggs (4) have found very comparable log  $K_{OW}$  values of 3.227 and 3.18, respectively, for fenamiphos. The literature solubility values which ranged from 400 (1) to 700  $\mu\text{g mL}^{-1}$  (24), almost placed the data point on the ideal line (Fig. 1). Even our lower solubility of 329  $\mu\text{g mL}^{-1}$  still placed the point of 0.65 log units above the regression line. Using our  $K_{OW}$  value, the log S vs log  $K_{OW}$  regression (Table 2) would have estimated fenamiphos solubility near 60  $\text{g mL}^{-1}$ . There was no evidence of any significant aqueous phase decomposition which would have erroneously increased the  $K_{OW}$  value. A much less soluble compound, temephos (#55) also had a  $K_{OW}$  value which was more than 0.5 log units (approximately 3-fold) above the regression line, while three compounds, azinphos methyl (#5), disulfoton sulfone (#23) and fensulfothion sulfone (#30) had  $K_{OW}$  values more than 0.5 log units below the line.

In summary, this study has shown:

- a) Variability in reported  $K_{OW}$  values was large for a considerable number of compounds, sometimes exceeding 180-fold.
- b) Although the melting point correction for the solubilities of solid compounds improved the  $K_{OW}$  - solubility correlation, two different regression equations best fit the data for liquid and solid compounds.
- c) Ten of the compounds examined did not fit the regression equation ( $>0.5$  log units away) but also did not give any suggestion of a systematic departure.
- d) The regression equations presented can serve as a good cross-check when determining  $K_{OW}$  or solubility values, but the relationship of  $K_{OW}$  to  $S$  has not been well enough defined to permit their use for accurate prediction.

Further  $K_{OW}$  - solubility studies should be independently done by other researchers to either verify or correct the results obtained here, especially for that group of compounds that did not fit the regression equation. Direct measurements of the heats of fusion of the solids need to be made to make the melting point corrections of the solubilities more reliable.

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