

FURTHER WATER SOLUBILITY DETERMINATIONS OF INSECTICIDAL COMPOUNDS

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ABSTRACT

The aqueous solubility of 39 insecticidal and related compounds was determined at $20 \pm 1.5^\circ\text{C}$, using a previously described shaking and centrifugation method. Fenamiphos, fenthion and methidathion produced values substantially less than those reported in the literature whereas, aminocarb, diazinon, dicapthon, pirimiphos-ethyl and pirimiphos-methyl gave solubilities substantially greater than reported literature values.

INTRODUCTION

This report is a continuation of an earlier solubility study in which a uniform procedure was used to determine the aqueous solubility of various insecticidal compounds. The purpose of this study was to provide reliable solubility values for use in characterizing and predicting pesticide behavior in environmental systems.

MATERIALS AND METHODS

Compound Purity. The purity of the compounds studied is shown in Table 1. The purity was not available for a number of compounds so they should be considered as being of technical purity. Several solids were re-crystallized three times from methanol at -20°C to improve their purity.

Sample Preparation. A three-fold excess of each compound (in triplicate) was dissolved in distilled water (pH 6) as was earlier reported¹. Successive samplings on a weekly basis were made until maximum solubility was attained. The temperature was maintained at 20±1.5°C during equilibration and centrifugation except for azinphos ethyl O-analog (10°C). There was still a visible excess of each compound present at the termination of each solubility experiment. All samples were centrifuged at 43,500 x g for 3 hr. prior to sampling and analysis.

Analytical. All samples were analyzed by gas-liquid chromatography using previously reported methods¹. The glass columns, 0.5 m x 2 mm I.D. were packed with either 3% OV-1 + 3% QF-1, or 10% QF-1 on Chromosorb W DMCS, 100/120 mesh.

RESULTS AND DISCUSSION

"Greater than" values are shown for seven compounds listed in Table 1 because of their high solubilities combined with a scarcity of material. Literature citations suggest that their solubilities are far in excess of our values, and they are included here for only reference purposes. The solubility of azinphos-ethyl O-analog at 10°C was 3350 µg ml⁻¹, and was estimated to be near 16 mg ml⁻¹ at 20°C, but due to the lack of material this was impossible to confirm. Fenamiphos, fenthion and methidathion, had solubilities substantially less than those reported in the literature.

Carbaryl and carbophenothion had conflicting literature values, of which one for each compound agreed reasonably well with the present data.

When lower solubility values are obtained than those reported in the literature, there is a tendency to believe, barring significant decomposition, that the centrifugation step was more efficient or complete than was the case for the higher reported values. Thus, it was puzzling that several of our values were considerably greater than were the literature values even after repeating the experiments. The value of $40 \mu\text{g ml}^{-1}$ for diazinon was reported by Hansens¹⁴ in 1953 and this value appears to have been used since then. Hansens apparently did not determine this value, nor did he acknowledge his source, possibly an earlier technical bulletin. Chiou et al.⁶ did not use a centrifugation step in their dicapthon solubility determination, but removed aqueous aliquots of the solution through a sintered-glass filter. In comparing their other solubility values with values obtained by our centrifugation method, there was no trend suggesting that one method systematically produced lower values than the other. There are no direct references to method(s) used to equilibrate and sample the two pirimiphos analogs, which were equilibrated at 30°C. Worthing¹² indicates that both compounds appear to be relatively stable, but have relatively high vapor pressures (ca. 10^{-4} mm Hg). The discrepancies become more pronounced considering the fact that our values were determined at 20°C, unless the values reported at 30°C were low because of significant vapor phase losses during the experiments. No solubility values were obtained for naled, bendiocarb (converted to its oxime), or the fungicide captan, which completely disappeared within a two week period.

The solubilities of fensulfothion sulfone and leptophos reported previously¹ were re-examined because of conflicting values in the literature and/or because they did not correspond with their octanol-water partitioning coefficients ($\log K_{OW} = 2.558$ and 5.881 , respectively). Reported solubility values for leptophos ranged from

TABLE 1
Aqueous Solubility Values for Insecticide Compounds at 20°C.

Compound	Physical State	Percent Purity	Solubility			
			Mean	Std. Dev.	Molar	Literature Citations
			$\mu\text{g ml}^{-1}$		mol L^{-1}	$\mu\text{g ml}^{-1}$
Acephate	S		>5000			65% (11,12)
Aminocarb	S	re-cryst.	915	29	4.394 E-03	sl.sol. (11,12)
Azinphos-ethyl	S	re-cryst.	10.5	1.2	3.040 E-05	insol. (11,12)
Azinphos-ethyl O-analog	S	re-cryst.	3350 ^g	60	1.017 E-02 ^g	
Azinphos-methyl	S	98.4	20.9	1.5	6.587 E-05	33 ^a (11,12), 29 ^c (4)
Carbaryl	S	99	104	12	5.164 E-04	40 ^b (11), 120 ^b (12)
Carbophenothion	L	95	0.63	0.13	1.838 E-06	<40 (12), <2 ^d (11), 1 ^a (9)
Carbophenothion-methyl	L	91.6	1.63	0.14	5.178 E-06	
Chlordimeform	L/S		270	2.1	1.373 E-03	250 (12)
Chlorfenvinphos	L	92	124	3.0	3.449 E-04	sl.sol. (12), 145 ^f (12)
Chlorpyrifos	S	99	0.73	0.04	2.082 E-06	2 ^c (11), 2 ^e (12), 0.4 ^f (6)
Chlorpyrifos-methyl	S	99	3.2	0.07	9.922 E-06	5 ^c (11), 4 ^c (12)
Diazinon	L	99.2	68.8		2.261 E-04	40 ^a (11,12)
Dicaphon	S	96	14.7	0.4	4.939 E-05	insol. (11), 6.25 ^d (6)
Dimethoate	S		>5000			3-4% (9), 2-3% (11), 2.5% ^d (12)
α -endosulfan	S		0.51	0.01	1.253 E-06	insol. (11,12)
β -endosulfan	S		0.45	0.01	1.106 E-06	
Endosulfansulfate	S		0.48	0.03	1.135 E-06	
Fenamiphos	S	99.2	329.	5.5	1.084 E-03	450 ^c (11), 700 ^a (12)

Fensulfothion sulfide	L	95.5	3.7	0.16	1.266 E-05	
Fensulfothion sulfone	S	re-cryst.	85.4	0.7	2.300 E-04	74.6 ^d (1)
Fenthion	L	97.1	7.51	0.31	2.698 E-05	54-56 ^a (9,11,12)
Isofenphos	S	92.6	22.1	0.7	6.399 E-05	23.8 ^d (12)
Leptophos	S	99+	0.021	0.006	6.095 E-08	0.0047 ^d (6), 0.03 (13), 0.07 ^d (1), 2.4 (12)
Malathion	L	95	143.	3.6	4.329 E-04	145 ^a (11,12),145 ^d (9)
Methamidophos	S		>3000			miscible (11)
Methidathion	S	99+	187	1.6	6.186 E-04	240 ^d (7), 240 ^c (9,12)
Methomyl	S	99+	>1000			sol (11), 58% ^c (12)
Mevinphos	L		>2000			miscible (11,12)
Oxamyl	S		>2000			28% ^d (12)
Phosalone	S	re-cryst.	2.6	0.05	7.069 E-06	insol. (11), 10 ^a (12)
Phosmet	S	94	24.4	3.0	7.690 E-05	25 ^c (11,12)
Phoxim	L	98.3	4.1	0.04	1.374 E-05	7 ^d (11,12)
Pirimiphos-ethyl	L	99.1	3.6	0.24	1.190 E-05	1.0 ^b (12)
Pirimiphos-methyl	L	99.3	20.2	1.7	7.363 E-05	5 ^b (11,12)
Propoxur	S	re-cryst.	1859	30.	8.885 E-03	2000 ^d (11,12)
Temephos	S	99	0.27	0.08	5.788 E-07	Insol. (12)
Triazophos	L	95	24.7	3.3	7.884 E-05	39 ^f (11,12)
Trichlorfon	S		>5000			15.4% ^c (11,12)
Trichloronat	L	95	0.59	0.04	1.769 E-06	insol. (11), 50 ^d (12)

a- Room temp.; b-30°C; c-25°C; d-20°C; e-35°C; f-23°C; g-10°C; h-except where expressed in %.

Numbers in parentheses following literature citations refer to References.

0.0047 to 2.4 $\mu\text{g ml}^{-1}$, with our new value falling at 0.021 g ml^{-1} , down from the earlier 0.07 g ml^{-1} . The new fensulfothion sulfone value increased from 74.6 g ml^{-1} to 85.4 $\mu\text{g ml}^{-1}$ after an extended equilibration period and more closely corresponded to the regression line of $\log K_{\text{OW}}$ on \log solubility values for 58 organophosphorus and carbamate insecticides (forthcoming publication).

In conclusion, it is hoped that these solubility values will be of use in predicting the environmental fate of insecticides. Further studies are being done to determine the effect of temperature on the water solubility of some of these compounds.

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