

EFFECT OF TEMPERATURE ON THE WATER SOLUBILITY OF INSECTICIDES

KEY WORDS: Differential Heat of Solution

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ABSTRACT

Water solubilities for 30 insecticides were determined at 10, 20, and 30°C. There was a positive correlation between solubility and temperature for all insecticides with the exception of diazinon and chlorfenvinphos. The magnitude of the effect generally appeared larger for solids than for liquids, and within the solids group, tended to increase with increasing molecular weight of the compound.

INTRODUCTION

Solubility values of insecticides can be useful predictors of their behavior in soil-water systems. Biggar and Riggs (1974) have reported an inverse temperature relationship with solubility for several organo-chlorine insecticides, but there appears to be little published temperature-solubility data for organophosphorus or carbamate insecticides. The purpose of this study is to obtain solubility data at 10, 20, and 30°C for a group of 30 insecticides for use in predicting environmental behavior of these compounds.

MATERIALS AND METHODS

Compound Purity. The purity of the insecticides used has been reported previously (Bowman and Sans 1979, 1983).

Sample Preparation. A several-fold excess (in excess of projected solubility) of each compound (in triplicate) was dispersed in distilled water (pH 6) and tumbled continuously in Pyrex glass bottles. Successive samplings on an approximately 3-day basis were made until two consecutive samplings gave the same solubility value. Sample temperatures were maintained at 10, 20 or $30 \pm 1.5^\circ\text{C}$ during both tumbling and centrifugation procedures. All samples were centrifuged at $43,000 \times g$ for 3 hr prior to analysis by gas-liquid chromatography (GLC). Considerable caution had to be exercised during removal of centrifuged sample by pipet (with centrifuge tubes remaining in rotor). Occasionally small droplets or particles of undissolved insecticide remained floating on the aqueous surface of the centrifuged sample, due to surface tension effects and it was necessary to avoid them with the pipet tip. The volumetric pipet (3 to 5 mL) was inserted very carefully into the centrifuge tube, containing a 30 mL-volume, on the side opposite to where the excess insecticide was thrown during centrifugation, and away from the bottom of the tube. After withdrawing the pipet (filled above reference mark) from the centrifuge tube, the tip was wiped with a tissue, the volume was lowered to the reference mark and the sample was transferred to a volumetric flask.

Analytical. All samples were analyzed by GLC as methanol-water mixtures, using external standards of the same solvent composition, as previously reported (Bowman and Sans 1979, 1983). 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

The solubility values of the 30 compounds in Table 1 were re-determined at 20°C , despite the fact we had previously reported them

TABLE 1**SOLUBILITIES OF 30 INSECTICIDES AT 10, 20 AND 30°C**

| COMPOUND | SOLUBILITY | | | | | | |
|----------|-----------------------|-------|-----------|-------|-----------|---------|-----------|
| | 10°C | | 20°C | | 30°C | | |
| | µg/mL | mol/L | µg/mL | mol/L | µg/mL | mol/L | |
| 1 | Aminocarb | 872 | 4.187E-03 | 915 | 4.394E-03 | 1360 | 6.540E-03 |
| 2 | Azinphos-Et | 6.7 | 1.940E-05 | 10.5 | 3.040E-05 | 24.7 | 7.152E-03 |
| 3 | Azinphos-Me | 9.5 | 2.994E-05 | 20.9 | 6.587E-05 | 43.6 | 1.374E-04 |
| 4 | Bromophos | 0.24 | 6.558E-07 | 0.34 | 9.290E-07 | 0.96 | 2.634E-06 |
| 5 | Bromophos-Et | 0.21 | 5.329E-07 | 0.34 | 8.629E-07 | 0.50 | 1.269E-06 |
| 6 | Carbaryl | 72.4 | 3.444E-04 | 104 | 4.947E-04 | 130 | 6.184E-04 |
| 7 | Carbofuran | 291 | 1.315E-03 | 320 | 1.446E-03 | 375 | 1.695E-03 |
| 8 | Carbophenothion | 0.61 | 1.779E-06 | 0.63 | 1.838E-06 | 0.73 | 2.129E-06 |
| 9 | Carbophenothion-Me | 1.47 | 4.670E-06 | 1.6 | 5.083E-06 | 2.82 | 8.958E-06 |
| 10 | Chlordimeform | 203 | 1.032E-03 | 270 | 1.373E-03 | decomp. | |
| 11 | Chlorfenvinphos | 125 | 3.476E-04 | 124 | 3.449E-04 | 107 | 2.976E-04 |
| 12 | Chlorpyrifos | 0.45 | 1.284E-06 | 0.73 | 2.082E-06 | 1.3 | 3.708E-06 |
| 13 | Chlorpyrifos-Me | 1.8 | 5.581E-06 | 3.2 | 9.922E-06 | 6.9 | 2.139E-05 |
| 14 | Diazinon | 71.1 | 2.336E-04 | 53.5 | 1.758E-04 | 43.7 | 1.436E-04 |
| 15 | Dicaphon | 12.6 | 4.233E-05 | 14.7 | 4.939E-05 | 44.2 | 1.485E-04 |
| 16 | Dieldrin | 0.08 | 2.100E-07 | 0.14 | 3.676E-07 | 0.20 | 5.251E-07 |
| 17 | Ethion | 0.57 | 1.483E-06 | 0.68 | 1.769E-06 | 0.76 | 1.977E-06 |
| 18 | Fenamiphos | 306 | 1.009E-03 | 329 | 1.085E-03 | 419 | 1.381E-03 |
| 19 | Fensulfothion sulfone | 40.3 | 1.243E-04 | 85.4 | 2.633E-04 | 116 | 3.576E-04 |
| 20 | Fenthion | 6.4 | 2.300E-05 | 9.3 | 3.244E-05 | 11.3 | 4.074E-05 |
| 21 | Leptophos | 0.003 | 8.707E-09 | 0.021 | 6.095E-08 | 0.045 | 1.306E-07 |
| 22 | Malathion | 141 | 4.268E-04 | 145 | 4.389E-04 | 164 | 4.964E-04 |
| 23 | Parathion | 10.3 | 3.536E-05 | 12.9 | 4.429E-05 | 15.2 | 5.219E-05 |
| 24 | Parathion-Me | 21.8 | 8.283E-05 | 38.0 | 1.444E-04 | 58.5 | 2.223E-04 |
| 25 | Phosalone | 1.2 | 3.263E-06 | 2.6 | 7.069E-06 | 3.7 | 1.006E-05 |
| 26 | Phoxim | 3.3 | 1.106E-05 | 4.1 | 1.374E-05 | 4.9 | 1.643E-05 |
| 27 | Pirimiphos-Me | 21.8 | 7.946E-05 | 30.7 | 1.119E-04 | 45.0 | 1.640E-04 |
| 28 | Propoxur | 1740 | 8.316E-03 | 1930 | 9.224E-03 | 2440 | 1.166E-02 |
| 29 | Temephos | 0.009 | 1.929E-08 | 0.27 | 5.788E-07 | 0.70 | 1.501E-06 |
| 30 | Trichloronat | 0.82 | 2.458E-06 | 0.88 | 2.638E-06 | 1.07 | 3.208E-06 |

(Bowman and Sans 1979, 1983). We found that eight compounds had different solubility values than previously determined, of which the changes in five (ethion, fensulfothion sulfone, leptophos, propoxur, trichloronat) were within experimental error. The new value for diazinon was 53.5 g mL⁻¹, down from an earlier reported value of 68.8 µg mL⁻¹. The solubilities of both fenthion and pirimiphos-Me increased from 7.51 to 9.03 µg mL⁻¹ and from 20.2 to 30.7 µg mL⁻¹, respectively. Repeated solubility determinations for these two compounds failed to produce the previously obtained lower values.

The solubility values of all compounds excepting diazinon and chlorfenvinphos increased with increasing temperature over the 10 to 30°C range. The chlorfenvinphos sample was a technical mixture of cis- and trans-isomers (92% purity) in a 10:90% ratio. Preliminary solubility determinations of the two pure isomers showed that the trans-isomer was approximately twice as soluble as the cis-isomer, and that the solubility of the cis-isomer exhibited a negative temperature relationship. Unfortunately, there was insufficient trans-product to establish solubility values at all-three temperatures (at 30°C: cis- 52, trans- 115 µg mL⁻¹).

When the solubility data for diazinon indicated a substantial negative temperature relationship, a new pure sample was obtained. It also exhibited the same trend, but tended to give somewhat lower values than the older sample for which the 20°C solubility value was previously reported at 68.8 µg ML⁻¹. This temperature-solubility relationship suggests an endothermic dissolution process (negative heat of solution). A thorough search of the literature failed to reveal any other pesticidal compounds with a negative temperature relationship.

An Apparent Differential Heat of Solution ($\Delta\bar{H}^*(\text{soln})$) for the insecticides in a saturated nonideal solution can be determined from the following relationship:

$$\frac{d(\ln X)}{dT} = \frac{\Delta\bar{H}^*(\text{soln})}{RT^2} \quad (1)$$

where X = solubility of insecticide (mole fraction) at temperature T (deg K), R is the gas constant (1.98717 cal deg K⁻¹ mol⁻¹). Integration of Eq. 1 assuming $\Delta\bar{H}^*(\text{soln}) = \text{const.}$, produces

$$\ln X = \frac{-\Delta\bar{H}^*(\text{soln})}{R} \cdot \frac{1}{T} + \text{constant} \quad (2)$$

When the plot of $\ln X$ vs $1/T(K)$ is linear, the $\Delta\bar{H}^*(\text{soln})$ value can be easily calculated from the slope of the linear regression line. However, Hollenbeck (1980) has pointed out that in fact this calculated $\Delta\bar{H}^*(\text{soln})$ value is a combination of two factors: the real differential heat of solution, and a function characterizing the extent of deviation from ideal behavior. The actual differential heat of solution, $\Delta\bar{H}(\text{soln})$ is related to $\Delta\bar{H}^*(\text{soln})$ as follows:

$$\Delta\bar{H}^*(\text{soln}) = \Delta\bar{H}(\text{soln}) \cdot \frac{(\delta \ln X)}{(\delta \ln a)} \quad 3$$

where $a = \text{activity}$.

Also

$$\left[\frac{\delta \ln X}{\delta T} \right]_{\text{sat}} = \frac{\Delta\bar{H}(\text{soln})}{RT^2} \cdot \left[\frac{\delta \ln X}{\delta \ln a} \right]_T \quad (4)$$

Hollenbeck reported that $(\delta \ln X / \delta \ln a)$ is always a positive factor and that since most plots of $\ln X$ vs $1/T$ are linear for real (non-ideal) solutions, then this factor must be relatively constant in most solutions.

Apparent Differential Heat of Solution values $\Delta\bar{H}^*(\text{soln})$ shown in Table 2 were estimated by fitting a least-squares linear regression to the $\ln X$ vs $1/T$ variable using Eq. 2. Each $\Delta\bar{H}^*(\text{soln})$ value was derived using data from 3 temperatures and the average of 3 replicates/temperature for a total of 9 data points per value. Probably better precision and accuracy could have been obtained using additional temperatures, but that was beyond the scope of this study. With the exception of the technical chlorfenvinphos sample (corr. coeff., $R = 0.88$), all of the compounds fit Eq. 2 quite well giving R values exceeding 0.90 (for 23 compounds, $R > 0.95$; for 16 compounds, $R > 0.98$).

From these data (Table 2) it appears that temperature effects on solubility ($\Delta\bar{H}^*(\text{soln})$ values) were generally larger for solids than for

TABLE 2
PHYSICOCHEMICAL PROPERTIES OF 30 INSECTICIDES

| Compound | Physical State | Molecular Weight | Melting Point (deg. C) | Apparent Different. Heat of Solution (kcal/mol) |
|--------------------------|----------------|------------------|---------------------------|--|
| 1 Aminocarb | Solid | 208.26 | 93.5 | 3.76 |
| 2 Azinphos-Et | Solid | 345.37 | 53.0 | 11.07 |
| 3 Azinphos-Me | Solid | 317.31 | 73.5 | 12.98 |
| 4 Bromophos | Solid | 365.99 | 53.5 | 11.77 |
| 5 Bromophos-Et | Liquid | 394.04 | | 7.40 |
| 6 Carbaryl | Solid | 201.22 | 142.0 | 5.00 |
| 7 Carbofuran | Solid | 221.25 | 151.0 | 2.15 |
| 8 Carbophenothion | Liquid | 342.85 | | 1.52 |
| 9 Carbophenothion-Me | Liquid | 314.80 | | 5.50 |
| 10 Chlordimeform | Solid | 196.68 | 32.0 | |
| 11 Chlorfenvinphos | Liquid | 359.57 | | -1.31 |
| 12 Chlorpyrifos | Solid | 350.58 | 42.7 | 9.03 |
| 13 Chlorpyrifos-Me | Solid | 322.53 | 46.0 | 11.43 |
| 14 Diazinon | Liquid | 304.34 | | -4.15 |
| 15 Dicapthos | Solid | 297.64 | 51.5 | 10.60 |
| 16 Dieldrin | Solid | 380.90 | 175.5 | 7.82 |
| 17 Ethion | Liquid | 384.45 | | 2.46 |
| 18 Fenamiphos | Solid | 303.36 | 49.2 | 2.66 |
| 19 Fensulfothion sulfone | Solid | 324.34 | 44.0 | 9.05 |
| 20 Fenthion | Liquid | 278.32 | | 4.88 |
| 21 Leptophos | Solid | 344.55 | 70.4 | 23.18 |
| 22 Malathion | Liquid | 330.35 | | 1.28 |
| 23 Parathion | Liquid | 291.25 | | 3.32 |
| 24 Parathion-Me | Solid | 263.20 | 35.5 | 8.42 |
| 25 Phosalone | Solid | 367.80 | 48.0 | 9.63 |
| 26 Phoxim | Liquid | 298.30 | | 3.37 |
| 27 Pirimiphos-Me | Liquid | 274.35 | | 6.17 |
| 28 Propoxur | Solid | 209.24 | 85.5 | 2.87 |
| 29 Temephos | Solid | 466.50 | 30.0 | 37.32 |
| 30 Trichloronat | Liquid | 333.59 | | 2.25 |

liquids (due to energies associated with crystal structure) and that within the solids group, there was a tendency for the temperature effect to increase with increasing molecular weight of the compounds. Melting points of the compounds exhibited no direct relationship with $\Delta\bar{H}^*(soln)$ values, but would be indirectly involved through the heat of fusion of the supercooled liquid solute (Hollenbeck 1980).

These data have clearly demonstrated that the temperature-solubility relationship for this group of insecticides changes markedly with the compound, being dependent in the Apparent Differential Heat of Solution, $\Delta\bar{H}^*(\text{soln})$. These values should be quite useful in predicting solubilities of these compounds in the 10 to 30°C range and perhaps even for providing approximate solubility figures for temperatures 5 to 10°C on either side of this range.

REFERENCES

- J.W. Biggar and R.L. Riggs. *Hilgardia* 42, 383-391 (1974).
B.T. Bowman and W.W. Sans. *J. Environ. Sci. Health* B18, 625-634.(1979).
B.T. Bowman and W.W. Sans. *J. Environ. Sci. Health* B18,221-227.(1983).
R.G. Hollenbeck. *J. Pharm. Sci.* 69, 1241-1242 (1980).

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