Predicting and Measuring the Solubility of p,p'- DDT in Water

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In the course of developing techniques for studying the adsorption and movement in soil of extremely dilute aqueous p,p'-DDT suspensions, it was essential to determine the solubility or concentration of p,p'-DDT in water under identical experimental conditions to those experienced in adsorption and movement studies. Furthermore, it seemed desirable to determine whether the concentration of DDT in a stable suspension if not a true solution could be predicted by thermodynamic considerations for a set of conditions different from those examined experimentally.

The literature contains several values for the solubility of DDT obtained by a variety of analytical techniques. Richards and Cutkomp (8) reported a range of 0.2 to 1.0 ppb at 15°C determined by bio-assay with mosquito larvae while Roeder and Weiant (10) estimated 10 to 100 ppb at room temperature as determined by nerve reactions in cockroaches. Babers (2) and Bowman et al., (3) reported values of 37.4 ppb and not more than 1.2 ppb at 25°C respectively, determined by radiometric analysis. Gauvadan and Poussel (6) estimated a solubility of 100 ppb at 18°C by a

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nephelometric technique.

The "true" solubility of p,p'-DDT in water, where individual molecular species exist in the aqueous medium, is difficult to create and measure. The presence of clusters of molecules existing in a stable suspension as observed here and elsewhere (3) may be what commonly occurs in nature. (The fact that several workers have reported various values of the solubility may rest on this fact.) If the distribution of the chemical in the experiments reported was such as to produce the results obtained including estimates of solubility then this may be more significant than the presence of individual molecular species. Also if p,p'-DDT does exhibit colloidal properties it may be only of academic interest that centrifuging at higher and higher speeds for longer and longer periods of time produces lower and lower concentrations in solution. These same concentrations may not be encountered under natural conditions where centrifuging doesn't occur.

It is important to know, however, that particle size distributions (and/or single species) can occur, when studying adsorption, movement, absorption and degradation. Methods used in the study of such reactions may produce particle size distributions other than what is assumed to be complete molecular separation. The significance of this fact will be referred to later in the paper. Although it is not a principal objective of this paper to describe a method of analysis, it is evident that some details must be given. No claim is laid to originating the use of GLC in analysis of DDT in water. It is a highly sensitive method, which can provide a good

idea of the purity of the compound. From this point it is superior to radiometric methods reported previously (3). The latter method also has particular advantages that can be utilized when necessary. Where agreement is found between the two methods, confidence in the results should be considerably enhanced. Problems associated with codistillation and surface phase concentration have been avoided as pointed out previously (3, 4).

In the present paper analytical methods are described as well as solubility determinations and predictions of DDT in solution based on thermodynamic equations.

Theory

The use of the centrifuge in obtaining a particular particle size can be analyzed thermodynamically. The system to be considered is

$$DDT_{(l)} \equiv DDT_s$$

where (s) refers to solid phase p,p'-DDT and (l) refers to p,p'-DDT in solution. The chemical potential μ of DDT can be written as

$$\mu_I = \mu_I^\circ + RT \ln a_{(s)} - RT \ln a_{(l)} \qquad (2)$$

where μ_I° is the chemical potential in the reference state in a gravity field of unity; $a_{(l)}$ and $a_{(s)}$ are the activities in the solution and solid states respectively. By definition $a_{(s)} = 1.0$ for the solid phase and since at equilibrium $\Delta\bar{G} = \mu_I = 0$ equation 2 becomes

$$\mu^\circ_I = RT \ln a_l \qquad (3)$$

where $\bar{G}$ is the partial molar free energy. When the system is subjected to an external field such as that which occurs in a centrifuge in motion then the chemical potential μ and the partial molar free energy are not equivalent. An additional term must be added to the chemical potential to account for the increase in energy of the constituents as a result of the external field (7). Normally this is neglected for ions and in the case of DDT in the unit gravity field has been included in the reference state. We wish to compare the concentration in the solution after centrifugation with the concentration in the reference state of unit gravity.

For the centrifuged samples

$$G = \mu + \frac{1}{2} m v^2 \tag{4}$$

where G is the free energy, m the mass and v the linear velocity of the rotor.

Since

$$m = n_1 M_1 + n_2 M_2 + \ldots\ldots \tag{5}$$

where n_1 is the number of moles of constituent 1 and M_1 the molecular weight, then

$$\left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2 + \ldots} = \bar{G}_1 = \mu_1 + \frac{1}{2} v^2 \left(\frac{\partial m}{\partial n_1}\right)_{P,T,n_2 \ldots} \tag{6}$$

$$\bar{G}_1 = \mu_1 + \frac{1}{2} M_1 v^2 \tag{7}$$

For two different positions in the centrifugal field at constant temperature and pressure at equilibrium

$$\bar{G}_a - \bar{G}_b = \left(\mu + \frac{1}{2} M v^2\right)_a - \left(\mu + \frac{1}{2} M v^2\right)_b \tag{8}$$

where the subscripts a and b refer to two positions in the field.

Since $\bar{G}_a = \bar{G}_b$ at equilibrium and

$$\mu = \mu^\circ + RT \ln a$$

$$0 = RT \ln a_a - RT \ln a_b + \frac{1}{2} M (v_a^2 - v_b^2) \qquad (9)$$

$$RT \ln a_b/a_a = \frac{1}{2} M (v_a^2 - v_b^2)$$

For these dilute solutions the activity coefficient is assumed to be 1.0, and taking the activity equal to the concentration, equation (9) becomes

$$RT \ln C_b/C_a = \frac{1}{2} M (v_a^2 - v_b^2) \qquad (10)$$

where C_b refers to the solution concentration at 1.0 G ($v_b = 0$), and C_a the concentration at some velocity v_a in the centrifugal field.

Experimental

Preparation of Aqueous Suspensions. Pure p,p'-DDT(99.9%) was prepared from an original sample of 99.3% purity by repeated recrystallization from absolute methanol until a single chromatographic peak with no detectable decomposition was obtained. An acetone solution of p,p'-DDT was prepared, and an appropriate quantity was transferred to a glass-stoppered flask. Water, double distilled from glass, was added to the flask. The acetone was then removed from the suspension by vacuum. In this manner, suspensions of 25 ppb DDT were prepared. The suspension was heated on a steam bath and shaken for one hour, then shaken for 6 days at 25°C in a constant temperature bath. The

suspension was then filtered through a sintered glass filter funnel of 5 micron porosity. The filtrate was collected in a glass-stoppered flask and stored at 25°C until sampled or analyzed.

Method of Sampling. The filtrate was shaken immediately prior to each sampling to ensure uniform dispersion. Stainless steel centrifuge tubes (seven groups of four tubes) were filled to contain 50 ml. of filtrate each, and were capped to prevent loss during centrifuging. The tubes were centrifuged at 25°C ± 1°C for periods of 6, 12, 18, and 24 hours, at speeds of 5000 and subsequently 18000 r.p.m., in a Sorvall RC-2 centrifuge. At the end of each centrifuging, the top half of the filtrate was withdrawn from each tube by pipette and combined with others of the same group. The pipette was rinsed with redistilled n-hexane, the rinse being added to the sample, which was extracted once with 50 ml. of n-hexane, then twice further extracted with 25 ml. aliquots. The extracts were combined, concentrated to 1 ml. and chromatographed. Additional dilutions or concentrations were made when necessary to obtain a linear detector response.

Method of Analysis. The gas chromatographic analyses were performed on an Aerograph Model A-600-B gas chromatograph equipped with a 250 mc tritium foil concentric tube electron capture detector, operated at a potential of 90 volts. The 5' x 1/8" pyrex column was packed with 5% Dow 11 on 60/80 mesh Chromosorb W. Nitrogen suitable for GLC work was the carrier gas, at a flow rate of 100 ml/min. The column oven temperature was 180°C isothermal and

the injector and detector were maintained at 200°C. A pyrex injector insert was used to minimize decomposition, when the 5µl samples were injected with a 701N CH Hamilton syringe. The detector signal was recorded at a sensitivity of X8 with a Brown Electronik 15 1 mv-1 sec. recorder equipped with a 201-B Disc Integrator.

Results and Discussion

The approximate solubility of p,p'-DDT was estimated from suspensions of technical DDT and 10 p.p.m. suspensions of p,p'-DDT. It was observed that the minor components (26.2%) of technical DDT (o,p'-DDT, o,o'-DDT, p,p'-TDE and p,p'-DDE) had a greater solubility in water than did the p,p'-DDT. This could account for the high values reported by other workers. The o,p'-DDT, o,o'-DDT, and p,p'-TDE, and the dehydrohalogenation products of o,p'-DDT and p,p'-TDE, could not be resolved under the above conditions. Consequently the solubilities of the minor constituents were not further investigated.

The rate of adsorption of p,p'-DDT by stainless steel tubes was found to be less than that of any other centrifuge tube capable of withstanding the experimental conditions. It was found necessary to correct the data by subtracting the amount of DDT adsorbed on standing. Codistillation was avoided by employing closed systems. The efficiency of the liquid-liquid extraction procedure was 99-100%.

After preliminary work, the concentration of p,p'-DDT in the suspensions employed was 25 ppb and the filtrates of these suspensions contained less than 13 ppb.

Figure 1 presents the concentration of p,p'-DDT in the solution for various centrifuge speeds and times. It appears that after 24 hours an equilibrium has been established at 18000 r.p.m. (39,100 G), 12000 (17,300 G) and 0.0 r.p.m. (1G). The corresponding concentrations are 1.7 $\pm$ 0.17 ppb, 2.0 ppb, and 3.4 $\pm$ 0.17 ppb. Substituting in equation (10) M = 354.5, R = 8.314×10^7, T = 298°K, at 18000 r.p.m., the ratio $C_b/C_a = 2.1$. Taking C_a = 1.7 ppb, C_b = 3.57 ppb which compares with the measured value of 3.4 ppb the concentration at 1 x G or no centrifuging. For similar conditions except the speed is now 12000 r.p.m., the ratio $C_b/C_a = 1.54$ and for C_a = 2.0, C_b = 3.1 ppb compared to the measured value of 3.4 ppb at 24 hours. Hence the measured values and calculated values are all within 10% of each other which is satisfactory at these low concentrations.

One set of samples that was centrifuged until the concentration remained at 1.7 ppb were set aside at constant temperature conditions and sampled at various times. The slow increase in concentration is illustrated in Figure 1 by the curve with the 10 x; note the different time scale. After 200 hours, the concentration had reached 3.0 ppb in the upper half of the tubes and it appeared to be approaching a value of approximately 3.4 ppb,

the concentration approached from the other direction when the initial concentration was 9.5 ppb.

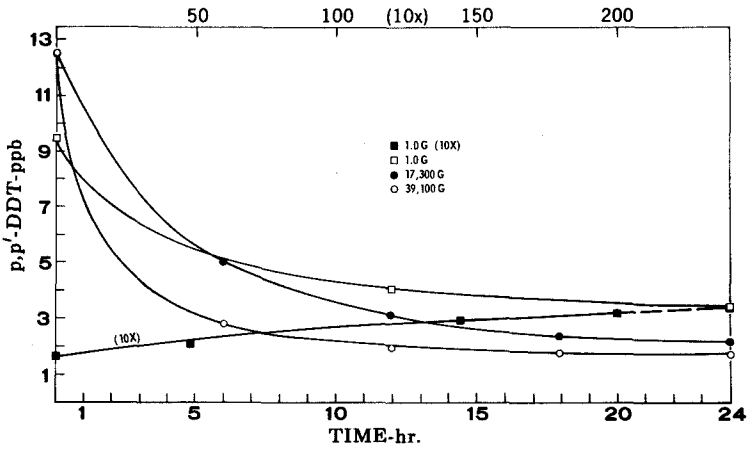

Figure 1. Changes in the concentration of p,p'-DDT in water with time for various treatments with and without centrifugation.

The value of 1.7 ppb obtained in this work is in close agreement with the value obtained by Bowman et al.,(3) who used the radiometric method and higher centrifugal force. However, our purpose was not only to measure the "solubility" in water of DDT by this method, but to develop a method consistent with methods for studying adsorption on particulate matter. It was also desirable to relate the concentration at some standardized centrifuged treatment to the concentration without centrifugation. This we are able to do.

It would appear for the present work that, considering the methods of preparation, etc., under natural conditions, the amount of p,p'-DDT in solution might be even less than 1.7 ppb. None of these values necessarily represent individual molecular species and, in fact, could be stable colloidal suspensions. It cannot be said that this species has several solubilities at one temperature but it may have different concentrations in solution at one temperature depending upon the previous history. These studies demonstrate that one must be aware of the possible size distribution when studying adsorption-desorption from aqueous solutions. Attempts to get even finer dispersal have been made using ultrasonic methods (9). A more adequate picture of the concentrations that might be encountered in nature may be had by desorption studies from various materials where an excess of solid phase DDT is present.

In lakes and streams the major portion of p,p'-DDT probably will be adsorbed to suspended colloidal matter which may or may not be absorbed by organisms. The pathway of DDT entry into lakes and streams most likely is by way of suspended or colloidal matter in discharge waters and from aerial applications. The low solubility of DDT in water probably accounts for its resistance to microbiol decomposition. Such considerations are complicated by the solubilizing effect that water soluble organic matter may have on the DDT. Some of these problems need additional investigation.

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