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Problems in Determining the Water Solubility of Organic Compounds

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We have been concerned for some time about the reliability of published water solubility data for organic compounds with low solubility. The problem was illustrated by the results of our studies on the solubility of the liquid trichlorobenzene (TCB). We found that the apparent solubility is strongly dependent on the method of introducing the solute into the water (Orr 1980). The results are summarized in Table 1 which show that the amount of TCB present in the water varies from 100 mg/L to 0.48 mg/L. The former value was obtained when the components were vigorously stirred and allowed to separate by gravity. The latter value was obtained by gentle stirring and separating by centrifugation at 48,400 x g.

It was apparent that we were not determining the amount of TCB actually dissolved in the water, but the amount that was present in solution plus that in suspended form.

In view of the variation in the results of solubility studies on TCB, we have determined the solubility of 1, 2, 4, 5 - tetrachlorobenzene (TTCB) for our toxicity studies under more carefully controlled conditions.

MATERIALS AND METHODS

Water sampling was started with the solution having the lowest nominal concentration. Using a sampler with a 50 µ sintered glass filter, a 50 - 100 mL volume of the test solution was aspirated, the sample shaken to coat the walls with the test solution, and the solution discarded.

A 400 mL portion of water, from test level 1, was aspirated and dispensed directly into a 500 mL volumetric flask. Distilled water (50 mL) and (non-spectro) hexane (50 mL) were added and the aqueous phase extracted overnight by magnetic stirring. The same procedure was followed for test levels 2 - 5. The TTCB content of the hexane solutions was determined by gas chromatography analysis and reported in Table 2 as glass sintered 50 µ.

A sample (500 mL) from test level 1 was filtered in the 50 µ filter sampler. A portion of the filtrate (100 mL) was added to the millipore apparatus (0.22 µ), shaken, filtered to coat the apparatus, and then discarded. The remainder of the initial filtrate (400 mL) was millipore filtered directly into a 500 mL volumetric flask. Water (50 mL) and non-spectro hexane (50 mL) were added and the aqueous phase extracted overnight by magnetic stirring.

The procedure was repeated on a second sample from the same test level, using a 0.45 µ millipore filter, and on a third sample using a 1.2 µ millipore filter. Test levels 2 - 5 were treated in the same manner. The TTCB content of the fifteen hexane extracts was determined by gas chromatography analysis and reported in Table 2 according to filter size.

Water (320 mL) from test level 4 was filtered through the 50 µ sintered glass filter as before. The water was divided among eight Nalgene centrifuge tubes and centrifuged at 20°C for 10 min at 43,500 x g, using a Sorvall RC2-B superspeed centrifuge. 25 mL aliquots were removed from each tube and combined. The combined aqueous phase was extracted with hexane and analyzed as before. Water from test level 5 was treated in the same manner.

All hexane extracts were analysed for TTCB using a Hewlett-Packard 5730A gas chromatograph equipped with an electron capture detector (^{63}Ni) and a model 7671A automatic sampler. The carrier gas was 5% methane in argon at a flow rate of 35 mL/min. The 80 cm x 0.3 cm(id) glass column was packed with 8% Bentone - 34/10% DC-200 on 80 - 100 mesh Gas Chrom Q. The analyses were performed under the following conditions: injector temperature 150°C, column temperature 120°C, detector temperature 300°C. Results were recorded on a Hewlett Packard 3390A integrator, (electronically integrated) and compared to an internal standard (Hexachlorobenzene).

RESULTS AND DISCUSSION

In connection with toxicity studies of chlorinated benzenes, it was important to have at least an approximate value of the true solubility of those solutes.

In these toxicity studies, we used a flow through system in which the toxicant is nominally present at five concentration levels (Ozburn 1977). In the case of the solid 1, 2, 4, 5 tetrachlorobenzene (TTCB), the five concentration levels were nominally: level 1, 0.69 mg/L, level 2, 1.21 mg/L, level 3, 2.16 mg/L, level 4, 6.91 mg/L, level 5, 12.09 mg/L. In order to remove the bulk of the undissolved material, we sampled the tanks using a suction device which contained a sintered glass filter of 50 µ pore size. The amount of TTCB present in each of the five levels after this treatment was found to be: 0.15 mg/L, 0.36 mg/L, 0.70 mg/L, 1.86 mg/L, and 2.49 mg/L.

Table 1. Variation of trichlorobenzene content with mixing-separation procedure.

Mixing Procedure	Separation Method	Amt. trichlorobenzene present in mg/L
Fast magnetic stirring	gravity	100
Fast magnetic stirring	centrifugation 8×10^4 g	1.23 - 1.60
Blender	centrifugation 3×10^4 g	26.5
Shaking in separatory funnel	centrifugation 4.82×10^4 g	0.96
Slow magnetic stirring	centrifugation 4.82×10^4 g	0.48

After this initial filtration, three samples from each level were refiltered through millipore filters of three different sizes: 1.2 μ, 0.45 μ, and 0.22 μ. As can be seen from Table 2, the TTCB content of the water is a function of the size of the filter.

Table 2 shows no dramatic change in the amount of TTCB present when the water from the two lowest concentration levels was passed through filters with progressively smaller pore sizes. This could indicate that the bulk of the TTCB present is in solution, and hence cannot be removed by filtration, regardless of the filter size.

For the three high levels there is a dramatic change in the amount of TTCB present when the filtrate from the 50 μ pore filter is passed through a 1.2 μ pore filter. For level 5, containing 2.49 mg/L after the initial filtration, there is a five-fold reduction in the amount of TTCB contained in the water. Clearly, the bulk of the TTCB present is not in solution.

If one plots (Figure 1) concentration of TTCB (mg/L) vs pore size (μ) of the filter and extrapolates the curve to zero pore size, the three high levels give a TTCB concentration of 0.30 mg/L. This number could represent an approximate value for the true solubility. A similar plot for the two lowest levels shows that the extrapolated curve gives values of 0.07 mg/L for level 1 and 0.20 mg/L for level 2. We believe these values to be lower than the true solubility, because either the nominal concentration of the solute is below true solubility, or there was insufficient time to saturate the water.

The solubility of TTCB that we found by this method is in agreement with the amount of TTCB remaining in the water after centrifuging at 43,500 x g for ten min. Level 4 contains 0.31 mg/L of TTCB and level 5 contains 0.30 mg/L after centrifuging.

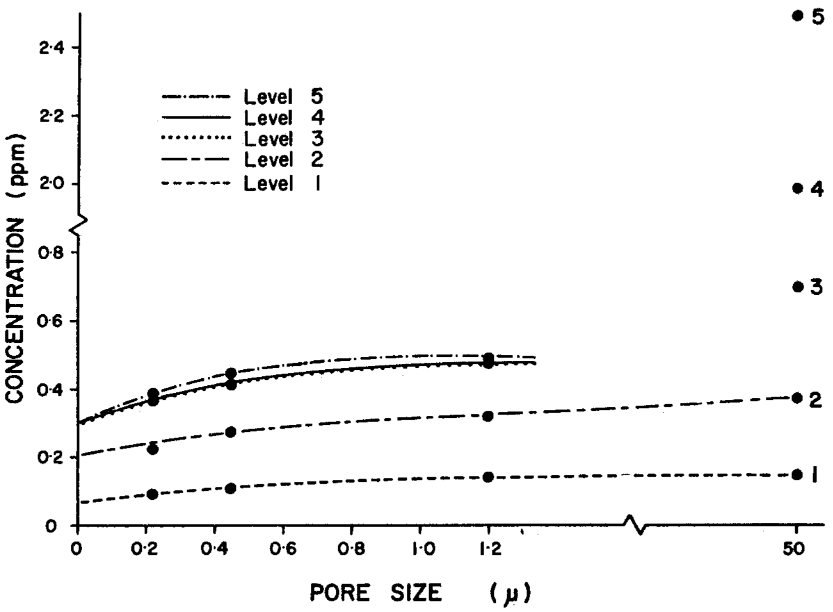

Table 2. Variation of tetrachlorobenzene content with pore size of filter.

Test Level	Nominal concentration mg/L	Concentration of 1,2,4,5-tetrachlorobenzene (mg/L) ($\bar{X}$ ± S.D.) Glass sintered 50 μ	Filter pore size 1.2	 0.45	 0.22
1	0.69	0.148±0.009	0.139±0.009	0.108±0.008	0.093±0.005
2	1.21	0.363±0.055	0.317±0.061	0.274±0.024	0.245±0.040
3	2.16	0.695±0.050	0.471±0.033	0.412±0.030	0.365±0.025
4	6.91	1.855±0.326	0.472±0.046	0.417±0.041	0.371±0.035
5	12.09	2.493±0.357	0.489±0.009	0.447±0.013	0.384±0.025

The results reported above from a flow-through system with the solubilities obtained by extrapolation to a zero filter size are reasonably consistent with our solubility results obtained by the following method.

TTCB was suspended in a conical flask and agitated for 120 days. If the bulk of undissolved TTCB is removed by filtration and the filtrate centrifuged at 43,500 x g for ten min. the mean amount of TTCB remaining is found to be 0.47±0.011 mg/L. If instead the undissolved TTCB is removed by filtration through a 0.45 μ filter, we find a value of 0.425 mg/L for the amount remaining.

The lower results obtained from the flow-through system may be a reflection of a non-saturated system due to the short-residence time (high water turnover rate) of TTCB particles in the water.

We found that the true solubility of TTCB is probably between 0.30 mg/L and 0.47 mg/L, the actual value depending on the experimental method. Hence, one must be cautious in using reported solubility data, as the "true value" is very much a function of how the solute was introduced into the aqueous phase, how long it was in contact with the water, and how the "resulting solution" was treated before analysis. We feel that many solubilities are reported high, as adequate procedures were not followed for removing undissolved material.

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