The Distribution of some Dialkylfluorophosphates in the Liquid Systems Carbon Tetrachloride/Water and Oil/Water

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The distribution of four dialkylfluorophosphates (I-IV) has been investigated in the systems carbon tetrachloride/water and whale-oil/water, and that of III also in the system peanut oil/water. In the systems whale-oil/water and carbon tetrachloride/water the following sequence for the distribution coefficient (K) was found: I < III < II < IV.

In connection with investigations on the inhibition of cholinesterase, it was desirable to determine the distribution of some dialkylfluorophosphates (I-IV) between an organic solvent and water, and an oil and water. The compounds investigated had the formula $(RO)_2P(O)F$. R = ethyl (I), R = propyl (II), R = isopropyl (III), R = butyl (IV).

The distribution of III between peanut oil and water has been investigated by Augustinsson¹ who used the cholinesterase inhibiting effect of the water phase as a measure of the amount of III present.

In the work described herein two different methods were used for the quantitative determination of the dialkylfluorophosphates. The one is a *o*-tolidine perborate method for colorimetric estimation of dialkylfluorophosphates. The other is a method based upon analysis of fluoride. The values of the distribution coefficients found all refer to room temperature (20-24°C).

The results of a typical experiment, *viz.* the determination of the distribution coefficient (K) of III in the liquid systems whale-oil/water and carbon tetrachloride/water are given in Table 1.

A summary of the distribution coefficients (K) obtained is given in Table 2, which also includes the number of experiments made for each determination and the standard deviation.

The values of K vary widely with the length of the alkyl group. In the systems carbon tetrachloride/water and whale-oil/water the value of K varies in the following way with the alkyl group, ethyl < isopropyl < propyl < butyl.

Table 1. Data for the determination of the distribution of III between carbon tetrachloride and water and between whale-oil and water.

Solvent	Expt.	Total III mg	Vol.ratio solvent water	mg of dialkylfluoro- phosphate recovered		Reco- very %	K
				Solvent	Water		
Carbon tetra- chloride	1	18.80	1 : 5	17.44	2.23	104.6	39.2
	2	18.37	1 : 3	17.41	1.39	102.1	37.5
	3	13.78	1 : 7	11.86	2.17	101.8	38.2
Whale- oil	1	111.6	1 : 8.87	55.8 a)	55.8		8.87
	2	55.9	1 : 8.30	27.9 a)	28.0		8.26
	3	45.0	1 : 19.10	14.0 a)	31.0		8.64
	4	65.0	1 : 13.90	26.5 a)	38.5		9.57
	5	54.3	1 : 8.41	26.3 a)	28.0		7.90

a Calculated by difference.

EXPERIMENTAL

Syntheses of dialkylfluorophosphates. The dialkylfluorophosphates were prepared by a one stage method². Benzene was used as solvent. The products were redistilled until constant refractive index was obtained. No other test for purity was made. The refractive index was measured with a Hilger-Abbe refractometer, and the following values for n_D^{20} and boiling point respectively were found: I: 1.3722, 57°/11 mm; II: 1.3891, 80°/11.5 mm; III: 1.3817, 71°/14 mm; IV: 1.4013, 54°/0.02 mm.

Distribution coefficients of I–IV between carbon tetrachloride and water. The method used is a modification of the *o*-tolidine perborate method for estimation of phosphonofluoridates^{3,4}. The following reagents and organic solvents were used:

Acetone *pro analysi*, purified with potassium permanganate and distilled.

Carbon tetrachloride *pro analysi* (Merck).

o-Tolidine reagent. *o*-Tolidine dihydrochloride (B.D.H.) was purified by treatment with stannous chloride and active carbon until a concentrated aqueous solution was colourless. A 1 % solution in water was used (prepared daily).

Phosphate buffer 0.05 M, pH = 11.5, prepared by dissolving 8.7 g of K_2HPO_4 in 1 litre of distilled water, and adjusted to pH 11.5 with saturated NaOH solution.

Table 2. Distribution coefficients of dialkylfluorophosphates in the liquid systems carbon tetrachloride/water, whale-oil/water and peanut oil/water.

Dialkyl- fluoro- phosphate	Distribution carbon tetrachloride/water			Distribution whale-oil/water			Distribution peanut oil/water	
	No. of expts.	K	Stand. dev.	No. of expts.	K	Stand. dev.	No. of expts.	K
I	5	3.46	0.16	5	2.7	1.11		
II	4	60.2	1.02	6	15.0	2.04		
III	3	38.3	0.86	5	8.6	0.63	4	7.6
IV	3	102	10.74	9	62	7.52		

Sodium perborate reagent. 1.25 % aqueous solution of sodium perborate (prepared daily).

For estimation of the calibration curve a known solution of dialkylfluorophosphate in carbon tetrachloride was prepared, and the reagents mixed in the following quantities and sequence. Acetone (20 ml), phosphate buffer (2.0 ml), sodium perborate reagent (1.5 ml), *o*-tolidine reagent (1.0 ml), water saturated with carbon tetrachloride (6.5 ml), carbon tetrachloride saturated with water (1-n) ml and a solution of dialkylfluorophosphate in carbon tetrachloride (n ml).

The intensity of colour was measured after 20 min in a Fisher Electrophotometer (model AC) with a blue filter, and the colorimetric readings, corrected for blanks, were plotted against mg of dialkylfluorophosphate.

For the determination of the distribution coefficient a measured volume of a known solution of dialkylfluorophosphate in carbon tetrachloride was shaken vigorously for 1 min with a known volume of distilled water. The phases were allowed to separate and samples of both of them were with-drawn and analyzed for dialkylfluorophosphate as described for the calibration. In analyzing the water phase (6.5-n) ml of water, n ml of water phase and 1 ml of carbon tetrachloride were used. The concentration in each phase was determined by comparison of the net colorimetric readings with the calibration curve.

Distribution coefficients of I-IV between whale-oil and water. The amount of dialkylfluorophosphate in the water phase was determined by colorimetric estimation of fluoride by interaction with a thorium lake⁵. The following reagents were used:

Refined whale-oil from De-No-Fa, Fredrikstad, Norway.

Thorium reagent, 0.001 M with respect to thorium nitrate and 1.0 M with respect to sodium sulphate, formic acid and sodium formate.

Alizarin indicator 0.00025 M. 0.0855 g of alizarin monosodium sulphonate was dissolved in 1 litre of distilled water.

For estimation of the calibration curve 20-40 mg of dialkylfluorophosphate was dissolved in 100 ml of distilled water. Samples of not more than 25 ml were boiled with reflux for 90 min with 10 ml of 0.1 M NaOH solution. The samples were filtered through paper filter and quantitatively transferred to 100 ml flasks. 20 ml of alizarin indicator was added, and the samples were titrated with 0.6 M nitric acid until a pure yellow colour was obtained. Then 20 ml of thorium reagent was added and the solution diluted to 100 ml with distilled water. The intensity of colour was measured after 30 min in a Fisher Electrophotometer (model AC) with a green filter, and the colorimetric readings, corrected for blanks, were plotted against mg of dialkylfluorophosphate.

For estimation of the distribution coefficient the density of a 3 % solution of dialkylfluorophosphate in oil was determined. A calculated volume (about 5 ml) of a known solution of dialkylfluorophosphate, about 3 % in oil, was shaken cautiously with 50 ml of distilled water for 5 min. The two phases were allowed to separate and samples of 5 ml of the water phase were withdrawn for analyses. The analyses were performed as described for the calibration, and the concentration of dialkylfluorophosphate in the water phase was determined by comparison of the net colorimetric readings with the calibration curve.

We did not succeed in analyzing the oil phase. The amount of dialkylfluorophosphate in the oil phase therefore was calculated by difference.

Distribution coefficient of III between peanut oil and water. The first part of the procedure was as described for the system whale-oil/water. The second part, the analyzing of the water phase, was performed by the *o*-tolidine perborate method as described before.

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