

Studies on the Extraction of Metal Complexes

XXX. The Dissociation, Distribution and Dimerization of Di-*n*-butyl Phosphate (DBP)

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The solubility and acidity of DBP in water and the distribution of DBP between chloroform or hexone (methyl *isobutyl* ketone) and HClO₄-NaClO₄ solutions has been studied at 25°C. The distribution of DBP has been chiefly measured with DBP labelled with radioactive ³²P. It was thus possible to measure *q*, the net distribution ratio of DBP, at very low concentrations of DBP and to determine the very high dimerization constant, *k*₂, in chloroform.

From the data, the following constants were calculated by fitting the normalized curve, $\log y = \log (x+1)$ (*cf.* Refs. ^{17, 18}).

Dissociation of DBP in 0.1 M and 1 M HClO₄-NaClO₄

$$pk_a = 1.00 \pm 0.01$$

Distribution of DBP between chloroform or hexone and 0.1 M HClO₄-NaClO₄

$$\log k_d = 0.34 \pm 0.01 \text{ (chloroform)}$$

$$\log k_d = 1.36 \pm 0.01 \text{ (hexone)}$$

Dimerization of DBP in

$$\text{chloroform (wet): } \log k_2 = 4.48 \pm 0.04$$

$$\text{hexone (wet): } \log k_2 = 1.19 \pm 0.03$$

$$\text{water (sat.soln.): } \log k_2 = 1.11 \pm 0.07$$

Complex formation of DBP and TBP in chloroform

$$\log k_B = 1.6$$

These constants are discussed together with data for some carboxylic acids, and it is shown that the dimerization of DBP is much more pronounced than for these acids. Furthermore it is possible to calculate the distribution constant, *k*_D, for some of the dimers.

Di-*n*-butyl phosphate (DBP) has been shown to be a very suitable complexing agent for the extraction of elements such as scandium¹, yttrium^{2, 3}, zirconium³, lanthanum¹, hafnium¹ and uranium^{1, 4, 5}. It is also known that

DBP interferes with TBP extractions in reactor fuel processes⁶. In order to obtain a more complete understanding of the reactions of DBP in these systems it was necessary to determine the dissociation constant and partition coefficients of DBP. During these studies we found that DBP had a pronounced tendency to dimerize, and the values of the association constants in chloroform, hexone (methyl *isobutyl* ketone) and water were determined. Previously the dissociation constants for some dialkyl phosphates have been determined by van Hove⁷, Drushel and Felty⁸, and Kumler and Eiler⁹. Recently Peppard *et al.*¹⁰ have reported that dialkyl phosphates in benzene solution are dimeric, and in measurements of the infrared spectra of DBP in non-polar solvents¹¹ it has not been possible to find any evidence of free hydroxyl-group absorption.

Symbols and formulas

$[]$ or $[]_{\text{aq}}$	concentrations in the aqueous phase
$[]_{\text{org}}$	concentrations in the organic phase
C_A	initial total concentration of DBP in the organic phase
$C_{\text{org}}, C_{\text{aq}}$	equilibrium total concentrations of DBP
HA	di- <i>n</i> -butyl phosphate (DBP), (C_4H_9O) ₂ P(OH)
H_2A_2	dimer of DBP
B	solvent molecule
$k_a = [H^+][A^-]/[HA]$	stoichiometric acid dissociation constant
$k_B = [HA \cdot B]_{\text{org}}/[HA]_{\text{org}}[B]_{\text{org}}$	association constant of HA and B
$k_d = [HA]_{\text{org}}/[HA]$	distribution constant for HA
$k_D = [H_2A_2]_{\text{org}}/[H_2A_2]$	distribution constant for H_2A_2
$k_2 = [H_2A_2]_{\text{org}}/[HA]_{\text{org}}^2$	dimerization constant in the organic phase
$k'_2 = [H_2A_2]/[HA]^2$	dimerization constant in the aqueous phase
q	net distribution ratio of DBP
$V_{\text{org}}, V_{\text{aq}}$	phase volumes

The experimental errors given were estimated from the fit obtained between the normalized curve $\log y = \log(x+1)$ and the experimental points.

REAGENTS AND APPARATUS

Our general experimental techniques have been described previously by other papers in this metal extraction series (*cf.* Ref. 12). The DBP was kindly supplied by Albright & Wilson Ltd., London. Titration with alkali and analysis for C (Found: 45.0. Calc. for $C_8H_{16}PO_4$: 45.7) and H (Found: 8.7. Calc: 9.1) showed the compound to be at least 99 % pure. DBP labelled with radioactive ³²P was purchased from Radiochemical Centre, Amersham, England. This product was free of any non-acidic ³²P-products (*e.g.* TBP or pyrophosphate, TBPP). The specific activity was 4.7 mc per gram of DBP. The chloroform was washed three times with twice the volume of water to remove the 1 % alcohol. The hexone and TBP were washed with alkali, acid, and finally with water.

The radioactivity of DB³²P was measured in 10 ml liquid counter tubes (type M6, 20th Century Electronics) with an approximate wall-thickness of 35 mg/cm². In order to determine the influence of the solvent on the counting rate, solutions were made of 0.5 ml of acetone with DB³²P and 9.5 ml of different solvents. These values are given in Table 1

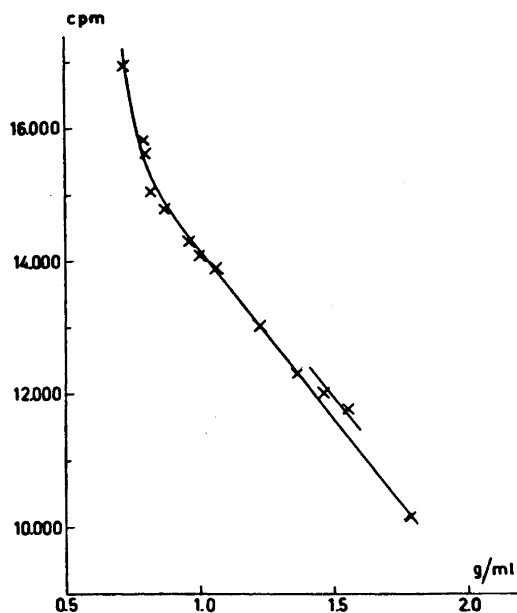


Fig. 1. Effect of solvent density on the counting rate of ^{32}P in a liquid counter.

and plotted in Fig. 1. The values of chloroform and carbon tetrachloride fall above the curve because of the comparatively low electron density of these two solvents. Similar results have been reported earlier^{13, 14}.

All experiments were carried out at 25°C, and all counting rates given are corrected for background activity and resolving time. Measurements of the hydrogen ion concentration were carried out with a Radiometer pHM3i valve potentiometer, equipped with a Radiometer glass electrode G 100 and a calomel electrode K 100. The two-phase titrations¹⁵ were performed with the same potentiometer but with other types of glass and calomel electrodes.

THE SOLUBILITY AND ACIDITY OF DBP IN WATER

The solubility of DBP in water at 25°C was found to be 0.0818 M by titration with alkali. The pH of the saturated solution was 0.022 units higher than for a solution of 0.05 M $\text{HClO}_4 + 0.05 \text{ M NaClO}_4$. If we use values of the activity coefficients given by Kielland¹⁶ and the value of $\text{p}k_a = 1.00$ in 0.1 M ClO_4^- , which was determined in other experiments reported here, we may calculate the following values for the saturated aqueous solution of DBP.

$$-\log [\text{H}^+] = 1.340$$

$$[\text{H}^+] = [\text{A}^-] = 0.0457 \text{ M}$$

$$\text{p}k_a = 1.036 = \log [\text{HA}] - \log [\text{H}^+] - \log [\text{A}^-]$$

$$[\text{HA}] = 0.0227 \text{ M}$$

$$[\text{H}_2\text{A}_2] = \frac{1}{2} (0.0818 - 0.0227 - 0.0457) = 0.0067 \text{ M}$$

Table 1. The effect of the solvent on the counting rate of DB³²P for a Century Electronics M6 liquid counter tube.

Solvent	Density g/ml	Density of DB ³² P solution ^a	<i>I</i> ^b cpm
Ether	0.714	0.72	16 964
Acetone	0.792	0.792	15 830
Hexone	0.802	0.80	15 623
Kerosene	0.82	0.82	15 054
Benzene	0.879	0.87	14 793
TBP	0.973	0.96	14 304
0.1 M NaClO ₄	1.006	1.00	14 089
1 M NaClO ₄	1.076	1.06	13 897
4.32 M H ₂ SO ₄	1.252	1.23	13 033
7.11 M H ₂ SO ₄	1.395	1.36	12 307
Chloroform	1.498	1.46	12 022
Carbon tetrachloride	1.595	1.55	11 770
18 M H ₂ SO ₄	1.836	1.78	10 164

^a 2.5 × 10⁻⁵ M DBP, 5 % acetone

^b Corrected for the decay of ³²P. Standard error approx. ±130 cpm.

The assumption, that DBP dimerizes also in water, will explain the low value of [HA] that is obtained from the value of pK_a found in distribution experiments with radioactive DBP. The association constant may then be calculated as

$$k'_2 = [\text{H}_2\text{A}_2]/[\text{HA}]^2 = 13 \pm 2$$

THE ACIDITY IN THE AQUEOUS PHASE AS A FUNCTION OF THE CONCENTRATION OF DBP IN THE ORGANIC PHASE

Solutions of DBP (conc. C_A) in chloroform or hexone were shaken with an equal volume of 0.1 M NaClO₄, and the value of $-\log [\text{H}^+]$ was measured in the aqueous phase (the potentiometer was set to pH = 2.000 for a solution of 0.01 M HClO₄ + 0.09 M NaClO₄). The results are given in Figs. 2 and 3. With chloroform there seemed to be mainly dimers present in the concentration range studied (10⁻⁴ to 1 M). The following equations are valid in these experiments.

$$C_A = C_{\text{org}} + C_{\text{aq}} \quad (1)$$

$$C_{\text{org}} = 2[\text{H}_2\text{A}_2]_{\text{org}} + [\text{HA}]_{\text{org}} \quad (2)$$

$$C_{\text{aq}} = [\text{HA}] + [\text{A}^-] \quad (3)$$

$$[\text{A}^-] = [\text{H}^+] \quad (4)$$

Additional results were obtained by a two-phase titration^{12, 15} of 0.5 mmoles of DBP in 75 ml chloroform or hexone. From these titrations C_{org} and $[\text{H}^+][\text{A}^-]$ were calculated.

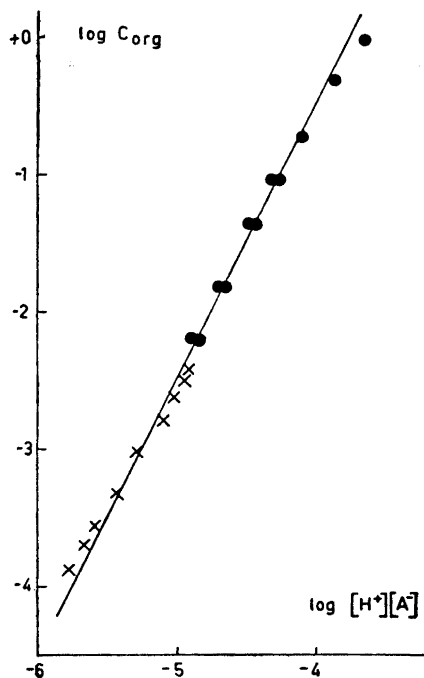


Fig. 2. Distribution of DBP between chloroform and 0.1 M NaClO₄. ● [H⁺] measured in the aqueous phase after equilibration and separation of the two phases. × [H⁺] measured in a two-phase titration.

From eqn. (2) and the definitions of k_2 , k_d and k_a given above, the following equation may be derived

$$C_{\text{org}} = 2k_2(k_d/k_a)^2[\text{H}^+]^2[\text{A}^-]^2 + (k_d/k_a)[\text{H}^+][\text{A}^-] \quad (5)$$

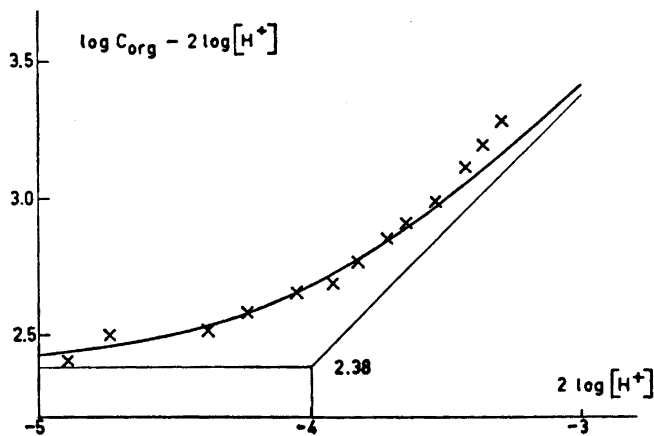


Fig. 3. Distribution of DBP between hexone and 0.1 M NaClO₄. [H⁺] measured in the aqueous phase. Position of horizontal asymptote ($pK_a + \log k_d = 2.38$) determined from a two-phase pH-titration.

Table 2. Distribution of DB³²P between chloroform and 0.1 M perchloric acid for different conc. of DBP. $V_{\text{org}} = V_{\text{aq}} = 15$ ml.

C_A M	I_{org} cpm	I_{aq} cpm	$\log q^a$	$\log C_{\text{org}}^b$
0.987	7 800	57	+2.210	-0.009
0.500	8 003	75	+2.102	-0.305
0.333	7 289	64	+2.130	-0.481
0.200	8 074	78	+2.089	-0.703
0.133	7 530	95	+1.980	-0.880
0.100	8 000	128	+1.869	-1.006
0.0500	7 739	159	+1.761	-1.309
0.0200	7 969	250	+1.577	-1.710
0.0100	7 470	325	+1.435	-2.016
0.00501	7 747	468	+1.293	-2.322
0.00201	7 070	672	+1.096	-2.730
0.00101	6 495	877	+0.943	-3.043
5.13×10^{-4}	6 029	1 106	+0.810	-3.352
2.13×10^{-4}	5 521	1 571	+0.620	-3.765
1.13×10^{-4}	4 890	1 912	+0.481	-4.071
5.33×10^{-5}	18 285	9 418	+0.362	-4.430
2.67×10^{-5}	7 258	5 330	+0.224	-4.777
1.33×10^{-5}	13 120	9 918	+0.195	-5.088
6.67×10^{-6}	1 867	1 590	+0.143	-5.412

$$^a q = I_{\text{org}} \cdot 1.186 / I_{\text{aq}}$$

$$^b C_{\text{org}} = C_A \cdot q / (1 + q)$$

For chloroform (Fig. 2) the points follow a straight line with a slope equal to 2 when $\log C_{\text{org}}$ is plotted against $\log [H^+][A^-]$. This means that the monomer HA in the chloroform phase can be neglected (last term in eqn. (5)). From this line we obtained

$$\log k_2(k_d/k_a)^2 = +7.22 \pm 0.05$$

Table 3. Distribution of DB³²P between hexone and 0.1 M perchloric acid for different conc. of DBP. $V_{\text{org}} = V_{\text{aq}} = 15$ ml.

C_A M	I_{org} cpm	I_{aq} cpm	$\log q^a$	$\log C_{\text{org}}^b$
0.973	8 631	118	+1.825	-0.018
0.500	8 665	159	+1.698	-0.310
0.200	9 046	249	+1.521	-0.712
0.100	9 078	317	+1.418	-1.017
0.0500	8 638	404	+1.291	-1.322
0.0200	8 315	511	+1.173	-1.727
0.0100	8 290	567	+1.126	-2.032
0.00503	8 157	580	+1.109	-2.332
0.00203	8 131	666	+1.048	-2.730
0.001027	7 957	661	+1.043	-3.027
1.33×10^{-5}	11 741	950	+1.053	-4.912

$$^a q = I_{\text{org}} \cdot 0.915 / I_{\text{aq}}$$

$$^b C_{\text{org}} = C_A \cdot q / (1 + q)$$

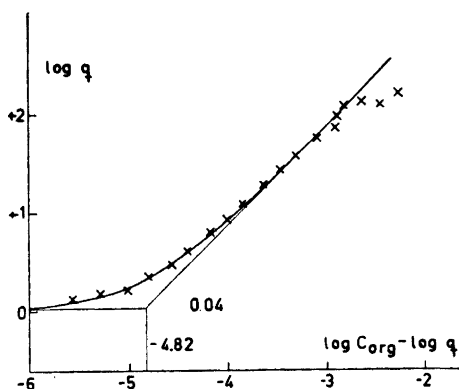


Fig. 4. The distribution ratio of DB³²P between chloroform and 0.1 M perchloric acid as a function of the DBP conc. in the chloroform phase.

For hexone a plot (Fig. 3) of $\log C_{\text{org}} - 2\log [H^+]$ against $2\log [H^+]$ does not give a straight line. The normalized curve $\log y = \log (x+1)$ (cf. Refs. 17, 18) fits the data except for the highest DBP concentrations (0.5 and 1 M). The horizontal asymptote ($\log y = 0$) to the curve was obtained from a two-phase titration

$$pk_a + \log k_d = +2.38 \pm 0.01$$

The point of intersection of the two asymptotes ($\log y = 0$ and $\log y = \log x$) gives

$$\log 2k_2k_d/k_a = +4.00 \pm 0.03$$

$$i.e., \log k_2 = +1.32 \pm 0.04$$

THE DISTRIBUTION OF DBP AS A FUNCTION OF THE CONCENTRATION OF DBP IN THE ORGANIC PHASE

In these experiments the distribution of DBP was measured by means of DBP labelled with radioactive ³²P. The results for chloroform and hexone are given in Tables 2 and 3 and in Figs. 4 and 5. The aqueous phase was 0.1 M

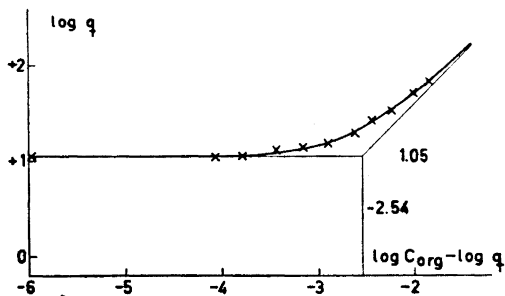


Fig. 5. The distribution ratio of DB³²P between hexone and 0.1 M perchloric acid as a function of the DBP conc. in the hexone phase.

perchloric acid. Eqns (1)—(3) given above are also valid here. As C_{aq} is always low any formation of dimers in the aqueous phase can be neglected. The net distribution ratio is

$$q = C_{\text{org}}/C_{\text{aq}} \quad (6)$$

and from eqns. (2), (3), and (6) and the definitions of k_2 , k_d and k_a follows that

$$q = 2k_2(k_d/\varphi)^2 C_{\text{org}}/q + k_d/\varphi \quad (7)$$

where φ is a constant in these experiments

$$\varphi = 1 + k_a/[\text{H}^+] \quad (8)$$

In Figs. 4 and 5 $\log q$ is plotted against $\log C_{\text{org}} - \log q$.

The normalized curve $\log y = \log (x+1)$ fits the data very well except for 0.5 and 1 M DBP in chloroform. The horizontal asymptote ($\log y = 0$) gives

$$\log k_d/\varphi = +0.04 \pm 0.02 \text{ for chloroform (Fig. 4)}$$

$$\text{and } \log k_a/\varphi = +1.05 \pm 0.01 \text{ for hexone (Fig. 5)}$$

and the point of intersection between the two asymptotes gives

$$\log 2k_2k_d/\varphi = +4.82 \pm 0.02 \text{ for chloroform}$$

$$\log 2k_2k_d/\varphi = +2.54 \pm 0.02 \text{ for hexone}$$

i.e., $\log k_2 = +4.48 \pm 0.04$ (chloroform) and $+1.19 \pm 0.03$ (hexone).

The latter value for hexone is definitely lower than the value of 1.32 obtained in the previous part.

If we use the value of $k_a = 10^{-1.00 \pm 0.01}$ that was obtained in the experiments reported below, φ will be equal to 2.00 ± 0.02 (eqn. 8). The distribution coefficient of the monomeric form HA may then be calculated as

$$\log k_d = +0.34 \pm 0.02 \text{ for chloroform}$$

$$\log k_d = +1.35 \pm 0.01 \text{ for hexone}$$

For comparison with the results obtained from the acidity measurements with inactive DBP (given in brackets), the following values may be calculated

$$\log k_2(k_d/k_a)^2 = +7.16 \pm 0.06 \text{ for chloroform } (7.22 \pm 0.05)$$

$$pk_a + \log k_d = +2.35 \pm 0.02 \text{ for hexone } (+2.38 \pm 0.01)$$

$$\log 2k_2k_d/k_a = +3.84 \pm 0.04 \text{ for hexone } (+4.00 \pm 0.03)$$

Except for the value of $\log k_2$ for hexone the agreement seems to be rather good. We consider the value of $\log k_2$ obtained with radioactive DBP to be more reliable.

THE DISTRIBUTION OF DBP AS A FUNCTION OF THE ACIDITY IN THE AQUEOUS PHASE

These experiments were carried out in order to determine both the distribution coefficients and the acidity constant of DBP. The distribution of DBP was again measured with radioactive DB³²P. The results for chloroform and

Table 4. Distribution of DB³²P between chloroform and HClO₄-NaClO₄ solutions. Initial conc. of DBP in the chloroform layer 1.33×10^{-5} M.

Ionic strength M	<i>I</i> _{org} cpm	<i>I</i> _{aq} cpm	log <i>q</i> ^a	-log [H ⁺]	log <i>q</i> _{corr} ^b
0.1	13 281	10 011	+0.196	1.00	+0.06
	10 510	12 500	-0.002	1.30	-0.13
	8 180	13 953	-0.158	1.48	-0.27
	6 226	17 203	-0.368	1.70	-0.43
	3 573	21 154	-0.699	2.00	-0.76
	2 084	23 601	-0.980	2.30	-1.01
	795	24 131	-1.408	2.70	-1.43
	307	9 211	-1.404	2.72	-1.42
	1	6 145	3 854	+0.265	0.00
6 832		3 582	+0.349	0.30	+0.19
6 615		3 645	+0.321	0.48	+0.16
6 426		3 917	+0.277	0.70	+0.13
5 733		4 443	+0.173	1.00	+0.03
4 850		5 728	-0.011	1.30	-0.16
3 333		7 388	-0.283	1.70	-0.38

^a $q = I_{\text{org}} \cdot 1.186/I_{\text{aq}}$ for 0.1 M ionic strength and $q = I_{\text{org}} \cdot 1.154/I_{\text{aq}}$ for 1 M.

^b corrected for the increase of *q* due to the formation of dimers in the chloroform phase.

hexone with both 0.1 and 1 M ionic strength (HClO₄-NaClO₄) in the aqueous phase are given in Tables 4 and 5 and in Figs. 6 and 7.

Even though the initial conc. of DBP in the chloroform layer was only 1.33×10^{-5} M we had to correct for the increase in *q* due to the formation

Table 5. Distribution of DB³²P between hexone and HClO₄-NaClO₄ solutions. Initial conc. of DBP in the hexone layer 1.33×10^{-5} M.

Ionic strength M	<i>I</i> _{org} cpm	<i>I</i> _{aq} cpm	log <i>q</i> ^a	-log [H ⁺]
0.1	11 740	953	+1.052	1.00
	11 308	1 317	+0.895	1.30
	10 748	1 731	+0.754	1.48
	10 244	2 449	+0.583	1.70
	8 567	3 774	+0.318	2.00
	6 657	5 535	+0.042	2.30
	3 771	8 230	-0.377	2.70
	1	11 298	368	+1.436
10 281		327	+1.446	0.30
10 618		388	+1.387	0.48
10 541		430	+1.339	0.70
10 344		6 622	+1.170	1.00
10 119		899	+1.001	1.30
8 450		1 651	+0.658	1.70

^a $q = I_{\text{org}} \cdot 0.915/I_{\text{aq}}$ for 0.1 M ionic strength and $q = I_{\text{org}} \cdot 0.890/I_{\text{aq}}$ for 1 M.

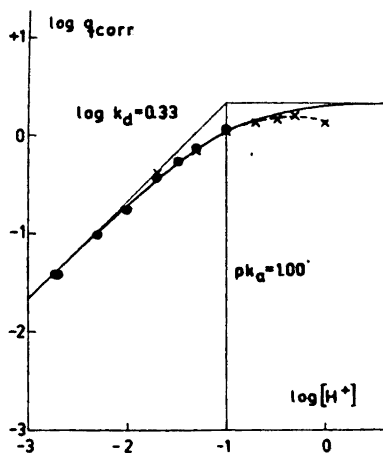


Fig. 6. Distribution of DB³²P between chloroform and HClO₄-NaClO₄ solutions. × = 1 M ionic strength. ● = 0.1 M ionic strength.

of dimers in the organic phase; for hexone no correction was needed. In these experiments the net distribution of DBP is given by

$$q = \frac{[\text{HA}]_{\text{org}}}{[\text{HA}] + [\text{A}^-]} \quad (9)$$

From the definitions of k_a and k_d it follows that

$$q = k_d / (1 + k_a [\text{H}^+]^{-1}) \quad (10)$$

The same normalized curve, $\log y = \log (x+1)$, is thus valid for these experimental data if $\log q$ is plotted against $\log [\text{H}^+]$. The horizontal asymptote ($\log y = 0$) gives $\log k_d$ and the point of intersection of this asymptote with the asymptote $\log y = \log x$ gives $\text{pk}_a = -\log [\text{H}^+]$. From Figs. 6 and 7 we obtained the following values by fitting the normalized curve (cf. Refs. 17, 18) to the data

$$\text{pk}_a = 1.00 \pm 0.01 \text{ for } 0.1 \text{ and } 1 \text{ M ClO}_4^-$$

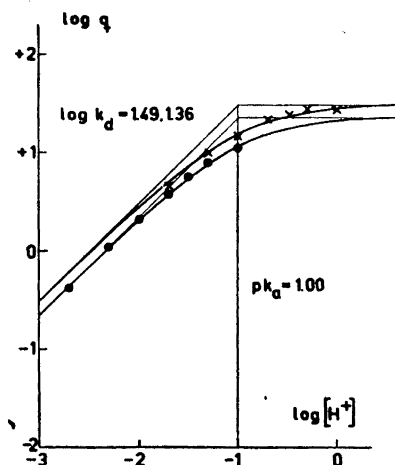


Fig. 7. Distribution of DB³²P between hexone and HClO₄-NaClO₄ solutions. × = 1 M ionic strength. ● = 0.1 M ionic strength.

Other acids, *e.g.* HCl and HClO₄ (*cf.* Ref. 16 p. 75), also have approximately the same mean activity coefficients in 0.1 M and 1 M solutions at 25°C.

$$\begin{aligned}\log k_d &= 0.33 \pm 0.02 \text{ for chloroform/0.1 and 1 M ClO}_4^- \\ \log k_d &= 1.36 \pm 0.02 \text{ for hexone/0.1 M ClO}_4^- \\ \log k_d &= 1.49 \pm 0.02 \text{ for hexone/1 M ClO}_4^-\end{aligned}$$

The values of $\log k_d$ for 0.1 M ClO₄⁻ agree with those found in the previous part.

For chloroform the more acid 1 M HClO₄-NaClO₄ solutions show a salt-in effect. Using activity coefficients given by Kielland¹⁶ the thermodynamic dissociation constant may be calculated

$$pk_a = 1.00 + 0.17 = 1.17$$

This value is definitely lower than the value of 1.72 reported by Kumler and Eiler⁹. However, their results on other dialkyl phosphates are about 0.4–0.6 units higher than dissociation constants given by van Hove⁷ and by Drushel and Felty⁸.

THE DISTRIBUTION OF DBP AS A FUNCTION OF THE CONCENTRATION OF TBP IN THE CHLOROFORM PHASE

If DBP reacts with TBP (tri-*n*-butyl phosphate) in the chloroform phase the net distribution ratio will increase according to

$$q = \frac{k_d}{\varphi} (1 + k_B [B]_{\text{org}}) \quad (11)$$

Table 6. Distribution of DBP between chloroform and 1 M HClO₄ for different concentrations of TBP in the chloroform phase. Initial conc. of DBP in the chloroform layer 3.33×10^{-5} M. $V_{\text{org}} = V_{\text{aq}} = 15$ ml.

ml TBP · H ₂ O per 15-v ml CHCl ₃	[TBP] _{org} M	I _{org} cpm	I _{aq} cpm	A	log q ^a
15	3.44	5 667	73.4	0.966	1.873
14.5	3.32	8 682	98.6	0.972	1.932
9	2.06	7 396	144	1.041	1.728
5	1.145	8 929	277	1.091	1.546
5	1.145	4 897	126	1.091	1.627
4	0.918	4 935	123	1.104	1.647
3	0.687	6 832	185	1.116	1.614
3	0.687	4 819	145	1.116	1.569
2.5	0.572	7 691	253	1.123	1.534
1	0.229	8 248	582	1.141	1.208
0.45	0.1031	6 778	739	1.148	1.022
0.2	0.0458	7 272	1 419	1.151	0.771
0.1	0.0229	5 805	1 352	1.153	0.695
0.05	0.01145	5 388	1 520	1.153	0.612
0.02	0.00458	4 957	1 569	1.154	0.562
0.01	0.00229	4 946	1 629	1.154	0.545
0	0	4 873	1 721	1.154	0.514
0	0	4 032	1 420	1.154	0.515

$$^a q = I_{\text{org}} \cdot A / I_{\text{aq}}$$

where φ is given by eqn. (8) and k_B is defined by

$$k_B = [\text{HA} \cdot \text{B}]_{\text{org}} / [\text{HA}]_{\text{org}} [\text{B}]_{\text{org}} \quad (12)$$

In a plot $\log q$ against $\log [\text{TBP}]_{\text{org}}$ ($= \log [\text{B}]_{\text{org}}$) the data would then follow the normalized curve $\log y = \log (x+1)$. With a high value of φ or a very high specific activity of the radioactive DBP we could have made the conc. of DBP dimers negligible. But with 1 M HClO_4 ($\varphi = 1.10$) and an initial conc. of DBP equal to 3.33×10^{-5} M, TBP has to compete with the dimerization of DBP. The expression for q will therefore contain an additional term.

$$q = \frac{k_d}{\varphi} (1 + 2k_2 \frac{k_d}{\varphi} \cdot \frac{C_A}{1+q} + k_B [\text{B}]_{\text{org}}) \quad (13)$$

With this expression we calculated for $(\text{TBP})_{\text{org}} < 0.4$ M

$$k_B = 40$$

As expected the tendency for DBP to dimerize ($k_2 = 3 \times 10^4$) is much stronger than the tendency to associate with TBP. However, the effective concentration of TBP in chloroform may be lower than $[\text{B}]_{\text{org}}$ as TBP is known to associate both with H_2O and CHCl_3 according to McKay *et al.*¹⁹ and Kosolapoff and McCullough²⁰ (*cf.* also Ref.²¹).

CONCLUSIONS AND DISCUSSION

From the experiments carried out the following data may be summarized: Dissociation of DBP in 0.1 M and 1 M HClO_4 - NaClO_4

$$pK_a = 1.00 \pm 0.01 \quad (pK_a = 1.17)$$

Dimerization (association) of DBP in

$$\text{chloroform (wet): } \log k_2 = 4.48 \pm 0.04$$

$$\text{hexone (wet): } \log k_2 = 1.19 \pm 0.03$$

$$\text{water (sat.soln.): } \log k_2 = 1.11 \pm 0.07$$

Distribution of DBP between

$$\text{chloroform and 0.1 M HClO}_4\text{-NaClO}_4: \log k_d = 0.34 \pm 0.01$$

$$\text{hexone and 0.1 M HClO}_4\text{-NaClO}_4: \log k_d = 1.36 \pm 0.01$$

$$\text{hexone and 1 M HClO}_4\text{-NaClO}_4: \log k_d = 1.49 \pm 0.02$$

$$\text{TBP and 1 M HClO}_4: \log k_d = 1.87$$

Association (complex formation) of DBP and TBP in chloroform

$$\log k_B = 1.60$$

According to Drushel and Felty⁸ and the result obtained by us the lower dialkyl phosphates are definitely stronger acids (10–20 times) than phosphoric acid ($pK_a = 2.12$). It might be suggested that H_3PO_4 is stabilized by three

Table 7. Summary of some dimerization constants in chloroform calculated from distribution measurements at 25°C.

Acid	pK_a	$\log k_d$	$\log k_2$	Ref.
Acetic	4.76	-1.36	1.05	22, 23
Propionic	4.87	-0.80; -0.75	1.50; 1.44	22, 24
<i>n</i> -Butyric	4.82	-0.27	1.68	22
<i>n</i> -Valeric	4.80	+0.32	1.73	22
Cinnamic	4.44	+1.20	2.22	26
Phenyl acetic	4.31	+0.46	1.75	22
Lactic	3.86	-1.81	2.33	22
Chloroacetic	2.87	-1.84	2.38; 3.10	22, 23
Benzoic	4.20	+0.53; +0.58	1.96; 1.87	22, 25
<i>m</i> -Nitrobenzoic	3.49	+0.39	1.99	22
3,5-Dinitrobenzoic	2.80	+0.18	no ass.	26
Salicylic	2.98	+0.48; +0.64	1.62; 1.22	26, 25
<i>o</i> -Chlorobenzoic	2.92	+0.89	1.04	22
<i>o</i> -Methoxybenzoic	4.09	+1.60	no ass.	22, 27
DBP	1.17	+0.34	4.48	this work

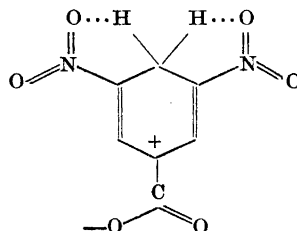
internal hydrogen bonds while the hydrogen bonding in the dialkyl phosphates is disturbed by the free rotation of the two ester groups. The degree of hydration is probably also different for the two acid-base pairs, $H_3PO_4-H_2PO_4^-$ and $(RO)_2PO(OH) - (RO)_2PO_2^-$.

The tendency for a dialkylphosphoric acid or a carboxylic acid to associate to double molecules depends on the tendency of the $P\begin{smallmatrix} \diagup O \\ \diagdown OH \end{smallmatrix}$ and $C\begin{smallmatrix} \diagup O \\ \diagdown OH \end{smallmatrix}$ groups to form hydrogen bonds. The dimerization is, however, very dependent on the solvent. Hitherto only the carboxylic acids have been investigated²³⁻³³. Usually very large dimerization constants are obtained in hexane, benzene and carbon tetrachloride. Smaller values (about 10 times) are obtained with chloroform, which is a weak donor for hydrogen bonds. The dimerization of carboxylic acids is very slight^{25, 26} in oxygen-containing solvents like ethers and ketones, which are good acceptors for hydrogen bonds. Finally the dimerization is almost negligible³¹⁻³³ in hydroxyl-containing solvents such as water. From Table 7 it may be seen that the dimerization constant for DBP is much larger than for any of the carboxylic acids. It is therefore not astonishing that a considerable dimerization also takes place in hexane and water. There seems to be a general trend for k_2 to increase with K_a and k_d . However, many of the k_2 -values in Table 7 are not very accurate. One of the reasons for this is that the aqueous phase has been unbuffered. Furthermore, the correction for ionization becomes too large when $K_a > 10^{-3}$. This emphasizes the necessity of measuring the distribution with constant ionic and acidity strength in the aqueous phase and carrying out the analysis of the acids, *e.g.* spectrophotometrically²⁶ or radiometrically as in this work. Table 7 shows furthermore the lowering effect on k_2 of OH, Cl and OCH₃ groups in the *ortho*-

Table 8. Distribution constants of some monomers and dimers.

Organic phase/acid	log k_d		log k_D	
	found	calc.	found	calc.
Chloroform/acetic	-1.36	-1.36	-0.39	-0.16
Chloroform/propionic	-0.76	-0.76	+1.22	+1.04
Chloroform/ <i>n</i> -butyric	-0.27	-0.16	+2.18	+2.24
Chloroform/ <i>n</i> -valeric	+0.32	+0.44	—	+3.44
Chloroform/DBP	+0.34	—	+4.05	—
Hexone/DBP	+1.36	—	+2.80	—

position of benzoic acid: Cl and OCH₃ act as acceptors for the carboxylic hydrogen while the OH group in salicylic acid can act both as a donor and acceptor. Careful work²⁶ on 3,5-dinitrobenzoic acid has revealed no evidence of association. This result has surprised us, especially when compared with *m*-nitrobenzoic acid. The result suggests that the carboxylic hydrogen is bound intramolecularly, *e.g.* as follows



The dimerization in water, which could be estimated from our measurements of the acidity of DBP in water, has been calculated for some fatty acids³¹⁻³³. Thus, if the dimerization constants in both the organic and aqueous phases and the distribution constant of the monomer are known, it is possible to calculate the distribution constant of the dimer

$$k_D = [\text{H}_2\text{A}_2]_{\text{org}}/[\text{H}_2\text{A}_2] = k_2 k_d^2 / k_2' \quad (14)$$

Some values of k_D are given in Table 8. Some estimations of k_d and k_D for the fatty acids can be made. Collander³⁴ found in his investigations of the distribution of organic compounds between ether and water that k_d increases 2 to 4 times when a CH₂ group is added in a homologous series; this factor is here denoted with m . Furthermore it is reasonable to assume that the dimerization makes the carboxylic groups less hydrophilic, *i.e.* increases k_d by a factor n regardless of the length of the hydrocarbon chain. If the distribution constant k_d for acetic acid is a , the values of log k_d and log K_D for the fatty acids will increase as log a , log am , log am^2 and log anm , log $anmm^2$, log $anmm^4$. The values calculated in Table 8 have been obtained with $m = n = 4$ and $a = 0.044$. The deviation from the rather uncertain experimental values is not too serious. The assumptions made here lead also to the following relation

$$k_2/k_2' = k_D/k_d^2 = mn/a = 16/0.044$$

In fact k_2 and k_2' do not vary much for the fatty acids (for k_2' see Ref.³²) and the ratio k_2/k_2' is thus rather constant. If the values in Table 8 for DBP with chloroform and hexone are compared, it may be seen that the increase of the distribution constant on dimerization is much larger for chloroform (5 100 times) than for hexone (27 times). This is also in agreement with Collander³⁵, who found that the distribution constants differed much less for *isobutanol* than for ether.

The association between chloroform and DBP is presumably rather weak (*cf.* Ref.²⁸). The lowering of k_2 in hexone may then be ascribed to complex formation between hexone and DBP according to eqn. (12). This can also explain the larger value of k_d for hexone. For comparison with k_B for TBP we may then calculate k_B for hexone as

$$k_B = \frac{10^{\frac{1}{2}(4.48-1.19)}}{[B]_{\text{org}}} = 5.5$$

The complex formation is thus somewhat lower for hexone than for TBP ($k_B = 40$). The tendency for DBP to dimerize is however much stronger. It would be interesting to know if the eight-membered dimer ring is planar or not (*cf.* Ref.³⁶).

The dimerization constant of DBP in chloroform is very large (3×10^4) and should be still larger in non-polar solvents such as carbon tetrachloride. This means that DBP will exist as dimers even at very low concentrations. Thus no shifts can probably be detected in the infra-red spectra within a measurable concentration range (*cf.* Ref.¹¹). The dimerization constant in carbon tetrachloride may however be determined with radioactive DBP if a larger value of φ in eqn. (7) (higher pH) or a higher specific activity of DBP than in the experiments reported here is used.

The dimerization constant for water, k_2' , has been determined with the distribution method for acetic acid³³. This method could probably be also used for the lower dialkyl phosphates (*e.g.* dimethyl phosphate). For DBP k_d and k_2 are too large, and the concentration of DBP in water will be too low.

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