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The Distribution and Dimerization of Di-*n*-butyl Phosphate (DBP) in Different Solvents

DAVID DYRSSEN and LIEM DJIET HAY

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

The distribution of DBP between a number of organic solvents and 0.1 M HNO_3 has been measured at 25°C using ^{32}P-labelled DBP. From the variation of the net distribution ratio, q, with the total concentration of DBP the distribution and the dimerization constants have been determined for the following solvents (log K_d and log K_2 given for each solvent): *n*-hexane (-2.34; $+6.87$), carbon tetrachloride (-1.44; $+6.49$), chloroform ($+0.24$; $+4.61$), *iso*propyl ether ($+0.52$; $+2.29$), tri-*n*-butyl phosphate ($+1.97$; -0.12), methyl*iso*butyl carbinol ($+2.21$, < -1).

An increase in K_d is combined with a decrease in K_2. The explanation given is based on the assumption that complex formation between DBP and the organic solvent molecules competes with the dimerization in the solvent and the solvation of DBP in the aqueous phase. The complex formation constant between DBP ($=$ HA) and TBP ($=$ B), $K_B = [HAB]_{org} [HA]_{org}^{-1} [B]_{org}^{-1}$, has been determined in carbon tetrachloride as log $K_B = 2.84$.

The results are discussed in relation to some recent work on DBP by Dyrssen [1] and by Hardy and Scargill [2].

It has been shown in previous work by Dyrssen [1] and by Hardy and Scargill [2] that the choice of solvent has great influence on the distribution of DBP ($=$ HA) between an organic solvent and acid aqueous solutions. This is partly due to the fact that the solvent may greatly influence the very pronounced tendency for dialkyl phosphates to dimerize. The purpose of this work was to study the distribution and dimerization of DBP in solvents of different types. The equilibrium constants determined in this work will be used in a study [3] of the extraction of Eu^{3+} and Am^{3+} with DBP in the same set of solvents. A more complete understanding of the reactions between the metal ions and DBP in the organic phase may thus be possible when the concentrations of H_2A_2 (org), HA (org and aq) and A^-(aq) can be calculated. This approach was shown to be fruitful in a study [4] of the extraction of UO_2^{2+} with DBP using chloroform and hexone as solvents.

The same symbols as previously [1] are used in this work except that in accordance with IUPAC K is used instead of k for equilibrium constants.

EXPERIMENTAL

The general procedure has been described earlier [1]. DBP has, however, been purified according to the following new technique (*cf.* Baes [5] *et al.* note 7): 10 ml of DBP was dissolved in 30 ml of petroleum ether (analytical grade). This layer was washed three times with water, and DBP was thereafter extracted with the equivalent amount of 1 M NaOH at 5°C, the cooling being done with ice. The aqueous layer containing the sodium salt of DBP was washed three times with petroleum ether, acidified with HCl and shaken with 30 ml of petroleum ether. The ether phase was washed three times with water and the ether distilled off. The final product, which was pale yellow, was dried at 130°C under reduced pressure (10 mm Hg, N_2 atmosphere) for half an hour. Potentiometric titrations evaluated by the Gran II method [6] for the detection of end-points indicated that the product was free from MBP and at least 99 % pure.

The chloroform (Merck-Darmstadt analytical grade) was washed three times with twice its volume of water to remove the 1 % alcohol. The carbon tetrachloride was of analytical grade (Merck-Darmstadt) and was not further purified. The hexone (methyl *iso*butyl ketone) was washed with $NaHCO_3$ solution, dilute perchloric acid and finally with water. The initial hexone (Kebo) had a boiling range of 114—117°C. The isopropyl ether, boiling range 65—70°C, and *n*-hexane (68—69°C) have a purity of at least 99 % (Kebo). These solvents were not further purified. The hexol (methyl *iso*butyl carbinol), of 99 % purity (Kebo) and boiling range 130—133°C, was treated as hexone. The tri-*n*-

Table 1. Distribution of DBP at 25°C between various solvents and 0.1 M HNO_3 for different initial concentrations of DBP in the organic layer (C_A). $V_{org} = V_{aq} = 15$ ml.

n-Hexane, log C_A (log q): −0.295(+1.119), −0.690(+0.690), −0.976(+0.492), −1.214 (+0.222), −1.690(−0.071), −1.976(−0.260), −2.301(−0.495), −2.580 (−0.796), −2.881(−1.046), −3.580(−1.637), −3.881(−1.947), −4.295(−2.108), −4.580(−2.154), −4.880(−2.546), −4.941(−2.520), −5.098(−2.520), −5.243 (−2.686), −5.465(−2.644), −5.641(−2.710), −5.941(−2.375), −5.941(−2.512).

Carbon tetrachloride, log C_A(log q): −0.304(+1.547), −0.691(+1.335), −0.991(+1.112), −2.311(+0.384), −2.696(+0.294), −2.996(−0.004), −3.696(−0.509), −3.996(−0.745), −4.270(−1.000), −4.627(−1.191), −4.750(−1.514), −4.771(−1.322), −5.149(−1.462), −5.273(−1.536), −5.403(−1.494), −5.432(−1.438), −5.593(−1.698), −5.750(−1.772).

Chloroform, log C_A(log q): −2.016(+1.368), −2.345(+1.204), −2.673(+1.060), −2.980 (+0.895), −3.294(+0.689), −3.692(+0.580), −3.972(+0.433), −4.914 (+0.076), −4.993(+0.080), −5.216(−0.018), −5.295(+0.008), −5.692(−0.036).

Isopropylether, log C_A(log q): −0.358(+1.354), −0.719(+1.168), −1.021(+1.015), −1.321(+0.858), −1.708(+0.549), −2.021(+0.669), −2.359(+0.433), −2.715(+0.318), −3.015(+0.305), −3.345(+0.259), −3.956(+0.256), −4.307(+0.238), −4.686(+0.253), −4.914(+0.212), −4.956(+0.238), −4.993(+0.215), −5.091(+0.210), −5.216(+0.212), −5.391(+0.162), −5.692(+0.188).

Mean value of log $K_d\varphi = 0.218 \pm 0.031$

Tri-n-butyl phosphate, log C_A(log q): −0.383(+1.830), −0.718(+1.754), −0.989(+1.731), −1.718(+1.664), −2.020(+1.680), −4.181(+1.676), −4.305(+1.678), −4.481(+1.638).

Mean value of log $K_d\varphi = 1.672 \pm 0.020$

Isobutyl methyl carbinol, log C_A(log q): −0.340(+1.845), −0.692(+1.917), 0.992(+1.896), −1.340(+1.915), −2.334(+2.005), −2.996(+1.937), −3.243(+1.903), −3.290(+1.906), −3.411(+1.916), −3.720(+1.891), −4.022(+1.958), −5.243(+1.842).

Mean value of log $K_d\varphi = 1.911 \pm 0.050$

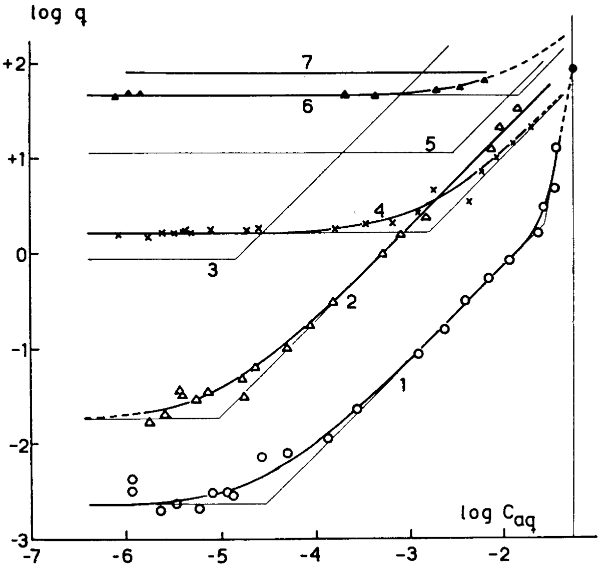

Fig. 1. Distribution of DBP between various solvents and 0.1 M HNO_3 as a function of the total concn. of DBP in the aqueous phase. The maximum value of C_{aq} is determined by the solubility of undiluted DBP in water. Solvents: 1 hexane, 2 carbontetrachloride, 3 chloroform (*cf.* Fig. 2), 4 *iso*propyl ether, 5 hexone (*cf.* Ref.[1]), 6 tributyl phosphate, 7 hexol (*cf.* Table 1). Normalized curve log Y = log (X + 1) is fitted to the data.

butylphosphate (Kebo) was purified by washing it first with an equal volume of 1 M NaOH solution, then with 0.1 M HNO_3 and finally with water.

The radioactive DBP was purchased as previously [1] from Radiochemical Centre, Amersham, England. The aqueous phase was always 0.1 M HNO_3 and the volumes of the two phases were equal.

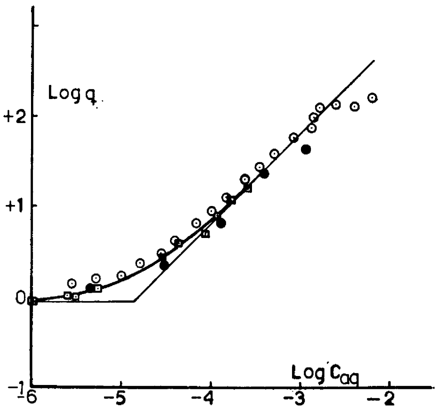

Fig. 2. Distribution of DBP between chloroform and 0.1 M HNO_3 as a function of the total concentration of DBP in the aqueous phase (open squares). Open circles: data from Ref.[1] (aq. phase 0.1 M $HClO_4$). Filled circles: data from Ref.[2] (aq. phase 0.1 M $HClO_4$).

RESULTS

The data are given in Table 1 as log C_A (initial conc. of DBP in the organic layer) and log q (net distribution ratio of DBP). The data, except those for methyl *iso*butyl carbinol where q is independent of C_A, are plotted in Figs. 1 and 2 as log q against log C_{aq} (equilibrium conc. of DBP in the aqueous phase). C_{aq} was calculated from the following relationship:

$$C_{aq} = C_A(1 + q)^{-1}$$

Assuming that $C_{org} = qC_{aq} = [HA]_{org} + 2[H_2A_2]_{org}$ and

$$C_{aq} = [HA] + [A^-] = [HA] + K_a[HA][H^+]^{-1}$$

the distribution constants, $K_d = [HA]_{org}[HA]^{-1}$, and dimerization constants, $K_2 = [H_2A_2]_{org}[HA]_{org}^{-2}$, were calculated as before [1] by fitting the normalized curve $\log Y = \log (X + 1)$ to the data $x = \log C_{aq}$, $y = \log q$.

The horizontal asymptote ($\log Y = 0$) gives

$$\log K_d\varphi^{-1} = \log Y_0$$

where $\varphi = 1 + K_a[H^+]^{-1} = 2.00$ is kept constant in these experiments and the point of intersection ($\log X_0$, $\log Y_0$) between the two asymptotes gives

$$\log 2\, K_2K_d\varphi^{-1} = -\log X_0;\ \log K_2 = -\log 2\, X_0Y_0$$

The values of K_d and K_2 determined in this manner are collected in Table 2 together with the constants for methyl *iso*butyl ketone (hexone) from earlier work [1] and some constants determined by Hardy and Scargill [2].

The complex formation between DBP and TBP (tri-*n*-butyl phosphate) was determined in a study of the distribution of DBP as a function of the TBP concentration in carbon tetrachloride ($= [B]_{org}$). The aqueous phase was

Table 2. Summary of distribution and dimerization constants for DBP in various two-phase systems.

System	log K_d	log K_2	Reference
Methyl-*iso*butyl carbinol/0.1 M HNO_3	+2.21 ± 0.05	< -1	this work
Tri-*n*-butyl phosphate/0.1 M HNO_3	+1.97 ± 0.02	(−0.12)[1]	this work
Methyl-*iso*butyl ketone/0.1 M $HClO_4$	+1.36	+1.19	1
*Iso*propyl ether/0.1 M HNO_3	+0.52 ± 0.03	+2.29	this work
Chloroform/0.1 M HNO_3	+0.24	+4.61	this work
Carbon tetrachloride/0.1 M HNO_3	−1.44	+6.49	this work
n-Hexane/0.1 M HNO_3	−2.34	+6.87	this work
Nitrobenzene/1 M HNO_3	−0.14	+3.55	2
Benzene/1 N HNO_3	−0.42	+4.88	2
Carbon tetrachloride/1 M HNO_3	−0.91	+5.33	2
Kerosene/1 M HNO_3	−1.96	+5.78	2
n-Butyl ether/0.1 M $HClO_4$	−0.14	+2.84	9

[1] Uncertain, H_2A_2B complex may be formed [7].

Table 3. Distribution of DBP between carbon tetrachloride and 0.1 M HNO_3 for different concentrations of TBP in the organic layer. $[DBP]_{org} < 10^{-4}$ M $\ll [TBP]_{org}$.

$[TBP]_{org}$ M	log q	log q $[TBP]_{org}^{-1}$
3.43 (no CCl_4)	+1.672	1.137
2.86	+1.658	1.201
2.06	+1.432	1.118
1.145	+1.139	1.079
0.916	+1.064	1.103
0.686	+0.929	1.094
0.571	+0.904	1.147
0.229	+0.361	1.001
0.103	+0.048	1.034
0.0458	−0.345	0.994
0.0229	−0.513	1.127
0.01145	−0.770	1.170

Mean value of log $K_d K_B \varphi^1 = 1.100 \pm 0.064$

0.1 M HNO_3.* With $[DBP]_{org} < 10^{-4}$ M and $[TBP]_{org} \gg [DBP]_{org}$ it is possible to neglect $[HA]_{org}$ and $[H_2A_2]_{org}$ (cf. Dyrssen [1], eqns (11) and (13)). The principal reaction studied is then

$$HA\ (aq) + B\ (org) = HAB\ (org)$$

$$q = \frac{[HAB]_{org}}{[HA] + [A^-]} = [HAB]_{org}\, [HA]^{-1}\, \varphi^{-1}$$

or if $K_B K_d = [HAB][B]_{org}^{-1}[HA]$ and $\varphi = 2.00$ is introduced

$$q = 0.50\ K_B K_d [B]_{org}$$

It may be seen from Table 3 that log $q[B]_{org}^{-1}$ is constant not only in dilute solutions of TBP in carbon tetrachloride, but also in highly concentrated solutions and undiluted TBP (3.43 M). This demonstrates the validity of the assumptions which lead to the expression for q above. Further evidence of a molecular interaction of this type is supplied by Baker and Baes [7], who studied the system dioctyl phosphate — trioctyl phosphine oxide, $(RO)_2PO(OH)$ — R_3PO, in octane by means of infrared spectroscopy and isopiestic measurements. The value of $K_B K_d$ calculated from the data in Table 3 is

$$\log K_B K_d = 1.40 \pm 0.06; \log K_B = 2.84 \pm 0.08$$

The value is very close to the value of log $K_B = 2.83$ for TBP in kerosene obtained by Hardy and Scargill [2] but considerably higher than the value for TBP in chloroform [1] (log $K_B = 1.60$). This is probably due to association of DBP and TBP [1] with $CHCl_3$.

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* It has been pointed out by Hardy and Scargill [2] that the nitric acid concentration in the aqueous phase must be kept low or else one has to consider the complex formation between TBP or DBP and HNO_3 also.

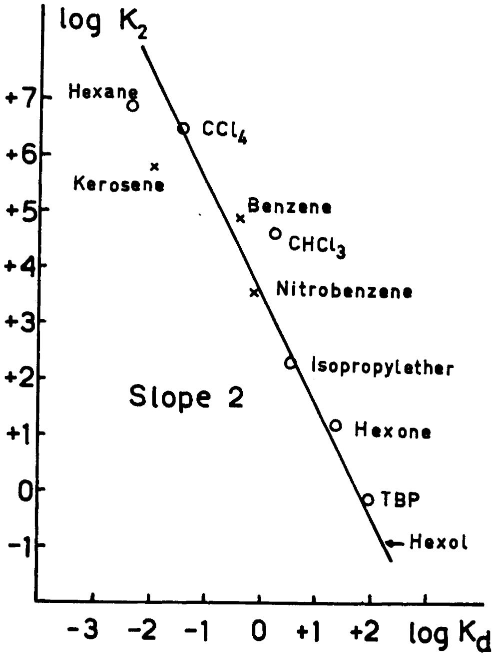


Fig. 3. The dimerization constant, K_2, of DBP in various solvents as function of the distribution constant, K_d. The data are taken from Table 2.

DISCUSSION

It is obvious from Table 2 that an increase in the distribution constant, K_d, is combined with a decrease in the dimerization constant, K_2. If log K_2 is plotted against log K_d as in Fig. 3 the data seem to fall fairly well on a line with a slope of —2. To explain this let us assume a complex formation between the DBP monomer, HA, and the solvent molecule B.

$$\text{HA (org)} + \text{B (org)} = \text{HAB (org)} \qquad \text{(eq. const. } K_B\text{)}$$

The expression for K_d and K_2 may then be written

$$K_d = \frac{[\text{HA}]_{org} + [\text{HAB}]_{org}}{[\text{HA}]} = \frac{[\text{HA}]_{org}}{[\text{HA}]} (1 + K_B[\text{B}]_{org})$$

or $K_d = \overset{\circ}{K}_d(1 + K_B[\text{B}]_{org})$

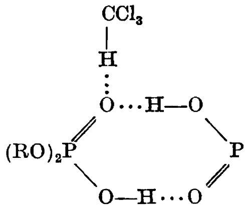
$$K_2 = \frac{[\text{H}_2\text{A}_2]_{org}}{([\text{HA}]_{org} + [\text{HAB}]_{org})^2} = \overset{\circ}{K}_2 (1 + K_B[\text{B}]_{org})^{-2}$$

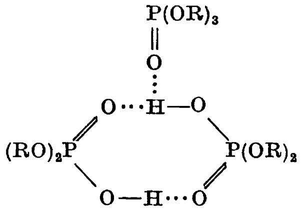
Combining these equations one obtains

$$K_2 = \overset{\circ}{K}_2 K_d^{-2} (\overset{\circ}{K}_d)^2$$

which satisfies the straight line in Fig. 3 (log $\overset{\circ}{K}_2(\overset{\circ}{K}_d)^2 = 3.7$).

The rather good fit of available data to this line means that, apart from the specific interaction due to complex formation between DBP and the solvent, the influence of the solvent on the distribution constant of the dimer ($K_D = [H_2A_2]_{org}[H_2A_2]^{-1}$)is rather independent of organic phase. The solvents have about the same molarity and the picture should therefore not change considerably in going over to mole fraction constants. However, two types of solvents do not fit to the straight line in Fig 3, namely the hydrocarbons, *n*-hexane and kerosene, and chloroform. In the first case it may be explained by assuming that the interaction between the solvent molecule and H_2A_2 is very weak giving a low value of $K_2K_d^2$. In the case of chloroform the reason might be that the interaction between $CHCl_3$ and the dimer is rather much stronger than for the other solvents due to hydrogen bonding with the phosphoryl groups.


$CHCl_3(DBP)_2$ complex


TBP$(DBP)_2$ complex

That a 1 : 1 complex is formed between solvents, which may act as acceptors for hydrogen bonds, and DBP, which is a donor of hydrogen, was proved in the case of TBP in CCl_4. Further support of a molecular interaction between DBP and solvents with phosphoryl groups has been supplied by Baker and Baes [7], who studied the system dioctyl phosphate — trioctyl phophine oxide, $(RO)_2PO(OH)$ — R_3PO, in octane by means of infrared spectroscopy and isopiestic measurements. — They also found some evidence of H_2A_2B complex at higher concentrations of HA. — Assuming that no complex formation occurs between CCl_4 and DBP ($K_B = 0$) we calculate approximately

$$\log \overset{\circ}{K}_d = -1.4 \text{ and } \log \overset{\circ}{K}_2 = 6.5$$

The acceptor tendency of the solvents for hydrogen bonds may thus be expressed by the value of K_B calculated from

$$\log K_d = -1.4 + \log (1 + K_B[B]_{org})$$

These values are collected in Table 4 together with values of the molarity of the solvent, $[B]_{org}$, and data for the solubility of water in the solvents. It may be seen from Table 4 that there is a close correlation between K_B and the solubility of water in g/l per mole of solvent. In Fig. 4 one may see that the solubility of water in the solvent is also related to K_d. It may thus be said that the acceptor tendency of the solvents for hydrogen bonds governs the solubility of water in the solvents as well. This fact can be used in choosing a suitable solvent for the extraction of metal ions with dialkyl phosphates. It will be shown in the following paper that the choice of the solvent has great

Table 4. Summary of values of $[B]_{org}$, K_B and the solubility of water (L_{H_2O}) for various solvents.

	$[B]_{org}$ [a] M	K_B	L_{H_2O} g/l	L_{H_2O} $[B]^{-1}_{org}$
Hexol $(CH_3)_2CHCH_2CH(OH)CH_3$	7.39	550	58	7.85
TBP $(n\text{-}C_4H_9O)_3PO$	3.43	680 (690)	50.8 [b] (61.8)	14.8
Hexone $(CH_3)_2CHCH_2COCH_3$	7.82	73	19	2.43
*Iso*propyl ether $(CH_3)_2CHOCH(CH_3)_2$	7.03	11.6	5.7	0.81
Nitrobenzene $C_6H_5NO_2$	9.74	1.8	2.4	0.25
Chloroform $CHCl_3$	12.53	3.4	1.46	0.12
Benzene C_6H_6	11.25	0.76	0.6	0.053
Carbon tetrachloride CCl_4	10.37	~0	0.154	0.015
Hexane $n\text{-}C_6H_{12}$	7.66	~0	0.0732	0.0096

[a] Calculated for the solvent saturated with water at 20°C.

[b] Approx. corrected for the amount of water dissolved due to the three ester groups.

influence on the extraction of Eu^{3+} and Am^{3+} with DBP. This can be explained by complex formation reactions between DBP and the solvent molecules as discussed here.

The results with hexane show a marked increase in log q (Fig. 1) for values of log C_{aq} higher than —1.80 (which corresponds to $C_{org} > 0.05$ M). This very

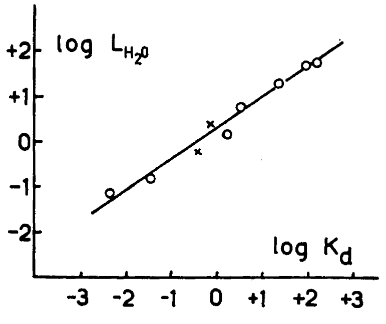
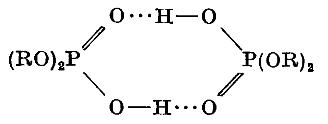
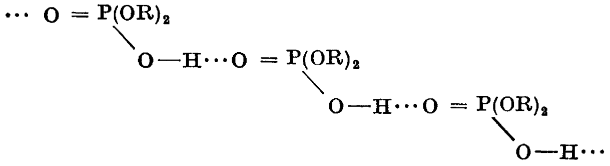


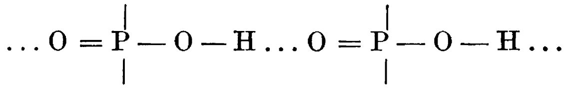
Fig. 4. Correlation between the solubility of water in the organic solvent and the distribution constant, K_d, of DBP between each solvent and 0.1 M HNO_3. The data are summarized in Table 4.

sharp increase of the slope indicates a conversion of the dimer in the form of a eight-membered ring to a polymer possibly in the form of an extended chain:





This proposal for the change in structure is supported by the fact the dibenzyl phosphate crystallizes with a structure [8] which is composed of spirals with the chain



$$\ldots O = \overset{|}{\underset{|}{P}} - O - H \ldots O = \overset{|}{\underset{|}{P}} - O - H \ldots$$

The distance between the two oxygen atoms in the link is very short, 2.494 Å, corresponding to a very strong hydrogen bond.

The transition of DBP in hexane from a dimer to a polymer may also explain the PMR-data and viscosity measurements of solutions of DBP in *n*-hexane. The same type of concentration shift in the proton magnetic resonance and viscosity was also found with carbon tetrachloride as a diluent. This emphasizes the need for great caution in drawing any conclusions about the DBP-species from distribution data where the concentration of DBP in the organic solvent is above 0.05 M. The PMR measurements and viscosity measurements will be extended to the other solvents in the near future and will be published separately.

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