

## Studies of the Distribution of Mixed Complexes between Dibutylphosphate (HDBP) and Tributylphosphate (TBP), Trioctylphosphine Oxide (TOPO) in Hexane and Carbon Tetrachloride

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The distribution of dibutylphosphate (= HDBP = HA) between 0.10 M  $H_2SO_4$  and hexane or carbon tetrachloride in the presence of tributylphosphate or trioctylphosphine oxide (= B) has been studied using  $^{32}P$ -labelled HDBP. Treatment of the distribution data with the LETAGROP VRID computer program<sup>19</sup> indicates the formation of the following species in the organic phase:

1) HA and  $H_2A_2$ , in hexane also  $(HA)_n$  ( $n \geq 4$ ) 2) with B = TBP, HAB, and  $H_2A_2B$ , in hexane also,  $HAB_2$  3) with B = TOPO, HAB, in hexane also  $H_2A_2B$ .

At  $A_{aq} > 1$  mM the data indicate the formation of HDBP dimers in the aqueous phase. A summary of the equilibrium constants for the formation of the various  $(HA)_pB_q$  species is given in Table 5.

Previous distribution studies by Dyrssen and Liem,<sup>9,12</sup> Hardy and Scargill<sup>17</sup> have shown that dibutylphosphate (HA = HDBP) forms complexes with tributylphosphate (B = TBP), which is found to influence their behaviour when used as metal extractants. In some cases, *e.g.* in the extraction of  $UO_2^{2+}$  with dialkyl phosphate, the addition of neutral organophosphorus compounds gives rise to a synergistic effect on the metal extraction,<sup>2,3,5,11,20,21,27,28,31,32</sup> *i.e.* the resulting distribution ratio  $D$  for the metal is greater than the sum of the distribution ratios obtained if HA or B is used separately. In other cases, however, *e.g.* in the extraction of Th(IV) by HDBP in the presence of TBP,<sup>10</sup> or under certain extraction conditions, such as in the extraction of  $UO_2^{2+}$  by HDBP in the presence of high concentrations of TBP,<sup>23,25</sup> an antagonistic effect in the metal extraction may occur. The synergistic effect in the extraction of  $UO_2^{2+}$ <sup>3,11,20,27,33,34</sup> has generally been explained by the formation of mixed ligand uranyl complexes  $UO_2A_2(HA)_pB_q$ , where the values of  $p$  and  $q$

can vary depending on the extraction conditions. The antagonistic effect has usually been explained by complex formation between HA and B decreasing the free concentration of HA for a given total concentration  $C_A$  of the extractant.<sup>10,13,14</sup> In order to understand the metal extraction equilibria involved when a combination of dialkylphosphate (= HA) and a neutral organophosphorus compound (= B) are used as extractant, one needs to know the distribution equilibria of HA and B species under the conditions used for the metal extraction. In the present work the various complex equilibria of HDBP—TBP and HDBP—TOPO in hexane and carbon tetrachloride and with 0.10 M  $H_2SO_4$  as aqueous phase have been studied using the  $\beta$ -active  $HDB^{32}P$  as tracer. The equilibrium constants obtained from this work are used in the treatment of the data on the extraction of U(VI) with HDBP in the presence of TBP or TOPO.<sup>25</sup> The preliminary results of this work have been reported earlier.<sup>27,28</sup>

### EXPERIMENTAL

*Reagents.* The HDBP,  $(n-C_4H_9O)_2PO_2H$ , purchased from Albright and Wilson Ltd., London, with a purity of approximately 95 %, was further purified by the procedure described previously.<sup>9</sup>

Tributylphosphate,  $(n-C_4H_9O)_3PO$ , (Kebo) was purified by washing it with an equal volume of 1 M NaOH solution, then with 0.1 M  $HNO_3$  and finally with water. The purified product was dried with an infrared lamp for half an hour at about 120°C under reduced pressure in an  $N_2$  atmosphere. Trioctylphosphineoxide,  $(n-C_8H_{17})_3PO$ , from Eastman Kodak Company, U.S.A., was used without further purification.

The carbon tetrachloride was of analytical grade (Merck-Darmstadt) and the hexane, boiling range 68–69°C, had a purity of at least 99 % (Kebo) the remainder presumably being inert hydrocarbon. These solvents were not further purified.

$H_2SO_4$  (*p.a.*, Merck-Darmstadt) was of analytical grade and was used without further purification.

The radioactive  $HDB^{32}P$  was purchased from the Radiochemical Centre, Amersham, England. The aqueous phase was always 0.1 M  $H_2SO_4$  and the volumes of the two phases were equal. All experiments were carried out at 25°C in thermostated rooms and the general procedure was the same as described previously.<sup>9,12</sup>

After equilibration we measure the numbers of impulses,  $i_{aq}$  and  $i_{org}$ , from equal volumes of the two phases during equal times.

We correct  $i_{aq}$  and  $i_{org}$  for dead time by means of the factor  $\tau$  and multiply  $i_{org}$  by  $\lambda$ , to correct for different absorptions of  $\beta$ -particles in the aqueous and organic phase. The corrected values are

$$i_{aq,corr} = i_{aq} + i_{aq}^2 \tau ; i_{org,corr} = \lambda(i_{org} + i_{org}^2 \tau)$$

The net distribution ratio of HA was calculated as:

$$D = i_{org,corr}/i_{aq,corr}$$

### SYMBOLS AND EQUILIBRIUM CONSTANTS

- HA = dibutylphosphoric acid  $(n-C_4H_9O)_2PO_2H$ , (HDBP) (or other dialkylphosphate)  
 B = tributylphosphate  $(n-C_4H_9O)_3P=O$ , (TBP), or trioctylphosphineoxide  $(n-C_8H_{17})_3P=O$ , (TOPO)  
 [ ] = equilibrium concentration in the aqueous phase  
 [ ]<sub>org</sub> = equilibrium concentration in the organic phase

$a$	$= [\text{HA}] + [\text{A}^-] = [\text{HA}]\varphi$
$C_A$	$=$ initial total concentration of HA in the organic phase
$C_B$	$=$ initial total concentration of B in the organic phase
$D$	$= A_{\text{org}}/A_{\text{aq}}$ net distribution ratio of HA
$K_a$	$= [\text{H}^+][\text{A}^-]/[\text{HA}]$ stoichiometric acid dissociation constant
$K_d$	$= [\text{HA}]_{\text{org}}/[\text{HA}]$ distribution constant of the monomers
$K_2$	$= [\text{H}_2\text{A}_2]_{\text{org}}/[\text{HA}]_{\text{org}}^2$ dimerization constant in the organic phase
$K_{2\text{aq}}$	$= [\text{H}_2\text{A}_2]/[\text{HA}]^2$ dimerization constant in the aqueous phase
$K_n$	$= [\text{H}_n\text{A}_n]_{\text{org}}/[\text{HA}]_{\text{org}}^n$ polymerization constant in the organic phase
$K_{pq}$	$= [(\text{HA})_p\text{B}_q]_{\text{org}}/[\text{HA}]_{\text{org}}^p[\text{B}]_{\text{org}}^q$ formation constant of the complex $(\text{HA})_p\text{B}_q$ in the organic phase
$K_{d2}$	$= [\text{H}_2\text{A}_2]_{\text{org}}/[\text{H}_2\text{A}_2]$ distribution constant of the dimers
$A_{\text{org}}$	$=$ total concentration of HA in organic phase, free or bound
$A_{\text{aq}}$	$=$ total concentration of HA in the aqueous phase
$\varphi$	$= 1 + K_a[\text{H}^+]^{-1}$
$\beta_{pq}$	$= [(\text{HA})_p\text{B}_q]_{\text{org}}a^{-p}[\text{B}]_{\text{org}}^{-q} = K_{pq}\beta_{10}^p$ ; $\beta_{10} = [\text{HA}]_{\text{org}}/a$
$\beta_{2\text{aq}}$	$= [\text{H}_2\text{A}_2]/a^2$

## DATA

The primary data are given in Table 1 as  $\log C_A$ ,  $\log D$ , in Tables 2 and 3 as  $C_B$ ,  $\log C_A$ , and  $\log D$ , and in Table 4 as  $C_A$ ,  $\log C_B$ ,  $\log D$ . The data are represented as diagrams,  $\log D$  against  $\log A_{\text{aq}}$  for different constant values of  $C_B$  (Figs. 1, 2, 6, 7) and as  $\log D$  against  $\log C_B$  (Fig. 3).  $A_{\text{aq}}$  was calculated from the following relationship<sup>1</sup>

$$A_{\text{aq}} = C_A(1 + D)^{-1} \quad (1)$$

Table 1. The distribution of HDBP at 25°C between hexane or carbon tetrachloride and 0.1 M  $\text{H}_2\text{SO}_4$  for different initial total concentrations of HDBP ( $C_A$ ).  $V_{\text{org}} = V_{\text{aq}} = 15$  ml.

<i>Hexane</i> , $\log C_A$ ( $\log D$ ):	-0.343 (+ 1.119), -0.887 (+ 0.666), -1.489 (+ 0.213), -2.120 (-0.251), -2.597 (-0.629), -3.120 (-1.099), -3.597 (-1.513), -4.120 (-1.937), -4.296 (-2.015), -4.596 (-2.203), -4.897 (-2.318), -5.293 (-2.361), -5.592 (-2.473), -6.912 (-2.353), -7.213 (-2.440)
<i>Carbon tetrachloride</i> , $\log C_A$ ( $\log D$ ):	-0.335 (+ 1.076), -0.895 (+ 0.935), -1.497 (+ 0.765), -2.019 (+ 0.542), -2.495 (+ 0.331), -3.015 (+ 0.032), -3.482 (-0.267), -3.971 (-0.618), -4.140 (-0.718), -4.228 (-0.874), -4.434 (-0.922), -4.531 (-1.002), -4.617 (-1.083), -4.939 (-1.328), -5.056 (-1.333), -5.354 (-1.505), -5.652 (-1.483)

Table 2. Distribution of HDBP at 25°C between hexane or carbon tetrachloride and 0.10 M  $\text{H}_2\text{SO}_4$  for different initial total concentrations of HDBP ( $C_A$ ) at different constant values of TBP ( $C_B$ ).  $V_{\text{org}} = V_{\text{aq}} = 15$  ml.

*Hexane:*

$C_B = 5.321 \times 10^{-2}$ M	
$\log C_A$ ( $\log D$ ):	-0.343 (+ 1.142); -0.826 (+ 0.779); -1.489 (+ 0.383); -2.120 (+ 0.001); -2.597 (-0.326); -3.148 (-0.515); -3.597 (-0.613); -4.120 (-0.665); -4.597 (-0.703); -7.789 (-0.703)
$C_B = 0.1017$ M	
$\log C_A$ ( $\log D$ ):	-0.373 (+ 1.152); -0.895 (+ 0.793); -1.497 (+ 0.452); -2.120

(+ 0.103); -2.597 (-0.104); -3.120 (-0.253); -3.597 (-0.324); -4.120 (-0.365);  
-4.597 (-0.406); -8.220 (-0.414)

$C_B = 0.2033 \text{ M}$

$\log C_A (\log D)$ : -0.396 (+ 1.236); -1.020 (+ 0.864); -1.497 (+ 0.606); -2.120  
(+ 0.310); -2.597 (+ 0.170); -3.120 (+ 0.077); -3.597 (+ 0.047); -4.120 (+ 0.015);  
-4.597 (+ 0.070); -8.220 (+ 0.051)

$C_B = 0.4964 \text{ M}$

$\log C_A (\log D)$ : -0.652 (+ 1.251); -0.941 (+ 1.109); -1.417 (+ 0.904); -1.895  
(+ 0.761); -2.366 (+ 0.658); -2.819 (+ 0.603); -3.296 (+ 0.593); -3.752 (+ 0.588);  
-4.295 (+ 0.583); -8.220 (+ 0.579)

#### Carbon tetrachloride

$C_B = 1.024 \times 10^{-2} \text{ M}$

$\log C_A (\log D)$ : -1.019 (+ 0.968); -1.496 (+ 0.779); -2.019 (+ 0.556); -2.494  
(+ 0.335); -3.010 (+ 0.072); -3.467 (-0.207); -4.051 (-0.484); -4.358 (-0.607);  
-4.714 (-0.739); -5.003 (-0.821)

$C_B = 0.1024 \text{ M}$

$\log C_A (\log D)$ : -0.383 (+ 1.133); -1.019 (+ 0.989); -1.497 (+ 0.856); -2.019  
(+ 0.629); -2.495 (+ 0.442); -3.015 (+ 0.262); -3.482 (+ 0.152); -3.971 (+ 0.091);  
-4.228 (+ 0.074); -4.336 (+ 0.078); -4.617 (+ 0.017); -5.642 (+ 0.035); -4.942  
(+ 0.037)

Table 3. Distribution of HDBP at 25°C between hexane or carbon tetrachloride and 0.10 M  $\text{H}_2\text{SO}_4$  for different initial total concentration of HDBP ( $C_A$ ) at different constant values of TOPO ( $C_B$ ).  $V_{\text{org}} = V_{\text{aq}} = 15 \text{ ml}$ .

#### Hexane

$C_B = 5.744 \times 10^{-3} \text{ M}$

$\log C_A (\log D)$ : -0.792 (+ 0.800); -1.491 (+ 0.254); -2.094 (-0.183); -2.713  
(-0.674); -3.191 (-1.021); -4.199 (-1.427); -4.597 (-1.449); -5.120 (-1.472)

$C_B = 5.474 \times 10^{-4} \text{ M}$

$\log C_A (\log D)$ : -0.792 (+ 0.759); -1.491 (+ 0.265); -2.093 (-0.151); -2.713  
(-0.524); -3.190 (-0.664); -3.491 (-0.724); -3.014 (-0.610); -3.491 (-0.719);  
-4.014 (-0.730); -4.491 (-0.726); -7.514 (-0.739)

$C_B = 5.474 \times 10^{-3} \text{ M}$

$\log C_A (\log D)$ : -0.889 (+ 0.698); -1.491 (+ 0.349); -2.093 (+ 0.141); -2.713  
(+ 0.146); -3.190 (+ 0.160); -3.491 (+ 0.164); -3.014 (+ 0.146); -3.491 (+ 0.157);  
-4.014 (+ 0.154); -7.514 (+ 0.154)

$C_B = 4.925 \times 10^{-2} \text{ M}$

$\log C_A (\log D)$ : -0.826 (+ 0.962); -1.489 (+ 0.963); -2.120 (+ 1.033); -2.597  
(+ 1.058); -3.120 (+ 1.076); -3.597 (+ 1.065); -4.597 (+ 1.072); -7.887 (+ 1.072)

#### Carbon tetrachloride

$C_B = 4.677 \times 10^{-3} \text{ M}$

$\log C_A (\log D)$ : -0.386 (+ 1.096); -1.022 (+ 0.935); -1.498 (+ 0.750); -2.016  
(+ 0.600); -2.481 (+ 0.476); -2.962 (+ 0.425); -3.342 (+ 0.386); -3.634 (+ 0.373);  
-3.773 (+ 0.381); -3.863 (+ 0.372); -4.164 (+ 0.371); -4.386 (+ 0.374)

$C_B = 4.677 \times 10^{-4} \text{ M}$

$\log C_A (\log D)$ : -0.386 (+ 0.993); -1.022 (+ 0.889); -1.498 (+ 0.712); -2.016  
(+ 0.553); -2.481 (+ 0.349); -2.962 (+ 0.151); -3.341 (-0.085); -3.773 (-0.230);  
-4.164 (-0.348); -4.386 (-0.295); -4.562 (-0.293); -3.634 (-0.169)

Table 4. Distribution of HDBP between hexane and 0.1 M  $\text{H}_2\text{SO}_4$  for different concentrations of TBP or TOPO ( $C_B$ ) in the organic phase and different constant values of initial total concentrations of HDBP ( $C_A$ ).

$B = \text{TBP}$

$C_A = 6.03 \times 10^{-9} \text{ M}$

$\log C_B (\log D)$ : -0.304 (+ 0.597); -0.692 (+ 0.051); -0.991 (-0.414);

$$\begin{aligned}
 C_A &= 1.63 \times 10^{-8} \text{ M} \\
 \log C_B (\log D) &: 0.003 (+ 1.043); -0.093 (+ 0.883); -1.276 (-0.703) \\
 C_A &= 3.06 \times 10^{-8} \text{ M} \\
 \log C_B (\log D) &: -0.407 (+ 0.430); -0.607 (+ 0.135); -0.796 (-0.114); -1.495 \\
 &(-0.927); -1.796 (-1.305); -1.959 (-1.479); -2.876 (-2.139)
 \end{aligned}$$

B = TOPO

$$\begin{aligned}
 C_A &= 3.06 \times 10^{-8} \text{ M} \\
 \log C_B (\log D) &: -1.000 (+ 1.356); -1.308 (+ 1.072); -1.698 (+ 0.686); -1.961 \\
 &(+ 0.461); -2.262 (+ 0.154); -2.536 (-0.070); -3.262 (-0.739)
 \end{aligned}$$

### CHEMICAL MODEL

The aqueous phase is assumed to contain the species HA, A<sup>-</sup>, and H<sub>2</sub>A<sub>2</sub>, and has the same [H<sup>+</sup>] = *h* in all experiments. As master variable we use for convenience

$$a = [\text{HA}] + [\text{A}^-] = [\text{HA}](1 + K_a h^{-1}) = \varphi \cdot [\text{HA}] \quad (2)$$

where  $\varphi = 1 + K_a[\text{H}^+]^{-1} = 1.879$ . Here the dissociation constant for HDBP is taken as  $K_a = 10^{-0.979} \text{ M}$  (cf. Refs. 11, 12) and [H<sup>+</sup>] = *h* in the aqueous phase may be calculated as 0.1195 M and the constant  $K = [\text{H}^+][\text{SO}_4^{2-}][\text{HSO}_4^-]^{-1} = 2.894 \times 10^{-2} \text{ M}$ , from the value of infinite dilution  $K_A^\circ = 1.01 \times 10^{-2}$  (cf. Ref. 36) and the activity factors given by Kielland.<sup>35</sup> If *a* is used, it is not necessary to know *K<sub>a</sub>* or *h*. The organic phase contains B (concentration *b*) and a series of complexes (HA)<sub>*p*</sub>B<sub>*q*</sub>. The concentration of the (*p*,*q*) complex is

$$[(\text{HA})_p\text{B}_q]_{\text{org}} = C_{pq} = \beta_{pq} a^p b^q \quad (3)$$

The "real" equilibrium constant for the formation of the (*p*,*q*) complex from HA(org) and B(org) is

$$K_{pq} = [(\text{HA})_p\text{B}_q]_{\text{org}} / [\text{HA}]_{\text{org}}^p [\text{B}]_{\text{org}}^q = \beta_{pq} \varphi^p K_d^{-p} = \beta_{pq} \beta_{10}^{-p}$$

Using the notation (*p*,*q*), the species HA(org), H<sub>2</sub>A<sub>2</sub>(org), HAB(org) are called the (1,0), (2,0), and (1,1) complexes, and the distribution constant *K<sub>d</sub>* for HA is thus

$$K_d = \frac{[\text{HA}]_{\text{org}}}{[\text{HA}]} = \frac{[\text{HA}]_{\text{org}}}{a} \quad \varphi = \beta_{10} \varphi$$

We now have the following relationships:

$$A_{\text{aq}} = [\text{A}^-] + [\text{HA}] + 2[\text{H}_2\text{A}_2] = a + 2\beta_{2\text{aq}} a^2 \quad (4)$$

$$A_{\text{org}} = \sum p [(\text{HA})_p\text{B}_q]_{\text{org}} = \sum p C_{pq} = \sum p \beta_{pq} a^p b^q \quad (5)$$

$$D = A_{\text{org}} / A_{\text{aq}} \quad (6)$$

$$C_A = A_{\text{org}} + V_{\text{fak}} A_{\text{aq}} \quad (7)$$

where *V<sub>fak</sub>* = volume aqueous phase/volume organic phase

$$C_B = B_{\text{org}} = b + \sum q [(\text{HA})_p\text{B}_q]_{\text{org}} = b + \sum q C_{pq} = b + \sum q \beta_{pq} a^p b^q \quad (8)$$

From (6) and (7) follows

$$A_{\text{aq}} = \frac{C_A}{D + V_{\text{fak}}} ; A_{\text{org}} = \frac{DC_A}{D + V_{\text{fak}}} \quad (9)$$

Given the values for  $\beta_{2\text{aq}}$  and the  $\beta_{p\text{q}}$ , we might insert  $A_{\text{aq}}$  from (9) into (4) and calculate  $a$ ; inserting this  $a$  and  $C_B$  into (8) we might calculate  $b$ . Inserting  $a$  and  $b$  into (5), finally, gives a calculated value  $A_{\text{org, calc}}$ .

#### TREATMENT OF THE DISTRIBUTION DATA WITH LETAGROP VRID COMPUTER PROGRAM

With the LETAGROP VRID computer program developed by Ingri and Sillén,<sup>19</sup> the computer is ordered to search for the set of values of unknown constants,  $k_1 k_2 \dots k_N$ , which will minimize the square sum of the relative error:

$$U = \sum w(y_{\text{calc}} - y_{\text{exp}})^2$$

where  $w$  is a weight factor,  $y_{\text{exp}}$  a measured quantity and  $y_{\text{calc}}$  a quantity calculated from a derived functional relationship:

$$y = f(k_1, k_2, \dots, k_N, a_1, a_2, \dots)$$

where  $a_1, a_2, \dots$  are quantities assumed to be known; the summation of the error-square sum  $U$  is taken over all available experimental points.

In the present work we may for instance minimize the error-square sum for  $A_{\text{org}}$ ,  $\log D$ , or any other experimental quantity. We chose to minimize the error-square sum

$$U = \sum \left( \frac{A_{\text{org, calc}} - A_{\text{org, exp}}}{A_{\text{org, exp}}} \right)^2 = \sum (D_{\text{calc}} - D_{\text{exp}})^2 D_{\text{exp}}^{-2}$$

Minimizing the  $U$  of  $A_{\text{org}}$  was found to give too low weight for measurements at low values of  $A_{\text{org}}$ . As input data to the computer we used the primary data 1)  $I_{\text{aq}}$  (activity in the aqueous phase in cpm) 2)  $I_{\text{org}}$  (activity in the organic phase in cpm) 3) the initial total concentration of HDBP ( $C_A$ ) 4) the total concentration of TBP or TOPO ( $C_B$ ).

The model sets of  $(\text{HA})_p\text{B}_q$  complexes and equilibrium constants, which are found to give the lowest value of the error-square sum  $U$  will probably give a better picture of the true chemical state of the system than the others.

#### EVIDENCE ON FORMATION OF HA DIMERS IN THE AQUEOUS PHASE

There have been conflicting reports on the formation of HDBP dimers in the aqueous phase.

In 0.1 M  $\text{HNO}_3$  medium Dyrssen and Liem<sup>9</sup> from distribution studies of HDBP between various organic solvents and nitrate solutions found no indications of dimeric species  $\text{H}_2\text{A}_2$  in the aqueous phase. Dyrssen<sup>12</sup> explained solubility data for HDBP in 0.05 M  $\text{HClO}_4$ —0.05 M  $\text{NaClO}_4$  aqueous solution by assuming the formation of  $\text{H}_2\text{A}_2$  species and calculated the constant  $K_{2\text{aq}} = 10^{1.14}$ .

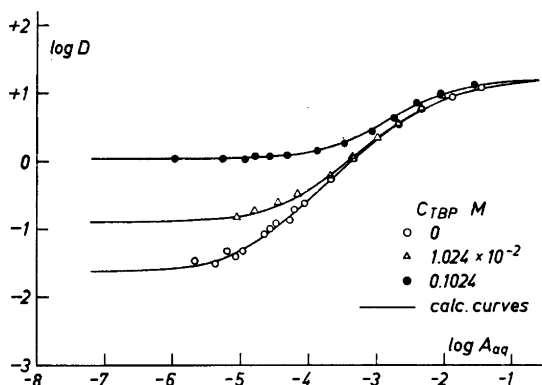


Fig. 1. Distribution of HDBP between 0.10 M  $\text{H}_2\text{SO}_4$  and carbon tetrachloride as a function of the total concentration of HDBP in the aqueous phase for different constant concentrations of TBP in the organic phase: 0 M ( $\circ$ ),  $1.024 \times 10^{-2}$  M ( $\triangle$ ), 0.1024 M ( $\bullet$ ). The lines are calculated assuming the HDBP–TBP species and equilibrium constants given in Table 5. The distribution data are given in Tables 1 and 2.

From distribution studies with  $^{32}\text{P}$ -labelled HDBP between carbon tetrachloride and nitrate medium, Kuča<sup>24</sup> reported the formation of HDBP dimers in concentrated nitrate medium.

In the present work the distribution data of HDBP between  $\text{CCl}_4$  and 0.10 M  $\text{H}_2\text{SO}_4$ , as shown in Fig. 1, indicate the formation of dimeric HDBP species in the aqueous phase at  $A_{\text{aq}} > 1$  mM, which can be seen from the levelling off of the distribution ratio  $D$  with increasing value of  $A_{\text{aq}}$ . Since the distribution experiments have been carried out at constant  $[\text{H}^+]$ , these data do not enable us to differentiate the several possible dimeric species  $\text{H}_2\text{A}_2$ ,  $\text{HA}_2^-$ , and  $\text{A}_2^{2-}$  from each other. Preliminary results<sup>26</sup> of distribution studies of HDBP between benzene and 0.10 M  $\text{H}_2\text{SO}_4$  also indicate the formation of HDBP dimeric species in the aqueous phase at  $A_{\text{aq}} > 1$  mM (corresponding to  $C_A > 1.5$  mM).

In Table 9 values of  $K_{2\text{aq}}$  for various aqueous media are compared. These differences in values for the dimerization constants in the aqueous phase may indicate a difference in interaction between HDBP and various ionic species.<sup>16,23,29</sup>

#### EVIDENCE ON POLYMERISATION OF DIALKYLPHOSPHATE IN THE ORGANIC PHASE

The existence of HDBP monomer, HA, and dimers,  $\text{H}_2\text{A}_2$ , in various organic solvents has been indicated previously.<sup>9</sup> Higher polymeric species are indicated in hexane at  $C_A > 0.05$  M, as can be seen from the steep increase of the distribution curve  $\log D$  versus  $\log A_{\text{aq}}$  in Fig. 2.

A similar phenomenon has been observed before by Dyrssen and Liem<sup>9</sup> when 0.1 M  $\text{HNO}_3$  was used as the aqueous phase, and the sharp increase of

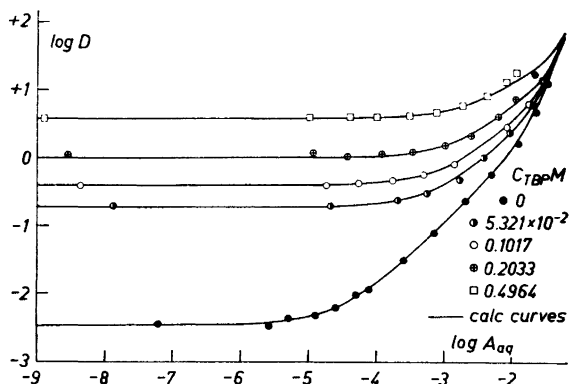


Fig. 2. The distribution of HDBP between 0.10 M  $\text{H}_2\text{SO}_4$  and hexane as a function of the total concentration of HDBP in the aqueous phase for different constant concentrations of TBP in the organic phase: 0 M ( $\bullet$ ),  $5.321 \times 10^{-2}$  M ( $\circ$ ), 0.2033 M ( $\oplus$ ) and 0.4964 M ( $\square$ ). The lines are calculated assuming the HDBP—TBP species and equilibrium constants given in Table 5. The distribution data are given in Tables 1 and 2.

the distribution ratio with increasing  $A_{\text{aq}}$  was taken as an indication of the breaking up of an eight-membered ring of the dimers to some polymeric species in the form of an extended chain. Similarly, from isopiestic studies of dioctylphosphoric acid in octane, Baes<sup>5,6</sup> reported the formation of trimeric species of DOP. Myers, McDowell and Coleman<sup>38</sup> reported from static differential vapour-pressure measurements with di-2-ethylhexylphosphoric acid, HDEHP, and with a mixture of HDEHP—NaDEHP in wet benzene, the formation of dimeric species for the pure acid and indications of acid dimer and “tetramers”,  $\text{NaA}(\text{HA})_3$ , in the acid-salt mixture. From distribution studies Courtemanche<sup>8</sup> found indications for the formation of polymeric species of dibenzylphosphate in toluene and carbon tetrachloride. Ferraro and Peppard<sup>15</sup> interpreted the results of proton magnetic resonance studies of acidic organophosphorus compounds in terms of polymer-dimer-monomer equilibria. Preliminary results<sup>26</sup> from distribution studies indicate the formation of polymeric species of HDEHP in hexane, carbon tetrachloride, chloroform, nitrobenzene, and toluene.

#### COMPLEX FORMATION BETWEEN HDBP SPECIES AND TBP

Fig. 1 shows the distribution of HDBP between 0.10 M  $\text{H}_2\text{SO}_4$  and carbon tetrachloride for different constant values of  $C_{\text{B}} = 0$ ,  $1.024 \times 10^{-2}$  and 0.1024 M. The experimental data are plotted as  $\log D$  versus  $\log A_{\text{aq}}$ . In the LETAGROP computer calculations the best fit to the available distribution data was found with the set of HDBP—TBP species shown in Table 5, *i.e.* the formation of HA,  $\text{H}_2\text{A}_2$ , and the 1:1 complex HAB and 2:1 complex  $\text{H}_2\text{A}_2\text{B}$  in the  $\text{CCl}_4$  phase. Addition of the complexes  $\text{HAB}_2$  and  $\text{H}_2\text{A}_2\text{B}_2$  gave no improvement to the error-square sum  $U$ .



Table 5. The distribution of HDBP between 0.10 M  $H_2SO_4$  and  $CCl_4$  or hexane in the presence of TBP or TOPO. Equilibrium constants <sup>a</sup> for formation of sets of  $(HA)_pB_q$  species which were found to give the minimum error-square sum  $U = \sum (D_{\text{calc}} - D_{\text{exp}})^2 D_{\text{exp}}^{-2}$ .

System	Chemical Equations	log $K$ values
HDBP - $CCl_4$ - 0.10 M $H_2SO_4$	$HA(\text{aq}) \rightleftharpoons HA(\text{org})$	$\log K_d = -1.36 \pm 0.08$
	$2 HA(\text{org}) \rightleftharpoons H_2A_2(\text{org})$	$\log K_2 = 6.37 \pm 0.04$
	$2 HA(\text{aq}) \rightleftharpoons H_2A_2(\text{aq})$	$\log K_{2\text{aq}} = 2.40 \pm 0.09$
	$HA(\text{org}) + B(\text{org}) \rightleftharpoons HAB(\text{org})$	$\log K_{11} = 2.65 \pm 0.04$
HDBP - TBP - $CCl_4$ - 0.10 M $H_2SO_4$	$H_2A_2(\text{org}) + B(\text{org}) \rightleftharpoons H_2A_2B(\text{org})$	$\log K_{21} = 0.22$ (max. 0.51)
	$HA(\text{org}) + B(\text{org}) \rightleftharpoons HAB(\text{org})$	$\log K_{11} = 4.36 \pm 0.06$
	$HA(\text{aq}) \rightleftharpoons HA(\text{org})$	$\log K_d = -2.18 \pm 0.04$
	$2 HA(\text{org}) \rightleftharpoons H_2A_2(\text{org})$	$\log K_2 = 6.66 \pm 0.02$
HDBP - TOPO - $CCl_4$ - 0.10 M $H_2SO_4$	$4 HA(\text{org}) \rightleftharpoons H_4A_4(\text{org})$	$\log K_4 = 14.62 \pm 0.07$
	$HA(\text{org}) + B(\text{org}) \rightleftharpoons HAB(\text{org})$	$\log K_{11} = 2.94 \pm 0.05$
	$HA(\text{org}) + 2 B(\text{org}) \rightleftharpoons HAB_2(\text{org})$	$\log K_{12} = 3.42 \pm 0.07$
	$H_2A_2(\text{org}) + B(\text{org}) \rightleftharpoons H_2A_2B(\text{org})$	$\log K_{21} = 1.27 \pm 0.02$
HDBP - TOPO - hexane - 0.10 M $H_2SO_4$	$HA(\text{org}) + B(\text{org}) \rightleftharpoons HAB(\text{org})$	$\log K_{11} = 4.88 \pm 0.04$
	$H_2A_2(\text{org}) + B(\text{org}) \rightleftharpoons H_2A_2B(\text{org})$	$\log K_{21} = 2.60$ (max. 2.91)

<sup>a</sup> The limits given correspond approximately to  $\log(K \pm 3\sigma(K))$  and if  $\sigma(K) > 0.2K$ , the maximum value  $\log(K + 3\sigma(K))$  is given.

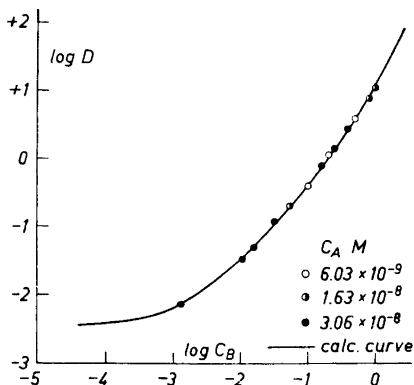


Fig. 3. The distribution of HDBP between 0.10 M  $\text{H}_2\text{SO}_4$  and hexane as a function of the concentration of TBP in the organic phase for different constant initial total concentration of HDBP;  $6.03 \times 10^{-9}$  (○),  $1.63 \times 10^{-8}$  (◐),  $3.06 \times 10^{-8}$  M (●). The lines are calculated assuming the HDBP—TBP species and equilibrium constants given in Table 5. The distribution data are given in Table 4.

In Fig. 1 the curves shown have been calculated assuming the HDBP—TBP species and equilibrium constants given in Table 5.

The value found for the formation of the HAB complex ( $\log K_{11} = 2.65 \pm 0.04$ ) is surprisingly much lower than that found in the two-phase system  $\text{CCl}_4/0.1 \text{ M HNO}_3$  ( $\log K_{11} = 2.84 \pm 0.08$ ),<sup>9</sup> which is unexpected, since the ionic medium would not be expected to be of importance for the complex formation in the organic phase. The deviation in value might be due to the extraction of  $\text{HNO}_3$  by HDBP<sup>16,23</sup> and by TBP<sup>1,18,30</sup> into the organic phase.

In Fig. 2 the distribution of HDBP between 0.10 M  $\text{H}_2\text{SO}_4$  and hexane are given for several constant values of initial total concentration of TBP in the organic phase:  $C_B = 0$ ,  $5.321 \times 10^{-2}$  M, 0.1017 M, 0.2033 M, and 0.4964 M. Fig. 3 shows the distribution of HDBP as a function of  $C_B$  for different constant values of  $C_A = 6.03 \times 10^{-9}$  M,  $1.63 \times 10^{-8}$  M and  $3.06 \times 10^{-8}$  M. In this system two opposing effects influence the distribution ratio  $D$  at higher concentration of HA ( $A_{\text{aq}} > 1 \text{ mM}$ ), *i.e.* 1) the formation of  $\text{H}_2\text{A}_2$  in the aqueous phase which should tend to lower  $D$ , and 2) the formation of polymeric species of HA in the organic phase which will cause a sharp increase of the extraction of HA.

In Table 6 a summary of the equilibrium constants is given for a number of sets of complexes  $(\text{HA})_p\text{B}_q$  and equilibrium constants  $\beta_{pq}$  which were found to minimize the error-square sum  $U$ . In all sets of  $(\text{HA})_p\text{B}_q$  tried, the formation of  $\text{HA}(\text{org})$ ,  $\text{HAB}(\text{org})$ ,  $\text{HAB}_2(\text{org})$ ,  $\text{H}_2\text{A}_2(\text{org})$  and  $\text{H}_2\text{A}_2\text{B}(\text{org})$  was indicated. In mechanism I—V only one more polymeric species of the form  $(\text{HA})_p$  was added. In the course of the computer calculation it was found that with the assumptions above the equilibrium constant for the HDBP dimers in the aqueous phase  $\beta_{2\text{aq}}$  could not be established satisfactorily, either  $\beta_{2\text{aq}}$  was reduced to zero or the standard deviation  $\sigma(\beta_{2\text{aq}})$  was found to exceed the value of the constant  $\beta_{2\text{aq}}$ . The results given in Table 6 for mechanism I—V were found by neglecting the dimeric species of HDBP in the aqueous phase. In this case the addition of a tetramer,  $\text{H}_4\text{A}_4$ , to the HDBP—TBP species HA,  $\text{H}_2\text{A}_2$ , HAB,  $\text{HAB}_2$ , and  $\text{H}_2\text{A}_2\text{B}$  was found to give a better  $U$  value than the addition of any other single polymeric HDBP species, like

$H_3A_3$ ,  $H_6A_6$ ,  $H_8A_8$ , or  $H_{10}A_{10}$ . However, the addition of the  $H_4A_4$  polymeric species and neglect of the aqueous  $H_2A_2$  can only be considered as a simplified way to describe formally the distribution of HDBP in the higher concentration range.

In mechanisms VI–XVII we tried to differentiate the two opposing effects mentioned before, *i.e.* the formation of dimeric HDBP in the aqueous phase and polymeric HDBP species in the hexane phase. To do this we assume the value  $K_{2aq} = [H_2A_2]/[HA]^2 = 10^{2.40}$ , found for the system HDBP– $CCl_4$ –0.10 M  $H_2SO_4$ , to apply for the system HDBP–hexane–0.10 M  $H_2SO_4$ . This constant was not varied during the course of computer calculations, and different HDBP–TBP polymeric species were added. Assuming that only HDBP-polymers of the form  $(HA)_p$  were formed, as can be seen from Table 7 in mechanism VI–XV, the best  $U$  values were found by adding of  $H_4A_4$  and  $H_8A_8$  or  $H_{10}A_{10}$  to the species HA, HAB,  $HAB_2$ ,  $H_2A_2$ ,  $H_2A_2B$  in the organic phase. The value of the error-square sum  $U \approx 1.400$  found assuming these sets of  $(HA)_pB_q$  species, however, is not as good as  $U = 0.567$  found in mechanism II, in which only the addition of HDBP tetramer was considered. A better fit to the data could, however, be found by the addition of other polymeric species  $(HA)_pB_q$ , besides HDBP tetramers and decamers. As seen in mechanism XVI and XVII in Table 6 the addition of the species  $H_2A_2B_2$ ,  $H_4A_4$ ,  $H_4A_4B$ ,  $H_4A_4B_2$ ,  $H_{10}A_{10}$ ,  $H_{10}A_{10}B$ , or  $H_{10}A_{10}B_2$ , considerably contribute to an improvement of the error-square sum  $U$  and  $\sigma(y)$ .

*Recalculation of HA distribution data between hexane and 0.1 M  $HNO_3$ .* Dyrssen and Liem<sup>9</sup> have studied the distribution of HA between hexane and 0.1 M  $HNO_3$ , in which polymeric species were indicated at high  $C_A$ . We now have recalculated the data and in Table 7 are given the equilibrium constants of different  $(HA)_p$  species which minimize the error-square sum  $U = \sum(\log D_{calc} - \log D_{exp})^2$ .

In this system where 0.1 M  $HNO_3$  was used as the aqueous phase we have neglected the HDBP dimerization in the aqueous phase, since there is no indication of its formation in the distribution curves for HDBP between 0.10 M  $HNO_3$  and other organic solvents, like  $CCl_4$ ,  $CHCl_3$ , and isopropyl-ether.

The results in Table 7 show that the addition of  $H_4A_4$  and  $H_{12}A_{12}$  to the monomers, HA, and dimers,  $H_2A_2$ , in the organic phase seems to give a somewhat better fit than adding  $H_4A_4$  with some other polymeric species like  $H_6A_6$ ,  $H_8A_8$ , or  $H_{10}A_{10}$ . The indication of the formation of  $(HA)_p$  with  $p \geq 4$  in hexane agrees with the results of the present work.

*Conclusions on the  $(HA)_pB_q$  polymeric species.* The results of our calculations indicate that in the greater part of our experimental range the set of complexes HA, HAB,  $HAB_2$ ,  $H_2A_2$ , and  $H_2A_2B$  suffices to describe the distribution data, as is also seen from the fact that their  $\beta_{pq}$  values are almost unchanged in the various mechanisms.

The additional complexes influence the calculated  $D$  values only for points at high  $C_A$  and low  $[B]_{org}$ . We may conclude from the distribution data in the system  $CCl_4/0.10$  M  $H_2SO_4$  that  $H_2A_2(aq)$  is formed, and that the hexane data indicate strongly that additional complexes  $(HA)_pB_q$  with  $p \geq 4$  are formed, both with  $q = 0$  and with positive  $q$  values.

Table 6. The equilibrium constants  $^a$  of different possible sets of complexes  $(HA)_pB_q$  between HDBP and TBP which give the lowest error-square sum  $U = \sum \frac{1}{I} \left( \frac{A_{org, calc} - A_{org, exp}}{A_{org, exp}} \right)^2$

Mechanism	(1,0)	(1,1)	(1,2)	(2,0)	(2,1)	Polymeric $(HA)_pB_q$ added	(2,0)aq <sup>b</sup> (not varied)	U	$\sigma$ (y)
I	-2.44 ± 0.08	0.48 ± 0.06	0.96 ± 0.09	1.67 ± 0.09	3.01 ± 0.10	(3,0) 3.34 ± 0.13		0.867	0.118
II	-2.46 ± 0.07	0.48 ± 0.05	0.96 ± 0.07	1.72 ± 0.06	3.03 ± 0.07	(4,0) 4.83 ± 0.09		0.567	0.096
III	-2.47 ± 0.07	0.48 ± 0.05	0.96 ± 0.08	1.76 ± 0.06	3.04 ± 0.08	(6,0) 7.70 ± 0.11		0.667	0.104
IV	-2.47 ± 0.09	0.48 ± 0.06	0.96 ± 0.09	1.77 ± 0.06	3.04 ± 0.09	(8,0) 10.54 ± 0.13		0.917	0.122
V	-2.48 ± 0.10	0.52 ± 0.07	0.96 ± 0.10	1.78 ± 0.07	3.04 ± 0.10	(10,0) 13.39 ± 0.17		1.124	0.135
VI	-2.46 ± 0.12	0.47 ± 0.08	0.96 ± 0.13	1.74 ± 0.13	3.34 ± 0.12	(4,0) 6.56 ± 0.09	1.85	1.708	0.166
VII	-2.49 ± 0.13	0.46 ± 0.09	0.96 ± 0.13	1.83 ± 0.11	3.39 ± 0.11	(6,0) 10.42 ± 0.10	1.85	1.886	0.174
VIII	-2.50 ± 0.16	0.46 ± 0.11	0.96 ± 0.16	1.85 ± 0.13	3.41 ± 0.13	(8,0) 14.19 ± 0.13	1.85	2.764	0.211
IX	-2.50 ± 0.19	0.46 ± 0.12	0.95 ± 0.19	1.86 ± 0.14	3.42 ± 0.14	(10,0) 17.94 ± 0.15	1.85	3.533	0.301
X	-2.47 ± 0.11	0.47 ± 0.08	0.96 ± 0.12	1.78 ± 0.18	3.36 ± 0.11	(4,0) (6.34, max. 6.57); (6,0) (10.09, max. 10.37)	1.85	1.445	0.154
XI	-2.47 ± 0.11	0.47 ± 0.08	0.96 ± 0.12	1.77 ± 0.12	3.36 ± 0.11	(4,0) (6.43 ± 0.17); (8,0) (13.77, max. 14.03)	1.85	1.401	0.152
XII	-2.47 ± 0.11	0.47 ± 0.08	0.96 ± 0.12	1.76 ± 0.12	3.36 ± 0.11	(4,0) (6.47 ± 0.14); (10,0) (17.50, max. 17.76)	1.85	1.400	0.152
XIII	-2.47 ± 0.11	0.47 ± 0.08	0.96 ± 0.12	1.76 ± 0.12	3.36 ± 0.11	(12,0) (6.49 ± 0.12); (21,24, max. 21.50)	1.85	1.418	0.153
XIV	-2.47 ± 0.11	0.47 ± 0.08	0.96 ± 0.12	1.76 ± 0.12	3.35 ± 0.11	(4,0) (6.50 ± 0.11); (14,0) (24.98, max. 25.26)	1.85	1.443	0.154
XV	-2.46 ± 0.11	0.47 ± 0.08	0.96 ± 0.12	1.76 ± 0.12	3.35 ± 0.11	(4,0) (6.51 ± 0.11); (16,0) (28.74, max. 29.03)	1.85	1.488	0.155

Table 6. Continued.

XVI	-2.48 ± 0.05	0.49 ± 0.03	0.95 ± 0.06	1.80 ± 0.05	3.06 ± 0.17	(4,0) (4,1) (10,0) (10,1)	(6.33 ± 0.09); (7.62 ± 0.12); (17.46 ± 0.20); (18.59 max. 18.98);	1.85	0.273	0.069
XVII	-2.48 ± 0.05	0.49 ± 0.03	0.96 ± 0.05	1.80 ± 0.05	3.11 ± 0.16	(2,2) (2,2) (4,0) (4,1) (4,2) (10,0) (10,2)	(3.23, max. 3.53) (3.02, max. 3.48); (6.35 ± 0.09); (7.46 max. 7.68); (7.60 max. 8.04); (17.47 ± 0.18); (20.09 max. 20.39)	1.85	0.245	0.066

<sup>a</sup> The equilibrium constants correspond to  $\beta_{pq} = K_{pq}\beta_{10}^p$ . The limits given correspond approximately to  $\log(\beta \pm 3\sigma(\beta))$  and if  $\sigma(\beta) > 0.2$ , the maximum value  $\log(\beta + 3\sigma(\beta))$  is given.

<sup>b</sup> (2,0)aq symbolizes the  $H_3A_2(aq)$ , the value of  $\beta_{2aq}$  was not varied during the course of computer calculations.

Table 7. Equilibrium constants <sup>a</sup> of sets of (HA)<sub>p</sub> species in hexane for HDBP which were found to minimize  $U = \sum_{i=1}^{20} (\log D_{calc} - \log D_{exp})^2$ . Data from Dyrssen and Liem.<sup>9</sup>

Mechanism	(1,0)	(2,0)	Added polymeric species		U	$\sigma(y)$
I	-2.64 ± 0.17	1.57 ± 0.15	(4,0)	(4.53, max. 4.62)	0.259	0.123
II	-2.65 ± 0.15	1.58 ± 0.13	(4,0)	(max. = 4.79);	0.202	0.109
III	-2.65 ± 0.14	1.59 ± 0.12	(4,0)	(max. = 4.57);	0.186	0.104
IV	-2.65 ± 0.14	1.60 ± 0.12	(4,0)	(max. = 4.50);	0.182	0.103
V	-2.65 ± 0.15	1.60 ± 0.13	(4,0)	(3.49, max. = 4.44); (12,0) (15.60, max. 15.96)	0.179	0.106

<sup>a</sup> The equilibrium constants correspond to  $\beta_{pq} = K_{pq}\beta_{10}^p$ . The limits given correspond approximately to  $\log(\beta \pm 3\sigma(\beta))$  and if  $\sigma(\beta) > 0.2$ , the maximum value  $\log(\beta + 3\sigma(\beta))$  is given.

The accuracy of the data does not permit us, however, to determine with certainty the predominating  $p$  and  $q$  values in the additional complexes. The various mechanisms listed in Table 6 must be understood as schematic descriptions which give a satisfactory fit with the data. To draw more definite conclusions on the nature of polymeric HDBP—TBP species, more detailed distribution studies should be carried out in systems where the formation of dimeric HDBP species in the aqueous phase may be neglected, such as in nitrate medium,<sup>9</sup> in combination with other physico-chemical methods, *e.g.* isopiestic,<sup>38</sup> IR spectroscopic,<sup>37,39</sup> or NMR studies.<sup>15</sup>

Figs. 4 and 5 show the calculated distribution as mole percentages over the different HDBP—TBP species in the two-phase systems hexane/0.10 M  $H_2SO_4$  for various concentrations of TBP in hexane at a constant  $C_A = 10^{-2}$  M (Fig. 4) and for various  $C_A$  at a constant  $C_B = 0.2033$  M (Fig. 5). The curves indicate competition between various  $(HA)_pB_q$  species under different distribution conditions. In Fig. 4 the formation of the  $H_2A_2B$  and HAB complexes is seen to increase to a maximum with increasing  $C_B$ , and at  $C_B > 1$  M the  $HAB_2$  complex becomes the predominant species.

In Fig. 5 the HAB and  $HAB_2$  species predominate at low values of HDBP concentration, while with increasing  $C_A$  first the  $H_2A_2B$  complex and then the HA polymeric species represented by the "tetramers" become predominant.

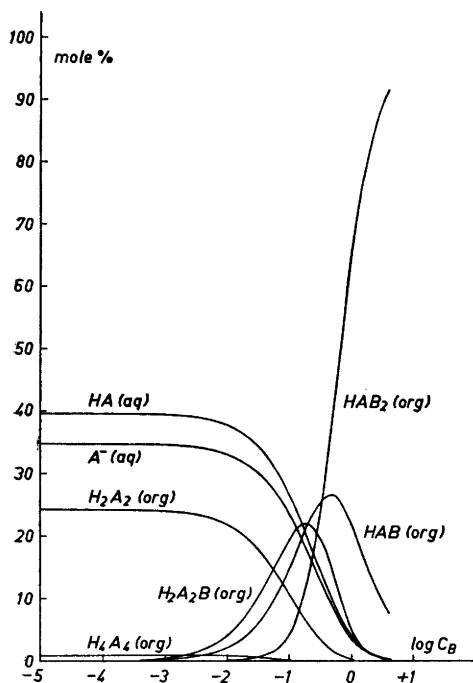


Fig. 4. The mole percentage of the different species of the complexes between HDBP and TBP in the two-phase systems hexane/0.10 M  $H_2SO_4$  as a function of the concentration of TBP in the organic phase.  $C_A = 10^{-2}$  M.

## COMPLEX FORMATION BETWEEN HDBP SPECIES AND TOPO

*Previous indication of HA-B interaction.* Trioctylphosphine oxide, TOPO, being a more basic reagent than tributylphosphate, TBP, might be expected to form more stable complexes with HDBP. From infrared study of dioctylphosphate (HDOP) and TOPO in octane, Baker and Baes<sup>4</sup> reported the formation of  $H_2A_2B$  and HAB species, with the equilibrium constants  $K_{21} = 100 \pm 50$  and  $K_{11}' = [HAB]_{org}[H_2A_2]_{org}^{-1}[B]_{org}^{-1} = 25 \pm 5$ . In explaining the experimental data of Blake *et al.*<sup>7</sup> on the synergistic effect in U(VI) extraction, Baes<sup>3</sup> assumed the formation of  $H_2A_2B$  ( $K_{21} = 33$ ) and HAB ( $K_{11}' = 8.3$ ) for the system HDOP and TBPO in kerosene. From infrared study of mono-butylphosphate (HMBP) and HDBP with tributylphosphine oxide (TBPO) in  $CS_2$ , Winand and Drèze<sup>37</sup> found evidence for the formation of the 1:1 complex HAB.

*Complex formation in  $CCl_4$ .* In Fig. 6 the distribution of HDBP between 0.10 M  $H_2SO_4$  and carbon tetrachloride is given as a function of the total concentration of HDBP in the aqueous phase for three constant concentrations of TOPO in the organic phase,  $C_B = 0$ ,  $4.677 \times 10^{-4}$  M, and  $4.677 \times 10^{-3}$  M. On computer treatment of the data, the best fit was found by assuming the formation of HA,  $H_2A_2$ , and HAB in the organic phase with the equilibrium constants given in Table 5. Just as when TBP was used, the data indicate the formation of dimeric species of HDBP in the aqueous phase at higher value of  $C_A$ . The addition of  $H_2A_2B$  to the model was found not to give any

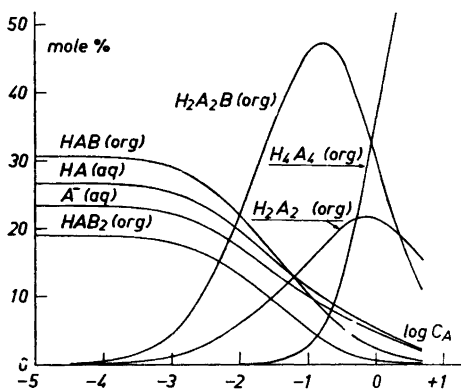


Fig. 5. The mole percentage of the different species of the complexes between HDBP and TBP in the two-phase systems hexane/0.10 M  $H_2SO_4$  as a function of  $C_A$  for  $C_B = 0.2033$  M.

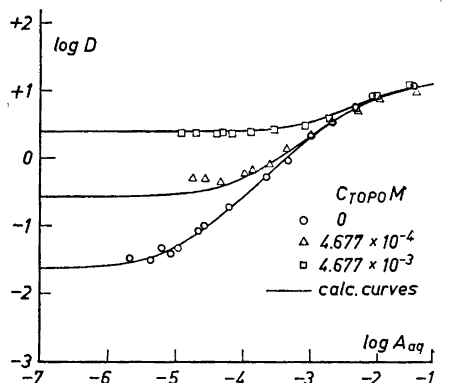


Fig. 6. Distribution of HDBP between 0.10 M  $H_2SO_4$  and carbon tetrachloride as a function of the total concentration of HDBP in the aqueous phase for different constant concentrations of TOPO in the organic phase: 0 M ( $\circ$ ),  $4.677 \times 10^{-4}$  M ( $\triangle$ ),  $4.677 \times 10^{-3}$  M ( $\square$ ). The lines are calculated assuming the HDBP-TOPO species and equilibrium constants given in Table 5. The distribution data are given in Tables 1 and 3.

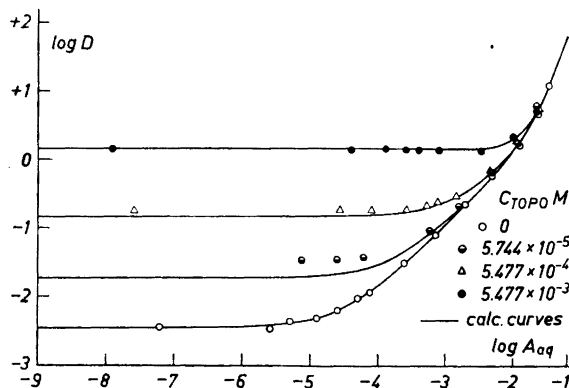


Fig. 7. The distribution of HDBP between 0.10 M  $\text{H}_2\text{SO}_4$  and hexane as a function of the total concentration of HDBP in the aqueous phase for different constant concentrations of TOPO in the organic phase: 0 M ( $\circ$ ),  $5.744 \times 10^{-5}$  M ( $\odot$ ),  $5.477 \times 10^{-3}$  M ( $\triangle$ ),  $5.477 \times 10^{-4}$  M ( $\bullet$ ). The lines are calculated curves assuming the HDBP–TOPO species and equilibrium constants given in Table 5. The distribution data are given in Tables 1 and 3.

improvement in the error-square sum  $U$ , thus in the concentration ranges studied the formation of a  $\text{H}_2\text{A}_2\text{B}$  complex between HDBP–TOPO seems to be of no importance.

*Complex formation in hexane.* Fig. 7 shows the experimental data for the distribution of HDBP between hexane and 0.1 M  $\text{H}_2\text{SO}_4$  aqueous solution for different constant concentrations of TOPO,  $C_B = 0$ ,  $5.744 \times 10^{-5}$  M,  $5.477 \times 10^{-4}$  M, and  $5.477 \times 10^{-3}$  M.

Just as was found for the system HDBP–TBP–hexane/0.10 M  $\text{H}_2\text{SO}_4$  at  $C_A > 0.05$  M, one may assume the formation of both HA polymeric species in the hexane phase and HDBP dimers in the aqueous phase. In Table 8 we summarize the equilibrium constants, the minimized error-square sum

$$U_{\min} = \sum_1^{58} \left( \frac{A_{\text{org,calc}} - A_{\text{org,exp}}}{A_{\text{org,exp}}} \right)^2$$

and the corresponding  $\sigma(y)$  for different possible sets of complexes  $(\text{HA}_p)_q$  between HDBP and TOPO. In mechanisms I–V the formation of HA dimers in the aqueous phase was formally neglected as was done and discussed before for the HDBP–TBP hexane/0.10 M  $\text{H}_2\text{SO}_4$  system. With this assumption the addition of  $\text{H}_4\text{A}_4$  to the set of  $(\text{HA}_p)_q$  species: HA, HAB,  $\text{H}_2\text{A}_2$ ,  $\text{H}_2\text{A}_2\text{B}$  in the hexane phase was found to give a better  $U$  value than adding any other single polymeric HA species like  $\text{H}_3\text{A}_3$ ,  $\text{H}_6\text{A}_6$ ,  $\text{H}_8\text{A}_8$ , or  $\text{H}_{10}\text{A}_{10}$  (see Table 8).

In mechanisms VI–XIII we take into account the formation of HDBP dimers in the aqueous phase and use the constant  $K_{2\text{aq}} = 10^{2.40}$  found for the system HDBP– $\text{CCl}_4$ /0.10 M  $\text{H}_2\text{SO}_4$ . The value of this constant was kept constant during the course of the computer calculations. In Table 8 the different sets of HDBP–TOPO species which minimize the error-square sum  $U$  are



Table 8. The equilibrium constants <sup>a</sup> of different possible sets of complexes (HA)<sub>p</sub>B<sub>q</sub> between HDBP and TOPO in hexane which minimize the error-square sum  $U = \sum_1^{58} \left( \frac{A_{\text{org. calc}} - A_{\text{org. exp}}}{A_{\text{org. exp}}} \right)^2$

Mechanism	(1,0)	(1,1)	(2,0)	(2,1)	Polymeric (HA) <sub>p</sub> B <sub>q</sub> added	(2,0)aq <sup>b</sup>	U	$\sigma(\beta)$
I	-2.44 ± 0.10	2.43 ± 0.04	1.73 ± 0.08	4.29, max. 4.63	(3,0)(3.22 ± 0.18)		1.096	0.144
II	-2.46 ± 0.09	2.42 ± 0.04	1.77 ± 0.06	4.31, max. 4.62	(4,0)(4.74 ± 0.16)		0.949	0.134
III	-2.47 ± 0.10	2.42 ± 0.04	1.80 ± 0.06	4.32, max. 4.64	(6,0)(7.64 ± 0.19)		1.134	0.146
IV	-2.47 ± 0.12	2.42 ± 0.08	1.82 ± 0.06	4.31, max. 4.65	(8,0)(10.46 ± 0.25)		1.405	0.163
V	-2.48 ± 0.13	2.42 ± 0.05	1.82 ± 0.06	4.30, max. 4.61	(10,0)(13.28, max. 13.51)		1.578	0.173
VI	-2.48 ± 0.11	2.42 ± 0.04	1.84 ± 0.08	4.67, max. 4.92	(4,0)(6.37 ± 0.21); (6,0)(9.79, max. 10.20)	1.85	1.056	0.143
VII	-2.48 ± 0.10	2.42 ± 0.04	1.83 ± 0.08	4.67, max. 4.90	(4,0)(6.41 ± 0.13); (8,0)(13.57, max. 13.92)	1.85	1.018	0.140
VIII	-2.47 ± 0.10	2.42 ± 0.04	1.83 ± 0.08	4.67, max. 4.91	(4,0)(6.43 ± 0.11); (10,0)(17.34, max. 17.68)	1.85	1.003	0.139
IX	-2.47 ± 0.10	2.42 ± 0.04	1.83 ± 0.08	4.66, max. 4.91	(4,0)(6.44 ± 0.09); (12,0)(21.10, max. 21.43)	1.85	1.002	0.139
X	-2.47 ± 0.10	2.42 ± 0.04	1.83 ± 0.08	4.66, max. 4.91	(4,0)(6.45 ± 0.09); (14,0)(24.86, max. 25.19)	1.85	1.006	0.139
XI	-2.47 ± 0.10	2.42 ± 0.04	1.83 ± 0.08	4.66, max. 4.91	(4,0)(6.45 ± 0.09); (16,0)(28.62, max. 28.96)	1.85	1.011	0.139
XII	-2.51 ± 0.15	2.42 ± 0.06	1.90 ± 0.09	4.73, max. 5.00	(6,0)(10.38 ± 0.11); (8,0)(max. = 14.11)	1.85	1.871	0.188
XIII	-2.51 ± 0.15	2.42 ± 0.06	1.90 ± 0.09	4.72, max. 5.00	(6,0)(10.38 ± 0.11); (10,0)(max. 17.72)	1.85	1.871	0.188

<sup>a</sup> The equilibrium constants correspond to  $\beta_{pq} = K_{pq}\beta_{10}^p$ . The limits given correspond approximately to  $\log(\beta \pm 3\sigma(\beta))$  and if  $\sigma(\beta) > 0.2$   $\beta$  the maximum value  $\log(\beta + 3\sigma(\beta))$  is given.

<sup>b</sup> (2,0)aq symbolizes the H<sub>2</sub>A<sub>2</sub>(aq), the value of  $\beta_{2aq}$  was not varied during the course of computer calculations.

compared. As can be seen from Table 8 the results indicate that adding of the polymeric species  $H_4A_4 + H_{10}A_{10}$  or  $H_4A_4 + H_{12}A_{12}$  to the species HA, HAB,  $H_2A_2$  and  $H_2A_2B$  seems to give a better U value compared with the other combinations tried, like  $H_4A_4 + H_6A_6$ ,  $H_4A_4 + H_8A_8$ ,  $H_4A_4 + H_{14}A_{14}$ ,  $H_4A_4 + H_{16}A_{16}$ ,  $H_6A_6 + H_8A_8$  or  $H_6A_6 + H_{10}A_{10}$ . Addition of complexes like  $H_2A_2B_2$ ,  $H_4A_4B$ ,  $H_4A_4B_2$ ,  $H_{10}A_{10}B$ , or  $H_{10}A_{10}B_2$  were found to give equilibrium constants with  $\sigma(\beta) > \beta$ . The results of the computer calculations indicate that the distribution data may in the greater part of our experimental range be described satisfactorily by the assumption of the formation of the species: (1,0), (1,1), (2,0), and (2,1), as may be seen from their values which are practically unaffected in the various mechanisms. Our results indicate strongly that at higher values of  $C_A$  additional complexes  $(HA)_pB_q$  with  $p \geq 4$  and mainly  $q = 0$  are formed, even if the predominating  $p$  and  $q$  cannot be deduced with certainty. The various mechanisms in Table 8 must be considered as a formal description of the experimental distribution data.

In Fig. 7 the lines shown have been calculated assuming the set of  $(HA)_pB_q$  species and equilibrium constants given in Table 5.

#### COMPARISON WITH RESULTS FROM SIMILAR STUDIES

From a general discussion of the solvent interaction of HA and  $H_2A_2$  for different organic diluents, Dyrssen and Liem<sup>10</sup> calculated the values of  $K_{11}$  and  $K_{21}$  for the interaction of HDBP and TBP in hexane, carbon tetrachloride and chloroform. In Table 9 the values of  $K_d$ ,  $K_{d2}$ ,  $K_2$ , and  $K_{2aq}$  found in this work are compared to corresponding values reported for other ionic media. In Table 10 the equilibrium constants for the formation of HAB,

Table 9. The distribution and dimerization constants of HDBP in hexane, carbon tetrachloride and various aqueous phases.

System	$\log K_d$	$\log K_{d2}$	$\log K_2$	$\log K_{2aq}$	Ref.
Hexane/0.1 M HNO <sub>3</sub>	-2.34	—	6.87		9
Hexane/0.1 M H <sub>2</sub> SO <sub>4</sub>	-2.18	—	6.66		This work
CCl <sub>4</sub> /0.1 M HNO <sub>3</sub>	-1.44	—	6.49		9
CCl <sub>4</sub> /0.1 M H <sub>2</sub> SO <sub>4</sub>	-1.36	1.25	6.37	2.40	This work
CCl <sub>4</sub> /0.1 M HNO <sub>3</sub> - 0.9 M NaNO <sub>3</sub>	-1.32 ± 0.06	—	6.28 ± 0.08		24
CCl <sub>4</sub> /1.0 M HNO <sub>3</sub>	-1.29 ± 0.06	—	6.12 ± 0.11		24
CCl <sub>4</sub> /0.1 M HClO <sub>4</sub> - 0.9 M NaClO <sub>4</sub>	-1.21 ± 0.03		6.19 ± 0.07		24
CCl <sub>4</sub> /1 M HClO <sub>4</sub>	-1.21 ± 0.03		6.01 ± 0.06		24
CCl <sub>4</sub> /0.1 M HNO <sub>3</sub> - 5.9 M NaNO <sub>3</sub>		2.15		4.65 ± 0.1	24
CCl <sub>4</sub> /1 M HNO <sub>3</sub> - 5 M NaNO <sub>3</sub>	0.12 ± 0.03	1.90	5.97 ± 0.1	4.31 ± 0.1	24
CCl <sub>4</sub> /6 M HNO <sub>3</sub>	-1.11 ± 0.03	1.86	5.58 ± 0.1	1.5	24
0.05 M HClO <sub>4</sub> + 0.05 M NaClO <sub>4</sub>				1.14	12

Table 10. Equilibrium constants for formation of  $(HA)_pB_q$  in various organic solvents.

System	$K_{11}$	$K_{12}$	$K_{21}$	Ref.
HDBP—TBP—hexane—0.1 M $H_2SO_4$	871	2630	18.6	This work
HDBP—TBP—hexane—0.1 M $HNO_3$			12.1 <sup>a</sup>	10
HDBP—TOPO—hexane—0.1 M $H_2SO_4$	$7.59 \times 10^4$	—	398	This work
HDBP—TBP— $CCl_4$ —0.1 M $H_2SO_4$	447	—	1.66	This work
HDBP—TBP— $CCl_4$ —0.1 M $HNO_3$	692 (749) <sup>a</sup>	—	(0.18) <sup>a</sup>	9
HDBP—TBP—kerosene—1 M $HNO_3$	676	—	—	17
HDBP—TOPO— $CCl_4$ —0.1 M $H_2SO_4$	$2.29 \times 10^4$	—	—	This work
HDBP—TBP— $CHCl_3$ —1 M $HClO_4$	40 (154) <sup>a</sup>	—	—0.28 <sup>a</sup>	12
HDBP—TBP—benzene—0.1 M $H_2SO_4$	86	—	—	26
HDOP—TOPO—octane	—	—	$100 \pm 50$	4
HDEHP—TBP— $CCl_4$ —0.1 M $HClO_4$	—	13.51	$8.446 \times 10^2$	26

<sup>a</sup> Calculated values (cf. Ref. 10.)

$HAB_2$  and  $H_2A_2B$  experimentally obtained are compared with values calculated in Ref. 10 and with constants for similar extractants reported by other workers.<sup>4,9,12,17,26</sup>

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