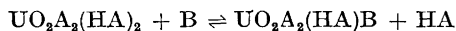


## The Extraction of Uranium(VI) with DBP in the Presence of TBP. The "Synergic" Effect: Substitution or Addition?

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The nature of the mixed complexes,  $\text{UO}_2\text{A}_2(\text{HA})_x\text{B}_y$ , of the uranyl ion with di-*n*-butyl phosphate (DBP = HA) and tri-*n*-butyl phosphate (TBP = B) in carbon tetrachloride has been investigated at 25°C by measuring the distribution ratio  $q$  of  $^{238}\text{U}$  between carbon tetrachloride and 0.1 M sulfuric acid. At concentrations of DBP between 0.0003 and 0.06 M, and of TBP between 0 and 0.1 M, two complexes are formed, namely  $\text{UO}_2\text{A}_2(\text{HA})_2$  at low  $[\text{B}]_{\text{org}}[\text{HA}]_{\text{org}}^{-1}$  and  $\text{UO}_2\text{A}_2(\text{HA})\text{B}$  at high  $[\text{B}]_{\text{org}}[\text{HA}]_{\text{org}}^{-1}$ . The value obtained for the equilibrium constant of the following reaction in carbon tetrachloride



is  $\log K_{11}^{-1}K_{20} = -3.0 \pm 0.2$ . The concentrations of free HA and B were calculated from data of Dyrssen and Liem<sup>9</sup>.

It may thus be stated that in the present case the «synergic» effect is due to substitution rather than addition.

Dialkyl phosphates have proved to be efficient extraction agents for lanthanide and actinide ions. At present, extraction with dialkyl phosphates has been developed by Brown and his co-workers at Oak Ridge to an industrial process for extraction of uranium from acid solutions<sup>1</sup>. In the course of systematic studies of various classes of organic phosphorus compounds as extracting agents for uranium, it was noticed that the addition of non-ionic phosphorylated reagent,  $\text{X}_3\text{PO}$  (X = alkyl group R or alkoxy group RO), to the dialkyl phosphate,  $(\text{RO})_2\text{POOH}$ , increased the distribution ratio considerably. This enhancement of U(VI) extraction has been called a «synergic» (synergistic, synergetic) effect.

Let us denote the dialkyl phosphate, which is an acid, by HA, and the non-ionic phosphorylated compound, *i.e.* TBP, by B. It should be noted that HA, dissolved in an inert organic solvent like  $\text{CCl}_4$  or hexane, exists predo-

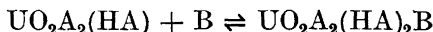
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minantly in the form of a dimer,  $H_2A_2$ . The extraction of uranyl, in the absence of B, may be expressed by the equation <sup>2-4</sup>:



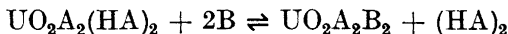
Two explanations of the »synergic» effect have been proposed, but neither has had up to now, adequate experimental support.

According to one hypothesis, which has been proposed by Brown *et al.*<sup>1</sup> the non-ionic molecule B is *added* to the previous complex through a hydrogen bond:



There is said to be some experimental evidence for this hypothesis <sup>5</sup>.

On the other hand, Kennedy <sup>6</sup> suggests that two molecules of B substitute for two molecules of HA:



Some indirect evidence <sup>7</sup> for this hypothesis is given by Kennedy's observation that a non-ionic phosphorylated resin absorbs uranium as  $UO_2A_2$  from a solution of uranium di-*n*-butyl phosphate in benzene, and liberates HA.

In two preceding papers from this laboratory <sup>8,9</sup>, the reactions of di-*n*-butyl phosphate (DBP = HA) with various solvents — among these tri-*n*-butyl phosphate (TBP = B) — was studied. The data make it possible to calculate the concentrations of individual species in the system DBP-TBP- $CCl_4$ - $H_2O$ , namely, HA and  $A^-$  in the aqueous phase, and HA,  $H_2A_2$ , B, and HAB in the organic phase.

The present work has aimed at studying the distribution of uranium (VI) between  $CCl_4$  and 0.1 M  $H_2SO_4$ . The experiments were so planned that either the concentration of free HA in the organic phase,  $[HA]_{org}$  was kept constant, and  $[B]_{org}$  was varied, or  $[B]_{org}$  was kept constant, and  $[HA]_{org}$  was varied.

Our results elucidate the mechanism of the so-called synergic effect for the DBP-TBP- $CCl_4$  system, and it seems possible in this case to decide between the two mechanisms proposed: addition or substitution.

## EXPERIMENTAL

The di-*n*-butyl phosphate (DBP = HA) was supplied by Albright and Wilson Ltd, London. It was purified in the way previously described <sup>9</sup>. Tri-*n*-butyl phosphate (TBP = B), Købo, Stockholm, was purified as follows: first it was stirred for several hours with the same volume of 4 % NaOH. After that, 4 %  $KMnO_4$  was added dropwise to the NaOH, still with vigorous stirring. At first, the solution was decolorized, but after the addition of a certain amount of  $KMnO_4$ , the color remained constant. The TBP was then washed with 0.1 M  $HNO_3$  and water, and finally dried at 130°C in a slow current of dry  $N_2$  gas at reduced pressure. Carbon tetrachloride (Merck) was of analytical grade and was not further purified.

A solution of <sup>233</sup>U(VI) in 0.1 M  $H_2SO_4$  was made from sulfuric acid, *pro analysi* (Merck). The  $\alpha$ -emitter <sup>233</sup>U was purchased in the form of  $UO_3(H_2O)_2$  from AERE, Harwell, England. In most experiments, the initial concentration of U(VI) in the aqueous phase was  $6.9 \times 10^{-6}$  M, which is negligible in comparison with the total concentration of HA(B).

In experiments with  $\log [\text{HA}]_{\text{org}} = -5.50$ , the concentration of uranium(VI) was  $3.7 \times 10^{-5}$  M. Also in this case, the concentration of U in the organic phase was negligible in comparison with the concentration of HA (see below).

All experiments were carried out at 25°C in thermostated rooms. The practical details of the distribution experiments have been described in a previous paper <sup>4</sup>. The  $\alpha$ -activity was measured in a Tracerlab SC-16 windowless proportional counter. The distribution ratio  $q$  of <sup>235</sup>U was calculated as before <sup>4</sup>.

In the measurements, the aqueous phase contained 0.1 M H<sub>2</sub>SO<sub>4</sub>; thus we may calculate  $[\text{H}^+] = 0.133$  M, using the data of Bray and Liebhafsky <sup>10</sup>.

We decided to work with sulfate medium in order to bring the distribution ratio into a suitable range for measurement ( $3 > \log q > -3$ ). A 1 M HClO<sub>4</sub> medium might have been used, but extraction of some HClO<sub>4</sub> with TBP <sup>11</sup>, and of some uranium as UO<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>(TBP)<sub>2</sub>, might occur. Nitrate medium would not be suited for these studies, since uranium would be extracted — in the form of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(TBP)<sub>2</sub> or UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DBP)<sub>2</sub> — to an even greater extent than from perchlorate medium <sup>12-15</sup>.

#### CALCULATION OF $[\text{HA}]_{\text{org}}$ AND $[\text{B}]_{\text{org}}$

The symbols are in general the same as in our earlier work on similar systems <sup>9</sup>. Let us denote the concentrations of free HA and B in the organic phase as:

$$[\text{HA}]_{\text{org}} = a; [\text{B}]_{\text{org}} = b$$

Let  $K_d$  be the distribution constant for monomer HA between organic and aqueous phase,  $K_a$  the acidity constant of HA in the aqueous phase,  $K_2$  the equilibrium constant for dimerization of HA in the organic phase and  $K$  the association constant of HA and B. Then we have ( $[\text{HA}]$  and  $[\text{A}^-]$  refer to the aqueous phase):

$$[\text{HA}] = \alpha K_d^{-1}; [\text{A}^-] = \alpha K_d^{-1} K_a h^{-1}; [\text{H}_2\text{A}_2]_{\text{org}} = K_2 a^2; [\text{HAB}]_{\text{org}} = Kab$$

Since the volumes of the organic and aqueous phases are equal, we may simply add the concentrations in two phases; the »total concentrations» of HA and B are then:

$$A = a(1 + K_d^{-1} + K_d^{-1} K_a h^{-1}) + 2K_2 a^2 + Kab$$

$$B = b(1 + Ka)$$

Since  $K$  and  $K_2$  refer to reactions in the organic phase only, it seems reasonable that they would be almost the same as in previous studies <sup>9</sup> on the distribution between CCl<sub>4</sub> and 0.1 M HNO<sub>3</sub>, namely:

$$\log K_2 = 6.49; \log K = 2.84$$

In the first calculation, a value of  $K_d$  (determined for the 0.1 M HNO<sub>3</sub> medium), was used:  $\log K_d = -1.44$ . Due to the difference in ionic strength between 0.1 M HClO<sub>4</sub> and 0.1 M H<sub>2</sub>SO<sub>4</sub>,  $\log K_a$  was chosen as  $-0.98$  instead of  $-1.00$  (Ref.<sup>8</sup>). These values were used initially, since no radioactive DBP was available at the time, to measure the distribution of HA between CCl<sub>4</sub> and 0.1 M H<sub>2</sub>SO<sub>4</sub> directly. However, as we shall see later, the measurements on uranium distribution will suggest that the constants for the sulfuric acid system are somewhat different from those determined for 0.1 M HNO<sub>3</sub>. We

may note that Hardy and Scargill<sup>16</sup> give values of  $K_2$  and  $K_d$  with 1 M  $\text{HNO}_3$  that differ somewhat from our values<sup>9</sup> with 0.1 M  $\text{HNO}_3$ .

As already mentioned, the concentration of uranium is always so low in the organic phase that it can be neglected in comparison with A and B.

### THE DATA

The Tables 1 and 2 gives the primary experimental data which consist of the total concentrations  $A$  and  $B$ , the distribution ratio  $q$  and the calculated values for  $[\text{HA}]_{\text{org}} = a$  and  $[\text{B}]_{\text{org}} = b$ . The values of  $A$  and  $B$  have been chosen to give the values for  $a$  and  $b$ , using the known equilibrium constants.

*Table 1.* Data for the distribution of  $^{235}\text{U}$  between equal volumes of  $\text{CCl}_4$  and 0.1  $\text{H}_2\text{SO}_4$  at different total molar concentrations of DBP (=  $A$ ) and TBP (=  $B$ ). These concentrations have been calculated (see text) in such a manner that the concn. of free DBP was kept constant in the organic layer while the concn. of free TBP was varied stepwise. In Fig. 1 the distribution of  $\text{U(VI)}$  is plotted as  $\log q [\text{A}^-]^{-2}$  against  $\log [\text{HA}]_{\text{org}}$  (=  $\log a$ ) for different values of  $\log [\text{B}]_{\text{org}}$  (=  $\log b$ ).

$\log b$	$\log A$	$\log B$	$\log q$	$\log b$	$\log A$	$\log B$	$\log q$
$\log a = -3.5, \log [\text{A}^-] = -2.16$				$\log a = -4.75, \log [\text{A}^-] = -3.41$			
0	-0.070	0.086	2.01	0	-1.820	0.005	0.87
-1	-0.184	-0.914	2.10	-0.5	-2.172	-0.495	0.73
-2	-0.197	-1.914	2.08	-1.0	-2.390	-0.995	0.30
-3	-0.199	-2.914	2.06	-1.5	-2.492	-1.495	-0.10
-4	-0.199	-3.914	2.05	-2.0	-2.529	-1.995	-0.45
-5	-0.199	-4.914	2.04	-2.5	-2.542	-2.495	-0.69
$\log a = -4, \log [\text{H}^-] = -2.66$				$\log a = -5, \log [\text{A}^-] = -3.66$			
0	-0.866	0.029	1.96	-3	-2.545	-2.995	-0.77
-1	-1.133	-0.971	1.96	-4	-2.547	-3.995	-0.87
-2	-1.171	-1.971	1.86	-5	-2.548	-4.995	-0.90
-3	-1.175	-2.971	1.90	0	-2.097	0.003	-0.08, +0.03
-4	-1.176	-3.971	1.87	-0.5	-2.481	-0.498	-0.23
-5	-1.176	-4.971	1.94	-1	-2.745	-0.997	-0.65
$\log a = -4.25, \log [\text{A}^-] = -2.91$				$\log a = -5.25, \log [\text{A}^-] = -3.91$			
0	-1.213	0.017	1.84	-1.5	-2.876	-1.498	-1.16
-0.5	-1.461	-0.484	1.81	-2	-2.928	-1.997	-1.46
-1	-1.532	-0.983	1.85	-2.5	-2.947	-2.498	-1.60
-1.5	-1.629	-1.484	1.59	-3	-2.951	-2.997	-1.90
-2	-1.644	-1.983	1.47	-4	-2.955	-3.997	-1.92
-2.5	-1.650	-2.484	1.39	-5	-2.955	-4.997	-1.94
-3	-1.652	-2.983	1.37	0	-2.361	0.002	-0.89
-4	-1.652	-3.983	1.36	-0.5	-2.773	-0.499	-1.13
-5	-1.652	-4.983	1.37	-1	-3.065	-0.998	-1.58
$\log a = -4.5, \log [\text{A}^-] = -3.16$				$\log a = -5.5, \log [\text{A}^-] = -4.16$			
0	-1.529	0.009	1.42	-1.5	-3.225	-1.499	-2.01
-0.5	-1.836	-0.491	1.33	-2	-3.292	-1.998	-2.36
-1	-2.004	-0.991	1.17	-2.5	-3.314	-2.499	-2.78
-1.5	-2.075	-1.491	0.79	0	-2.620	0.001	-1.70
-2	-2.100	-1.991	0.67	-0.5	-3.040	-0.499	-1.88
-2.5	-2.108	-2.491	0.39	-1	-3.360	-0.999	-2.36
-3	-2.110	-2.991	0.40	-1.5	-3.544	-1.499	-2.87
-4	-2.111	-3.991	0.29				
-5	-2.112	-4.991	0.31				

Table 2. Data for the distribution of  $^{233}\text{U}$  between equal volumes of  $\text{CCl}_4$  and 0.1 M  $\text{H}_2\text{SO}_4$  or 0.133 M  $\text{HClO}_4$  at different total concentrations of DBP (=  $A$ ): In these experiments no TBP was added. The data are treated in Figs. 1 and 3.

aq medium	$\log A$	$\log q$	$\log A$	$\log q$
0.1 M $\text{H}_2\text{SO}_4$	-1.30	+1.74	-2.30	-0.24
	-1.70	+1.22	-2.70	-1.25
	-2.00	+0.48	-3.00	-1.97
			-3.30	-2.75
0.133 M $\text{HClO}_4$	-1.30	+1.89	-2.70	-0.48
	-2.00	+1.22	-3.00	-1.12
	-2.30	+0.81	-3.30	-1.71

In Fig. 1, the data are plotted in the form  $\log q[A^-]^{-2}$  versus  $\log [\text{HA}]_{\text{org}}$ . Points with the same symbol have the same calculated value for  $b$ . (The values of  $a$  and  $b$  were calculated with the set of constants for 0.1 M  $\text{HNO}_3$  and may thus have to be slightly corrected later on). The numbers in Fig. 1 denote the slope of the linear parts of the curves.

At the lowest value for  $b$ , up to  $\log b \sim -3$ , the experimental points approached the curve obtained for  $b = 0$ . As shown in earlier papers<sup>2-4</sup> this curve is determined in an inert solvent by the reaction



The slope of the limiting curve in Fig. 1 is not exactly 2.0 as one might have expected, but about 2.3. This discrepancy can probably be ascribed to small errors in the equilibrium constants used for the calculation of  $a$  and  $b$ .

At the highest values for  $a$ , the curves bend in the other direction, with a slope of  $-1.7$  instead of  $+2$ ; moreover, the addition of  $B$  now has no influence at all. This effect has not been studied more closely. It may be that  $\text{UO}_2\text{SO}_4$  is extracted to some extent and,  $\text{UO}_2^{2+}$  and  $\text{A}^-$  possibly form complexes in the aqueous phase. It should be noted also that in this region,  $\text{HA}$  is further polymerized in the organic phase according to physico-chemical experiments made at our institute. Furthermore, there may be minor impurities<sup>12,23</sup> in the sample of  $^{233}\text{U}$ , which could influence the measurements at  $100 > q < 0.01$ .

The fact that the curves spread out as  $\log b$  increases above  $-2.5$ , proves that  $B$  in some way enters into complexes with the uranium. (It should be noted that the complex between  $\text{HA}$  and  $B$  has been allowed for and the concentrations used in Fig. 1 are the calculated concentrations of free  $\text{HA}$  and  $B$ ).

As may be seen in Fig. 1 the slope of the curves decreases with increasing  $b$ . This indicates that some of the complexes, which may in general be written as  $\text{UO}_2\text{A}_2(\text{HA})_xB_y$ , contain less than 2  $\text{HA}$ . Thus the effect cannot be explained by addition compounds only.

At low  $[\text{HA}]_{\text{org}}$  the same upward bend in the curves is observed as previously<sup>4</sup> with the DBP-hexone system. In this case it was concluded, that in addition to  $\text{UO}_2\text{A}_2(\text{HA})_2$  a complex  $\text{UO}_2\text{A}_2(\text{hexone})_x$  was extracted at low  $[\text{HA}]$ .

Let us start with the simplest assumption that might be consistent with these data, namely that, besides  $\text{UO}_2\text{A}_2(\text{HA})_2$ , only the first substitution complex,  $\text{UO}_2\text{A}_2(\text{HA})\text{B}$ , appears in the organic phase.

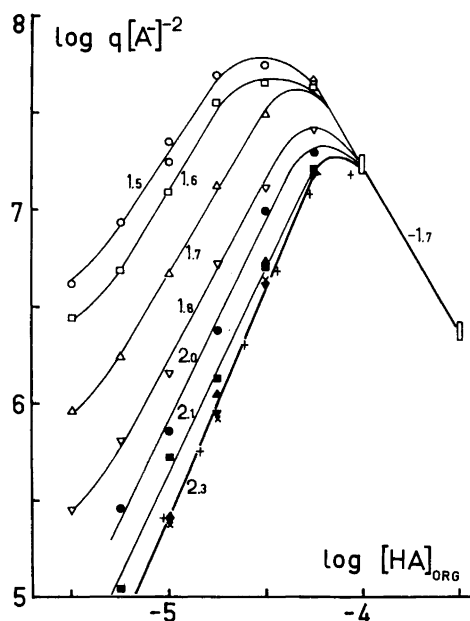


Fig. 1. The distribution of U(VI) between solutions of DBP (= HA) and TBP (= B) in  $\text{CCl}_4$  and 0.1 M  $\text{H}_2\text{SO}_4$ . Each curve represents a constant value of the pre-calculated molar concn. of free TBP,  $[\text{B}]_{\text{org}}$ . The limiting curve for  $[\text{B}]_{\text{org}} \leq 10^{-3}$  is shown as a thick line. The slopes of linear parts of the curves are noted in the figure. Symbols ( $\log [\text{B}]_{\text{org}}$ ):  $\circ$  (0),  $\square$  (-0.5),  $\triangle$  (-1),  $\nabla$  (-1.5),  $\bullet$  (-2),  $\blacksquare$  (-2.5),  $\blacktriangle$  (-3),  $\blacktriangledown$  (-4),  $\times$  (-5), and  $+$  ( $-\infty$ , no TBP). The distribution of  $^{233}\text{U}$  is independent of  $[\text{B}]_{\text{org}}$  at  $\log [\text{HA}]_{\text{org}} = -4$  and  $-3.5$ .

For this case, let us define the equilibrium constants

$$K_{20} = [\text{UO}_2\text{A}_2(\text{HA})_2]_{\text{org}} [\text{UO}_2^{2+}]^{-1} [\text{A}^-]^{-2} [\text{HA}]_{\text{org}}^{-2}$$

$$K_{11} = [\text{UO}_2\text{A}_2\text{HAB}]_{\text{org}} [\text{UO}_2^{2+}]_{\text{org}}^{-1} [\text{A}^-]^{-2} [\text{HA}]_{\text{org}}^{-1} [\text{B}]_{\text{org}}^{-1}$$

Moreover we use the conventional notation that  $[\text{UO}_2^{2+}]$  stands for the sum of all complexes of  $\text{UO}_2^{2+}$  including those with  $\text{SO}_4^{2-}$  with the aqueous medium\*. Assuming that  $\text{UO}_2\text{A}_2(\text{HA})_2$  and  $\text{UO}_2\text{A}_2\text{HAB}$  are the only species formed in the organic layer, the net distribution ratio is then:

$$q = ([\text{UO}_2\text{A}_2(\text{HA})_2]_{\text{org}} + [\text{UO}_2\text{A}_2\text{HAB}]_{\text{org}}) [\text{UO}_2^{2+}]^{-1} = [\text{A}^-]^{-2} (K_{20}a^2 + K_{11}ab)$$

$$\text{and } q[\text{A}^-]^{-2}a^{-2}K_{20}^{-1} = 1 + K_{11}K_{20}^{-1}ba^{-1}$$

\* The amount of  $\text{UO}_2^{2+}$  bound to  $\text{SO}_4^{2-}$  can be estimated from separate experiments with 0.133 M  $\text{HClO}_4$  (cf. Fig. 3). These data indicate that  $[\text{UO}_2^{2+}]_{\text{H}_2\text{SO}_4} [\text{UO}_2^{2+}]^{-1}_{\text{HClO}_4} = 1 + \beta_1[\text{SO}_4^{2-}] + \beta_2[\text{SO}_4^{2-}]^2 \sim 10$ , which agrees fairly well with the value that can be estimated from values of Davies and Monk<sup>17</sup> for  $\beta_1$  and  $\beta_2$ .

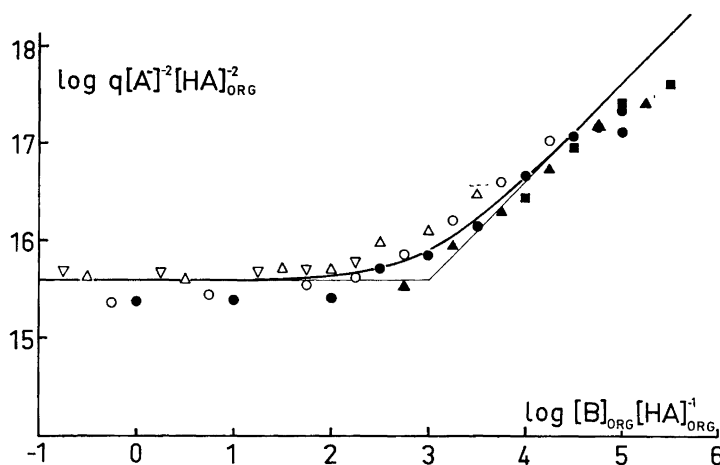


Fig. 2. Plot based on the assumption of the formation of a substitution complex in the  $\text{CCl}_4$  phase,  $\text{UO}_2\text{A}_2(\text{HA})\text{B}$ . The normalized curve  $\log Y = \log(1 + X)$  is fitted to the data.  $K_{20}$  and  $K_{20}K_{11}^{-1}$  (see text) are obtained from the position of the asymptotes (thin lines) to the curve. Symbols denote different constant values of  $\log [\text{HA}]_{\text{org}}$ :  $\nabla$  ( $-4.25$ ),  $\Delta$  ( $-4.50$ ),  $\circ$  ( $-4.75$ ),  $\bullet$  ( $-5.00$ ),  $\blacktriangle$  ( $-5.25$ ), and  $\blacksquare$  ( $-5.50$ ). The variables are calculated from data in Table 1.

In Fig. 2, the quantity  $\log q[\text{A}^-]^{-2}a^{-2}$  is plotted as a function of  $\log ba^{-1}$ . Values on the descending parts of the curves in Fig. 1 are not included in Fig. 2. It can be seen from the figure that the experimental points fall reasonably well on the normalized curve  $\log Y = \log(1 + X)$ . From the position of the asymptotes of the normalized curve one may calculate the values  $\log K_{20} = 15.6 \pm 0.2$  and  $\log K_{20} - \log K_{11} = 3.0 \pm 0.2$ . Hence  $\log K_{11} = 12.6 \pm 0.2$ .

It thus seems that the data may be rather well explained by assuming that one HA in the original complex is substituted with B. From the present data there is no strong evidence for the second complex,  $\text{UO}_2\text{A}_2\text{B}_2$ , which, in the diagram, Fig. 2, would have caused a steeper slope of the curve at high  $ba^{-1}$ . However, it is quite possible that the second type of substitution complex, which has been proposed by Kennedy<sup>6</sup>, may well exist with other more basic substituting substances B, for instance with phosphine oxides,  $\text{R}_3\text{PO}$ .

#### CONCLUSION

It does not seem possible to explain the data on the increased (synergic) extraction of uranyl by DBP in the presence of TBP by assuming the formation of addition compounds only, since with this assumption, one would have had a constant slope of 2 to the right in Fig. 1. In fact the slope really decreases with increasing  $b$ .

On the other hand, the substitution hypothesis seems to explain the data well; the diagram in Fig. 2 gives a good fit of the theoretical curve assuming

only one substitution. Thus, in addition to  $\text{UO}_2\text{A}_2(\text{HA})_2$  we would have  $\text{UO}_2\text{A}_2(\text{HA})\text{B}$  in the following concentration ranges: 0.0003 — 0.06 M DBP (= HA) and 0 — 1 M TBP (= B).

#### ADJUSTMENT OF $K_1K_d^2$

It remains however, to explain why in Fig. 1 the limiting slope for  $b \rightarrow 0$  is +2.3 rather than +2.0 because the difference is, we feel, outside of the experimental error. There seems to be no reason to doubt the formula  $\text{UO}_2\text{A}_2(\text{HA})_2$  for the predominant complex in the organic phase<sup>2-4</sup> since it has been proved in many other systems. Small amounts<sup>12,23</sup> of the decay products of  $^{232}\text{U}$  present in the sample of  $^{233}\text{U}$  would rather have decreased the slope, and it is therefore reasonable to suppose that the difference is due to small errors in the values assumed for the equilibrium constants that determine  $a$  and  $b$ . Let us consider the case of a solution with no B added. The total concentration of A is then

$$A = [\text{HA}]_{\text{org}} + [\text{HA}] + [\text{A}^-] + 2[\text{H}_2\text{A}_2]_{\text{org}} = a(1 + K_d^{-1}(1 + K_a h^{-1})) + 2a^2 K_2$$

With the previous definition of  $K_{20}$  we have

$$[\text{UO}_2\text{A}_2(\text{HA})_2]_{\text{org}} = K_{20}[\text{UO}_2^{2+}][\text{A}^-]^2 a^2 = [\text{UO}_2^{2+}]K_{20}a^4 h^{-2} K_d^{-2} K_a^2 = q[\text{UO}_2^{2+}]$$

In these experiments, the hydrogen ion concentration  $h$  is a constant, and we may simplify these equations. Normalizing, we find

$$A = \alpha + L_2 \alpha^2 \text{ and } q = L_1 \alpha^4, \text{ where}$$

$$\alpha = a(1 + K_d^{-1}(1 + K_a h^{-1})) \simeq a K_d^{-1}(1 + K_a h^{-1})$$

$$L_1 = K_{20} h^{-2} K_a^2 (1 + K_d^{-1}(1 + K_a h^{-1}))^{-4} \simeq K_{20} h^{-2} K_d^2 K_a^2 (1 + K_a h^{-1})^4$$

$$L_2 = 2K_2 (1 + K_d^{-1}(1 + K_a h^{-1}))^{-2} \simeq 2K_2 K_d^2 (1 + K_a h^{-1})^{-2}$$

$L_2$  and  $L_1$  may be obtained by plotting on one axis (Fig. 3)

$$\log A - \frac{1}{4} \log q = \log (1 + L_2 \alpha) - \frac{1}{4} \log L_1$$

and, on the other axis,

$$\frac{1}{4} \log q = \log \alpha + \frac{1}{4} \log L_1$$

Comparing this plot with the normalized curve,  $Y = \log (1 + X)$  we find, from the positions of the coordinates,

$$\frac{1}{4} \log L_1 - \log L_2 = 0.35 \text{ and } \frac{1}{4} \log L_1 = 2.74$$

Using  $K_a h^{-1} = 0.8$  we obtain

$$\log K_2 + 2 \log K_d = 3.3_0$$

whereas the value for this sum was 3.61 for nitrate medium. Fig. 3 also gives the corresponding data for 0.133 M  $\text{HClO}_4$ , which can be fitted, within the experimental error, with  $\log K_2 K_d^2 = 3.61$ , the same value as in 0.1 M  $\text{HNO}_3$ .

For 0.1 M  $\text{H}_2\text{SO}_4$  we may accept  $\log K_2 K_d^2 = 3.3_1$  assuming  $\log K_2 = 6.49$  as with 0.1 M  $\text{HNO}_3$  and thus giving  $\log K_d = -1.59$ . Using these constants



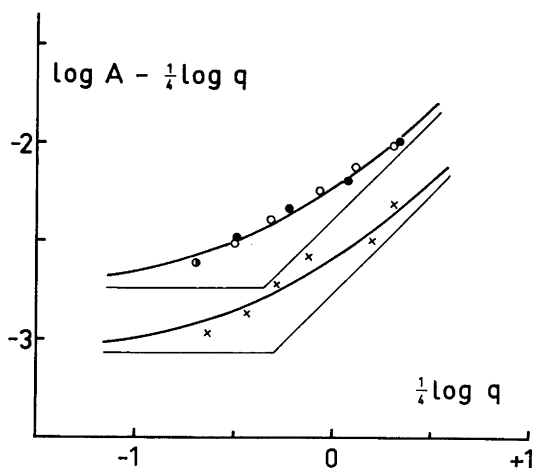


Fig. 3. Determination of  $K_2K_d^2$  for the 0.1 M  $H_2SO_4$  medium. The normalized curve  $\log Y = \log(1 + X)$  is fitted to the data:  $\circ$  experiments with no TBP,  $\bullet$  experiments with  $[TBP]_{org} \leq 10^{-2}M$ ,  $\times$  aq. phase 0.133 M  $HClO_4$ , no TBP. The point of intersection of the asymptotes to the curves gives the values of  $\frac{1}{4} \log L_1 - \log L_2$  and  $\frac{1}{4} \log L_1$  (see text).

the data in Table 1 were recalculated. They are plotted in Fig. 4, and it is seen that the spread is less than in Fig. 2. This gives additional support to the interpretation of the nature of the complexes  $UO_2A_2(HA)_xB_y$ . The deviation from the theoretical curve at high  $ba^{-1}$  is probably due to a decrease in

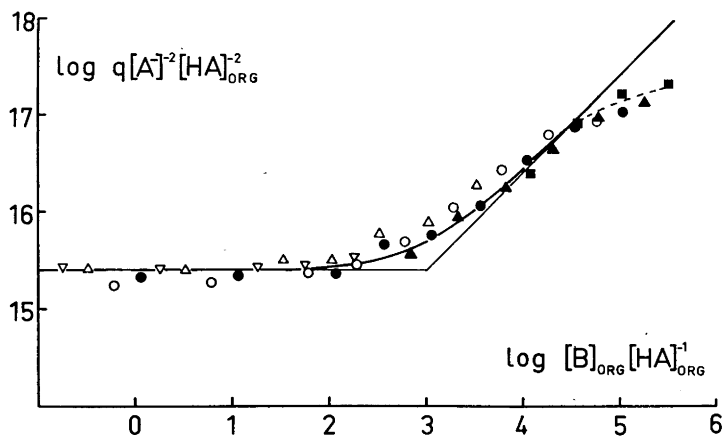


Fig. 4. Plot based on recalculated values of  $[HA]_{org}$  ( $= a$ ) and  $[B]_{org}$  ( $= b$ ) using  $\log K_d = -1.59$  instead of  $-1.44$  (cf. Fig. 2). The symbols refer to the same concentrations of DBP as in Fig. 2. The curve  $\log Y = \log(1 + X)$  is fitted to the data; deviation from this curve occurs with  $b = 0.0316$  and 1 M. The position of the asymptotes (thin lines) gives  $\log K_{20} = 15.4 \pm 0.2$  and  $\log K_{20}K_{11}^{-1} = 3.0 \pm 0.2$ .

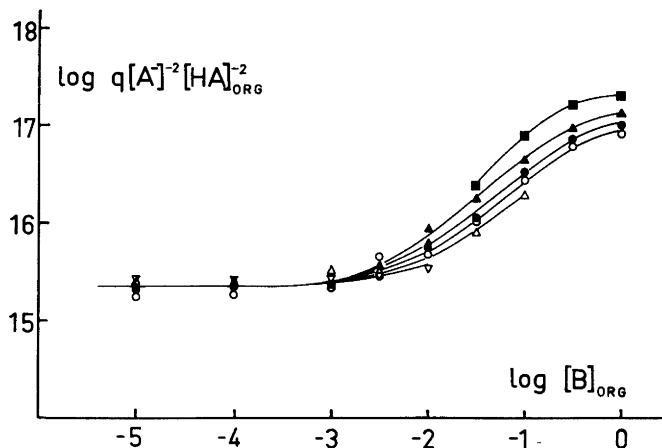


Fig. 5. Attempt to explain the synergic effect with the formation of  $\text{UO}_2\text{A}_2(\text{HA})_2\text{B}$ . The choice of the variables is explained in the text. The symbols are defined in Fig. 2.

the activity coefficient of TBP in  $\text{CCl}_4$  at  $b = 0.317$  and 1 M (undiluted TBP is 3.66 M). From Fig. 4 one may calculate  $\log K_{20} = 15.4 \pm 0.2$  and  $\log K_{11} = 12.4 \pm 0.2$ .

It may be worthwhile to see whether the data can be explained by a simple addition mechanism, as proposed by Brown *et al.*<sup>1</sup>, even if the curves in Fig. 1 are not favorable for such a hypothesis. If this were so, we would, instead of  $K_{11}$ , have to consider the equilibrium constant:

$$K_{21} = [\text{UO}_2\text{A}_2(\text{HA})_2\text{B}]_{\text{org}}[\text{UO}_2^{2+}]^{-1}[\text{A}^-]^{-2}[\text{HA}]_{\text{org}}^{-2}[\text{B}]_{\text{org}}^{-1}$$

As before, we would have obtained the expression

$$q[\text{A}^-]^{-2}a^{-2}K_{20}^{-1} = 1 + K_{20}^{-1}K_{21}b$$

Thus, if the experimental data had been plotted as  $\log q[\text{A}^-]^{-2}a^{-2}$  versus  $\log b$ , a single curve should have resulted, which would have been fitted with a normalized curve  $\log Y = \log(1 + X)$ . As seen in Fig. 5, the spread is considerable at high  $b$  where the complex  $\text{UO}_2\text{A}_2(\text{HA})_2\text{B}$  would be formed. As in Fig. 4 the curves fall off at  $b = 0.317$  and 1 M.

The calculations we have made in this part support the conclusion that was drawn from the uncorrected data in Figs. 1 and 2.

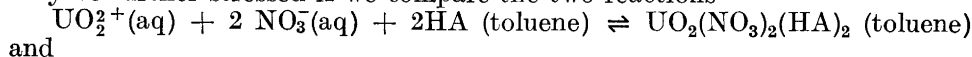
#### DISCUSSION

In calculating the economy of using the synergic effect with dialkyl phosphates, one must consider not only the formation of substitution complexes like  $\text{UO}_2\text{A}_2(\text{HA})\text{B}$  but also the dimerization of HA and the complex formation between HA and B in the organic phase.

• If the cost of organic phosphorus per mole of uranium to be extracted is important, then the economy of a process should gain if the more expensive

dialkyl phosphates (HA) can in part be replaced by the less expensive trialkyl phosphates (B). However, if the constants  $K_{20}$  and  $K_{11}$  are compared, it may be seen that the replacement of HA with B requires a large value for  $[B]_{\text{org}}[HA]_{\text{org}}^{-1}$  (cf. Figs. 2 and 4). The reason may be that the extra HA in  $UO_2A_2(HA)_2$  are not only bound with the phosphoryl oxygens to U (which probably has the coordination number of 8 as in  $UO_2(CH_3COO)_3$ , Ref.<sup>18</sup>), but also with strong hydrogen bonds to the oxygen atoms in  $UO_2^{2+}$ ; the basicity of the PO groups in DBP and TBP should be about the same.

The difference between DBP (= HA) and TBP (= B) as solvate molecules may be further stressed if we compare the two reactions



From data as Hardy<sup>12</sup> and of Healy and Kennedy<sup>19</sup> we may calculate the equilibrium constants of these reactions as  $\log K = 6.76$  and  $1.44$ . With the more basic compound tributyl phosphine oxide,  $Bu_3PO$ , the value of  $\log K$  is  $4.62$  for benzene.

It may be noted that Brown *et al.*<sup>1</sup> have shown that  $q$  increases more (using dioctyl phosphate as HA), if the more basic tributyl phosphine oxide (TBPO) is added than if TBP is added. It is possible that B = TBPO can replace two HA = DBP (cf. Kennedy<sup>7</sup>) at a value of  $[B]_{\text{org}}[HA]_{\text{org}}^{-1}$  where TBP only replaces one DBP. In the case of hexone<sup>4</sup>, which is 8 M, evidence was found of  $UO_2A_2$  at low [HA].

The complex formation between HA and B will diminish the loss of HA to the aqueous phase, but at the same time, this reaction will decrease the amount of free HA and B that can react with  $UO_2^{2+}$ . If the total load of organic phosphate per unit volume of the organic diluent, *e.g.* kerosene, needs to be kept low, then it might be more favorable to increase the concn. of HA than to add B. The situation should be different with a chelating agent like TTA, where the acid hydrogen is engaged in an intramolecular hydrogen bond and the tendency for the formation of  $H_2A_2$  and HAB is thereby weak (cf. Edgington and Irving<sup>20</sup>).

As the extraction of tri- and tetravalent ions seems to decrease on the addition of neutral esters of phosphoric acid (cf. Refs.<sup>21,22</sup>), it may be possible in many cases to increase the separation of di- and tri- or tetravalent ions by adding neutral ligands to the organic layer.

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