

## Some Reactions between Uranium(VI) and Di-*n*-butyl Phosphate(DBP) in Chloroform and Methyl *Isobutyl* Ketone (Hexone)

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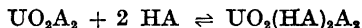
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The distribution of U(VI) between solutions of di-*n*-butyl phosphate (DBP=HA) in chloroform or hexone (methyl *isobutyl* ketone) and 1 M HClO<sub>4</sub>—NaClO<sub>4</sub> solutions has been investigated at 25°C.

The data demonstrate the presence of a complex UO<sub>2</sub>(HA)<sub>2</sub>A<sub>2</sub> with four molecules of DBP per uranyl ion in both solvents at low concentrations of uranium. The constants for the equilibrium

$UO_2^{2+} (aq) + 2 H_2A_2(org) \rightleftharpoons UO_2(HA)_2A_2 (org) + 2 H^+ (aq)$   
are 10<sup>3.58</sup> (chloroform) and 10<sup>4.50</sup> (hexone).

In addition to this complex an uranyl complex UO<sub>2</sub>A<sub>2</sub> with only two molecules of DBP was found in hexone at lower concentrations of DBP. The equilibrium constant for the reaction



in the hexone phase was 10<sup>4.78</sup>.

With increasing uranium concentration in the chloroform phase the ratio [U]<sub>org</sub>/[DBP]<sub>org</sub> approaches 0.5 thus indicating the composition (UO<sub>2</sub>)<sub>n</sub>A<sub>2n</sub> of the extractable uranyl complex. No definite conclusions about the degree of polymerization can be drawn from the distribution experiments, but isopiestic data of Baes *et al.*<sup>5</sup> indicate that *n* increases to 6 as [U]<sub>org</sub>/[DBP]<sub>org</sub> approaches 0.5.

Dialkyl phosphates, (RO)<sub>2</sub>PO<sub>2</sub>H, have proved to be very useful as liquid-extracting agents for lanthanide and actinide ions of various oxidation states. Extensive work on the extraction of U(VI) from acidic sulfate-process liquors has been carried out at Oak Ridge<sup>1</sup> (Dapex process) and several radiochemical separation procedures have been worked out at Argonne<sup>2</sup>. Di-*n*-butyl phosphate (DBP) has been used at FOA<sup>3</sup> for the separation of <sup>90</sup>Sr and <sup>90</sup>Y.

The reactions between metal ions and the dialkyl phosphates can be correctly understood only if one takes into account the very pronounced tendency of the dialkyl phosphates to dimerize. Although Kosolapoff and Powell<sup>4</sup> have reported dimerization of dialkyl phosphinic acids, R<sub>2</sub>PO<sub>2</sub>H,

no studies on the dialkyl phosphoric acids have been published in the open literature until recently<sup>5-7</sup>. It was shown by Dyrssen<sup>6</sup> that the dimerization constant of DBP in chloroform is much larger than for carboxylic acids, and that dimerization also takes place in oxygen-containing solvents like hexone and water.

The aim of the present investigation was to study the extraction of the uranyl ion from 1 M HClO<sub>4</sub>-NaClO<sub>4</sub> solutions with DBP in two different solvents, chloroform and hexone. Calculations on the distribution data throw some light on the reactions that can take place in the organic phase.

### EXPERIMENTAL

*Reagents.* The DBP, (C<sub>4</sub>H<sub>9</sub>O)<sub>2</sub>PO<sub>3</sub>H, was kindly supplied by Albright and Wilson Ltd., London. Potentiometric titration with alkali and analysis for C and H showed the compound to be at least 99 % pure. The remaining non-acidic impurities are probably tri-butyl phosphate and butanol. The chloroform was washed three times with twice its volume of water to remove the 1 % alcohol. The hexone (methyl isobutyl ketone) was washed with alkali, acid, and finally water. The 1 M HClO<sub>4</sub>-NaClO<sub>4</sub> solutions were prepared from analytical grade reagents. The solutions of U(VI) in 0.1 M HClO<sub>4</sub> + 0.9 M NaClO<sub>4</sub> were prepared from "nuclear grade" UO<sub>3</sub>. The <sup>233</sup>U was purchased from AERE, Harwell, England. The solution contained 5 μC of <sup>233</sup>U per mg of U.

*Distribution measurements.* Equal volumes (5 or 10 ml) of a solution of DBP in chloroform or hexone and a 1 M HClO<sub>4</sub>-NaClO<sub>4</sub> solution containing U(VI) were shaken for 2 h. The two liquid phases were then separated by centrifugation.

In the concentration range below 0.0025 M the uranium was analyzed by alpha-counting of 1 ml of the organic phase after evaporation of the solvent and removal of most of the DBP at 200°C. The distribution ratio, *q*, could then be calculated as

$$q = \frac{A}{C-A}$$

A = α-disintegrations per min and ml of the organic phase

C = total activity (cpm per ml) added.

For the determination of larger *q*-values part of the aqueous phase was shaken with an equal volume of a fresh solution of DBP (with the same concentration as in the first extraction). The distribution ratio is then calculated as

$$q = \frac{A-B}{B}$$

B = α-disintegrations per min and ml of the organic phase after the second extraction.

The alpha-activity was measured in a Tracerlab SC-16 windowless proportional counter.

Concentrations of uranium larger than 0.0025 M were analyzed spectrophotometrically at 375 mμ using a thiocyanate method<sup>8</sup>: The sample + 1 ml of 10 % SnCl<sub>2</sub> + 0.5 ml of conc. H<sub>2</sub>SO<sub>4</sub> + 15 ml of saturated NH<sub>4</sub>SCN in acetone was diluted with water to 25 ml and measured 3 min after addition of the reagent.

The following constants, from Ref.<sup>8</sup>, are used for the calculation of [H<sub>2</sub>A<sub>2</sub>]<sub>org</sub>, [HA]<sub>org</sub>, [HA] and [A<sup>-</sup>] (ionic strength = 1 M HClO<sub>4</sub>-NaClO<sub>4</sub>):

$$\begin{aligned} [H^+] [A^-] [HA]^{-1} &= 10^{-1.00} \\ [HA]_{org} [HA]^{-1} &= 10^{0.34} \text{ (chloroform), } 10^{1.49} \text{ (hexone)} \\ [H_2A_2]_{org} [HA]^{-2} &= 10^{4.48} \text{ (chloroform), } 10^{1.19} \text{ (hexone)} \end{aligned}$$

C<sub>A</sub> is the initial concentration of DBP in the organic phase. [ ]<sub>org</sub> and [ ] denote concentrations in the organic and aqueous phases, respectively.

Table 1. The distribution of  $^{233}\text{U}$  between chloroform and 1 M perchlorate solutions as a function of  $C_A$  and  $[\text{H}^+]$ . The initial conc. of U(VI) in the aqueous phase was  $2.69 \times 10^{-6}$  M.

$C_A$	A	B	$q = \frac{\log \frac{A-B}{B}}$	$q = \frac{\log A}{C-A}$	$\log [\text{HA}]$
[H <sup>+</sup> ] = 0.1 M					
0.5	6 419	5.0	+3.11		-2.89
0.2	8 137	14.7	+2.74		-3.09
0.1	7 419	25.8	+2.46		-3.24
0.08	7 712	33	+2.37		-3.29
0.05	8 165	57	+2.15		-3.39
0.03	7 529	126	+1.77		-3.50
0.02	8 282	211	+1.58		-3.60
0.015	7 344	410	+1.23		-3.66
0.01	6 733			+0.78	-3.75
0.004	4 294			+0.08	-3.96
0.002	1 581			-0.60	-4.12
0.001	423			-1.25	-4.28
[H <sup>+</sup> ] = 0.31 M					
0.05	8 333	322	+1.40		-3.39
0.01	2 896			-0.23	-3.75
0.004	916			-0.88	-3.96
0.002	218			-1.54	-4.12
0.001	48			-2.21	-4.27
[H <sup>+</sup> ] = 0.91 M					
0.05	6 110	1 449	+0.51		-3.39
0.01	720			-1.00	-3.75
0.004	113			-1.84	-3.96
0.002	36			-2.34	-4.12
0.001	6.0			-3.12	-4.27

## RESULTS

*A. Experiments with low concentrations of U(VI).* The results obtained with  $^{233}\text{U}$  are given in Tables 1 (chloroform) and 2 (hexone). If these data are plotted as  $\log q$  against  $\log C_A[\text{H}^+]^{-1}$ , a marked difference between the two solvents is revealed (Fig. 1). The chloroform values lie on a straight line with a slope of 2. The deviation from this line at higher values of  $C_A[\text{H}^+]^{-1}$  ( $> 10^{-0.2}$ ) may be ascribed to the formation of the complexes  $\text{UO}_2\text{A}^+$  and  $\text{UO}_2\text{A}_2$  in the aqueous phase<sup>9</sup>. The values from the distribution experiments with hexone, however, lie approximately on a line with a slope equal to 2.72. The deviation from this line at higher values of  $q$  is very abrupt and may be caused by an experimental error due to the fact that the aqueous phase may be slightly contaminated with the highly radioactive and lighter hexone phase when part of the aqueous bottom-layer is drawn off for the second extraction (and determination of B). This error will have a marked influence on the measurements only at high  $q$ -values.

Since the extraction of uranium by chloroform is proportional to  $C_A^2[\text{H}^+]^{-2}$  and since it is known<sup>6</sup> that the dimerization of DBP in chloroform is almost

Table 2. The distribution of  $^{238}\text{U}$  between hexone and 0.1 M  $\text{HClO}_4$  + 0.9 M  $\text{NaClO}_4$  as a function of the initial conc. of DBP in the hexone phase,  $C_A$ . The initial conc. of U(VI) in the aqueous phase was  $2.69 \cdot 10^{-6}$  M.

$C_A$	A	B	$q = \frac{\log \frac{A-B}{B}}$	$q = \frac{\log \frac{A}{C-A}}$	$\log [\text{HA}]$ ( $=\log [A^-]$ )
0.5	5 358	12.0	+2.65		-2.44
0.2	7 091	14.7	+2.68		-2.68
0.1	7 726	13.3	+2.76		-2.87
0.1	5 777	13.3	+2.65		-2.87
0.07	6 455	12.0	+2.73		-2.97
0.05	7 519	21.3	+2.55		-3.07
0.04	6 516	28	+2.36		-3.14
0.04	7 262	31	+2.37		-3.14
0.03	6 129	78	+1.89		-3.22
0.02	6 349	203	+1.48		-3.36
0.015	6 527	508	+1.07		-3.45
0.012	5 899	865	+0.76		-3.54
0.009	5 401	1 644	+0.36		-3.65
0.008	5 203	1 943	+0.22		-3.69
0.007	4 114			+0.17	-3.74
0.006	2 788			-0.17	-3.80
0.005	1 973			-0.40	-3.87
0.004	1 377			-0.60	-3.96
0.003	729			-0.93	-4.07
0.002	318			-1.32	-4.25
0.0015	158			-1.63	-4.37
0.001	87			-1.89	-4.55

complete at concentrations  $\geq 0.001$  M, the following reaction will describe the data in Fig. 1 when  $C_A[\text{H}^+]^{-1} < 10^{-0.2}$ :



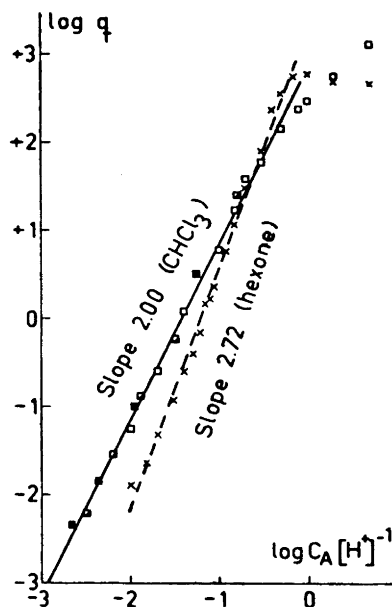
The equilibrium constant may approximately ( $C_A/2 = [\text{H}_2\text{A}_2]_{\text{org}}$ ) be calculated as

$$\log K = \log q + 2 \log [\text{H}^+] - 2 \log C_A/2 = 3.46$$

The same principle reaction was found in a study of the extraction of U(VI) with dioctyl phosphate in hexane from 2 M acid perchlorate solutions ( $\log K = 4.60 \pm 0.04$ ) recently published by Baes *et al.*<sup>5</sup> It has thus been demonstrated that the uranyl ion reacts with 4 molecules of dialkyl phosphates in inert solvents. Similar results have been found with other metal ions<sup>3,10</sup>, e.g.  $\text{Y}(\text{HA})_3\text{A}_3$ .

The results with hexone can be explained if one takes into account the existence of the DBP monomer and the uranyl complex  $\text{UO}_2\text{A}_2$  due to reactions between these species and the solvent. The reaction with DBP leads to a fairly low value of the dimerization constant  $k_2$  in hexone and a higher value of the distribution constant of the monomer as compared with chloroform<sup>6</sup>. The difference between the behavior of DBP in chloroform (fulldrawn curve)

Fig. 1. The distribution of  $^{238}\text{U}$  between a solution of di-*n*-butyl phosphate (DBP) in chloroform or hexane and 1 M  $\text{HClO}_4$ - $\text{NaClO}_4$ . Chloroform data:  $\square$  0.1 M  $\text{H}^+$ ,  $\blacksquare$  0.31 M  $\text{H}^+$ ,  $\blacksquare$  0.91 M  $\text{H}^+$ . Hexane data:  $\times$  0.1 M  $\text{H}^+$ .  $q$  = distribution ratio  $[\text{U}]_{\text{org}}/[\text{U}]_{\text{aq}}$ .  $C_A$  = initial conc. of DBP in the organic phase. The data are given in Tables 1 and 2.



and hexane (dashed curve) is shown in Fig. 2 and may be explained by the fact that the oxygen atom in hexane is a good acceptor for the hydrogen atom in DBP.

Some conclusions on the reactions between  $\text{UO}_2\text{A}_2$  and HA in hexane may be drawn from a plot of  $\log q[\text{A}^-]^{-2}$  against  $\log [\text{HA}]$  (or  $\log [\text{HA}]_{\text{org}}$ ). The

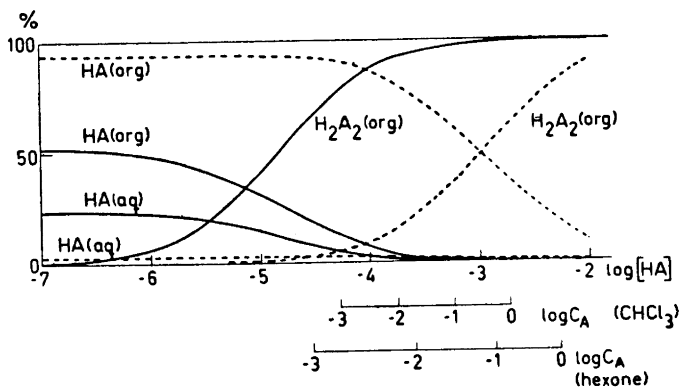


Fig. 2. The percentage of different DBP species in the two-phase systems chloroform/0.1 M  $\text{HClO}_4$  + 0.9 M  $\text{NaClO}_4$  (full-drawn curves) and hexane/0.1 M  $\text{HClO}_4$  + 0.9 M  $\text{NaClO}_4$  (dashed curves) as a function of the conc. of HA (DBP monomer) in the aqueous phase. The volumes of the two phases are equal.  $[\text{H}^+] = k_a$  and  $[\text{HA}] = [\text{A}^-]$ . The diagram is based on data given in the text.

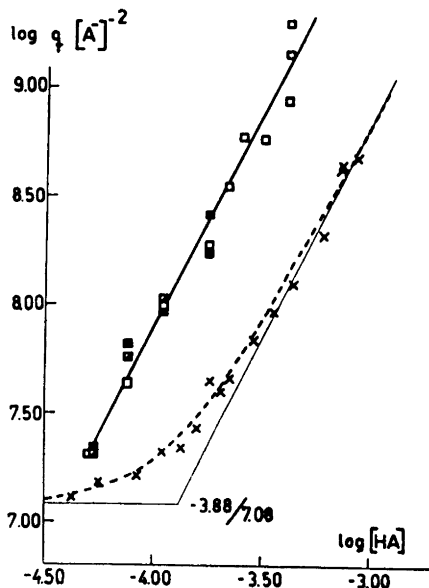


Fig. 3. Variation of  $q[A^-]^{-2}$  with  $[HA]$ . These functions are calculated from data given in Tables 1 and 2. Fulldrawn line: chloroform-DBP system. Dashed curve: hexone-DBP system. The symbols and experimental points are the same as in Fig. 1. The horizontal asymptote to the hexone curve corresponds to  $q[A^-]^{-2} = \lambda_2\beta_2$  and the equation for the asymptote with slope 2 is  $q[A^-]^{-2} = \kappa\lambda_2\beta_2[HA]^2$ ; the constants  $\lambda_2$ ,  $\beta_2$  and  $\kappa$  are defined in the text.

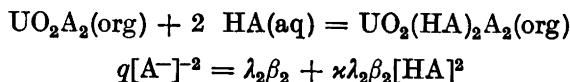
data in Fig. 1 (except those for  $\log C_A[H^+]^{-1} > -0.2$ ) are therefore replotted in Fig. 3. Again the values for chloroform lie on a straight line with a slope of 2 demonstrating the presence of the complex  $UO_2(HA)_2A_2$ . The distribution with hexone is proportional to  $[A^-]^2(1 + [HA]^2)$ , which demonstrates the presence of both  $UO_2A_2$  and  $UO_2(HA)_2A_2$  in the hexone phase. The expression for the distribution ratio thus contains an additional term:

$$q = \frac{[UO_2A_2]_{org} + [UO_2(HA)_2A_2]_{org}}{[UO_2^{2+}]}$$

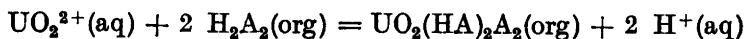
or, if we introduce the complexity and distribution constants  $\beta_2$  and  $\lambda_2$

$$\beta_2 = [UO_2A_2][UO_2^{2+}]^{-1}[A^-]^{-2}; \quad \lambda_2 = [UO_2A_2]_{org}[UO_2A_2]^{-1}$$

and the constant  $\kappa$  of the equilibrium



The values of  $\log \lambda_2\beta_2 = 7.08$  and  $\log \kappa = 7.76$  may be calculated from Fig. 3. The data give no evidence for the existence of an intermediate complex  $UO_2(HA)A_2$  in appreciable amounts. Using the constants given above for the dissociation, distribution and dimerization of DBP the values of  $\log K$  for the reaction



may be calculated as 3.58 (chloroform) and 4.50 (hexone).

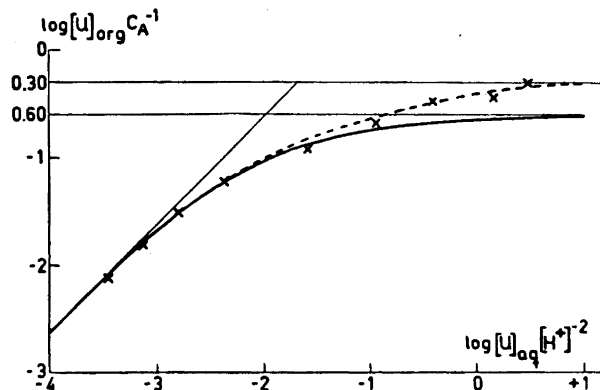


Fig. 4. The effect of increasing uranium concentration on the extraction of U(VI) by a solution of 0.04 M DBP in chloroform. The data are plotted as  $\log [U]_{\text{org}} C_A^{-1}$  against  $\log [U]_{\text{aq}} [H^+]^{-2}$ . The full-drawn curve is calculated assuming only the complex  $UO_2(HA)_2A_2$  in the chloroform phase. The dashed curve is calculated assuming that, in addition to  $UO_2(HA)_2A_2$ , the dinuclear complex  $(UO_2)_2A_4$  is formed in the chloroform phase.

Although such experiments as these cannot decide whether a complex is formed between hexone and  $UO_2A_2$ , the presence of  $UO_2A_2$  in hexone and not in chloroform is very likely due to such a complex formation. Reactions between  $UO_2A_2$  and hexone might be studied by distribution experiments with solutions of hexone in chloroform. Calculations on such data presuppose, however, a corresponding study of DBP in order to be able to calculate the variation of  $[HA]$  with  $[\text{hexone}]_{\text{CHCl}_3}$ .

It is thus possible to explain that the hexone data in Fig. 1 do not follow a straight line with a slope 2 by assuming the presence of HA and  $UO_2A_2$  in the hexone phase. Similar values of the slope, that are higher than 2 have been reported by Stewart and Hicks<sup>11</sup>. However, their results are probably further complicated by the fact that they use nitric acid. It is therefore quite

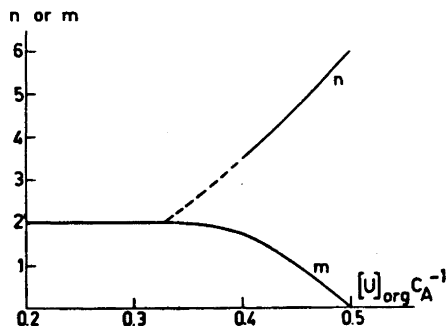


Fig. 5. Calculated mean values of  $n$  and  $m$  of the complex  $(UO_2)_n(HA)_m A_{2n}$  in dioctyl phosphate-hexane solutions as a function of  $[U]_{\text{org}} C_A^{-1}$ . The calculations (see text) are based on data given by Baes *et al.*<sup>5</sup>, Fig. 2.

Table 3. The distribution of U(VI) between a solution of 0.04 M DBP in chloroform and 0.1 M HClO<sub>4</sub> with increasing conc. of uranium. The volumes of the two phases are equal.

$[\text{UO}_2^{2+}]_{\text{aq}}$ <sup>a</sup> M	$q$	$[\text{H}^+]^{\text{b}}$ M	$\log \frac{[\text{U}]_{\text{aq}}}{[\text{H}^+]^2}$	$\log \frac{[\text{U}]_{\text{org}}}{0.04}$
0.08	0.332	0.1399	+0.49	-0.30
0.04	0.595	0.1298	+0.17	-0.43
0.02	2.09	0.1270	-0.40	-0.47
0.01	5.32	0.1168	-0.94	-0.68
0.005	15.0	0.1094	-1.58	-0.93
0.0025	54.4	0.1048	-2.38	-1.22
0.00125	76.2	0.1024	-2.81	-1.51
0.0006277	81.4	0.1012	-3.13	-1.81
0.0003152	88.3	0.1006	-3.46	-2.11
0	95.5	0.1000	-	-
(extrapol.) $2.69 \times 10^{-6}$	95.5 <sup>c</sup>	0.1000	-	-

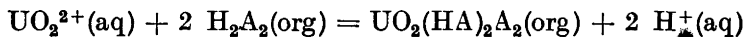
<sup>a</sup>) Initial conc. of U (VI) in the aqueous phase.

<sup>b</sup>) Calculated from  $0.1000 + 2[\text{U}]_{\text{org}}$ .

<sup>c</sup>) Interpolated from values in Table 1.

possible that some uranium was extracted as uranyl nitrate into the organic phase (butyl ether or hexane), DBP acting like a tri-alkyl phosphate (*e.g.* TBP). Other oxygen-containing solvents such as TBP, ethers, esters, and alcohols may react in a similar way to hexone.

*B. Experiments with increasing uranium concentration.* In order to study the possible formation of  $\text{UO}_2\text{A}_2$  from  $\text{UO}_2(\text{HA})_2\text{A}_2$  at higher concentrations of uranium a separate investigation was carried out with 0.04 M DBP in chloroform. The data are given in Table 3 and plotted in Fig. 4. A similar plot has been published by Baes *et al.*<sup>5</sup>, Fig. 3 for the dioctyl phosphate-hexane system. It is seen from Fig. 4 that the ratio  $[\text{U}]_{\text{org}}/C_A$  is increased above 0.25 to a limiting value of 0.5. The simple equilibria



can thus not explain the whole extraction process.

The lower full-drawn curve in Fig. 4 is based on the reaction above using the value of  $10^{3.38}$  at  $C_A = 0.04$  M for the equilibrium constant,  $K$ , and calculating the free conc. of  $\text{H}_2\text{A}_2$  in the chloroform phase as  $C_A/2 - 2[\text{U}]_{\text{org}}$ . The equation for this curve is

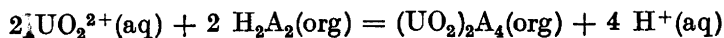
$$[\text{U}]_{\text{org}} = K[\text{U}]_{\text{aq}}[\text{H}^+]^2(C_A/2 - 2[\text{U}]_{\text{org}})^2$$

This equation seems to be valid up to  $[\text{U}]_{\text{org}}C_A^{-1} \sim 0.1$ . The same result was found by Baes *et al.*<sup>5</sup> for the dioctyl phosphate-hexane system.

In order to explain the increase of  $[\text{U}]_{\text{org}}C_A^{-1}$  above 0.25 several simple reactions may be considered. One might assume the formation of only mononuclear complexes,  $\text{UO}_2(\text{HA})\text{A}_2$  and  $\text{UO}_2\text{A}_2$ , or the formation of dinuclear com-



plexes such as  $(\text{UO}_2)_2(\text{HA})_2\text{A}_4$  and  $(\text{UO}_2)_2\text{A}_4$ . With constants for the formation of two complexes in addition to the formation constant of  $\text{UO}_2(\text{HA})_2\text{A}_2$  ( $K$ ) it should be possible to explain the data in Fig. 4 very well. In fact the dashed curve in Fig. 4 has been derived assuming only the reaction (equilibrium constant = 2.25  $K$ )



in addition to reaction given above (eq. const. =  $K$ ). Also there might be complexes such as  $\text{UO}_2\text{A}^+$  and  $\text{UO}_2\text{A}_2$  formed in the aqueous phase. It is therefore not possible to draw any definite conclusions from the distribution data about the reactions in the chloroform phase at higher concentrations of uranium.

Baes *et al.*<sup>5</sup> have published, for solutions of U(VI) and dioctyl phosphate in *n*-hexane, some isopiestic results which indicate the formation of polymers with more than two uranyl ions. Calculations \* on Fig. 2 in the work of Baes *et al.*<sup>5</sup> allow an approximate determination of the mean values of  $n$  and  $m$  in  $(\text{UO}_2)_n(\text{HA})_m\text{A}_{2n}$  as a function of  $[\text{U}]_{\text{org}}C_A^{-1}$ . The curves obtained are shown in Fig. 5. It may be seen that no change in  $m$  ( $= 2$ ) seems to occur at values of  $[\text{U}]_{\text{org}}C_A^{-1}$  below 0.33. It seems as if Baes *et al.*<sup>5</sup> have not considered a decrease in  $m$ . Viscosity measurements have lead them assume the presence of complexes with considerably higher values of  $n$  than 6. However, the viscosity properties of the dioctyl phosphate with its longer hydrocarbon groups may differ considerably from DBP (*i.e.*, micelles may be formed much more readily).

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\* For the calculation of the curves in Fig. 5 we have used the following approximate equations:

$$\begin{aligned} C_m &= [(\text{UO}_2)_n(\text{HA})_m\text{A}_{2n}] + [\text{H}_2\text{A}_2] \\ [\text{U}]_{\text{org}} &= n[(\text{UO}_2)_n(\text{HA})_m\text{A}_{2n}] \\ C_A &= (2n + m)[(\text{UO}_2)_n(\text{HA})_m\text{A}_{2n}] + 2[\text{H}_2\text{A}_2] \\ C_A - 2 C_m &= \frac{2n + m - 2}{n} \cdot [\text{U}]_{\text{org}} \end{aligned}$$

If we apply this equation to the data of Baes *et al.*<sup>5</sup>, Fig. 2, read from a smoothed curve, we obtain  $\frac{2n + m - 2}{n} = 2$  for  $[\text{U}]_{\text{org}}C_A^{-1} < 0.33$ ; *i.e.*,  $m = 2$ ; whereas  $n$  is undetermined. With decreasing  $[\text{U}]_{\text{org}}C_A^{-1}$  the complex  $\text{UO}_2(\text{HA})_2\text{A}_2$  should finally dominate, *i.e.*,  $n \rightarrow 1$ . For values of  $[\text{U}]_{\text{org}}C_A^{-1} > 0.4$  we might plausibly neglect  $[\text{H}_2\text{A}_2]$  and then estimate  $n$  from  $C_m C_A^{-1} = \frac{1}{2n + m}$  and  $[\text{U}]_{\text{org}}C_A^{-1} = \frac{n}{2n + m}$ .

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