ACTA CHEMICA SCANDINAVICA 22 (1968) 773–790

The Synergistic Effect in the Extraction of $^{233}U(VI)$ by Dibutylphosphate (HDBP) in the Presence of Tributylphosphate (TBP), Trioctylphosphine Oxide (TOPO) in Hexane and Carbon Tetrachloride

DJIET HAY LIEM

Department of Inorganic Chemistry, Royal Institute of Technology (KTH), Stockholm 70, Sweden

The extraction has been studied of $^{233}U(VI)$ from aqueous 0.1 M H_2SO_4 into hexane or carbon tetrachloride by dibutylphosphate (= HA) in the presence of tributylphosphate or trioctylphosphine oxide. Computer analysis of the distribution data with the LETAGROPVRID [1] program indicates the formation in the organic phase of the following extractable uranyl species:

1) $UO_2A_2(HA)_2$ 2) with B = TBP, $UO_2A_2(HA)_2B$, $UO_2A_2(HA)B$, in hexane also $UO_2A_2B_2$ and $UO_2SO_4B_2$
3) with B = TOPO, UO_2A_2B, $UO_2A_2B_2$, UO_2SO_4B, in CCl_4 also $UO_2A_2(HA)B$

A summary of the equilibrium constants for the formation of the various extractable uranyl species is given in Table 4.

The results indicate that both addition-type uranyl species ($UO_2A_2(HA)_2B$) and substitution-type species ($UO_2A_2(HA)B$, $UO_2A_2B_2$) may contribute to the synergistic effect found in the extraction of U(VI).

Many studies have been published dealing with the synergistic effect * found in the extraction of UO_2^{2+} by dialkylphosphate (= HA) in the presence of neutral organophosphorus compounds (= B).[2–10] Similar effects have also been reported for other combinations of extractants.[11] When only dialkylphosphoric acid (= HA) was used as the extractant, the extracted

* The enhancement of the distribution ratio in metal extraction when a combination of two extractants is used, compared with the sum of distribution ratios due to each of the extractants separately is called a synergistic effect. However, when the combination of the two extractants leads to a decrease in the distribution ratio, the combination is said to cause an antagonistic effect on the metal extraction.

complex has been found to be $UO_2A_2(HA)_2$ by a number of authors.[10,12–17] The equilibrium constants for the extraction of U(VI) with different HA and extraction systems are summarized in Table 5. There are, however, different opinions regarding the nature of the extracted complexes when a mixture of HA and B is used as extractant. Brown *et al.*[3] and Blake *et al.*[18] from data on U(VI) extractions by dioctylphosphate (HDOP) in the presence of TBP proposed the formation of the complex $UO_2A_2(HA)_2B$ *via* the *addition* reaction $UO_2A_2(HA)_2(org) + B(org) \rightleftharpoons UO_2A_2(HA)_2B(org)$. On the other hand, Kennedy *et al.*[4–6] suggested the formation of the uranyl species $UO_2A_2B_2$ corresponding to a *substitution* reaction:

$$UO_2A_2(HA)_2(org) + 2B(org) \rightleftharpoons UO_2A_2B_2(org) + 2HA(org)$$

The latter conclusion was based partly upon the observation that a non-ionic phosphorylated resin-diethylpolystyrene-methylene-phosphonate quantitatively absorbed one mole of UO_2A_2 and liberated approximately two moles of HA from every mole $UO_2A_2(HA)_2$, and partly upon results from IR-studies of the formation of mixed complexes $UO_2A_2B_2$ and $UO_2A_2(HA)B$ (HA = HDBP and B = TOPO).

Neither of these two groups of authors have determined any equilibrium constants for the formation of the proposed uranyl species.

Dyrssen and Kuča,[2] from a quantitative study on the extraction of UO_2^{2+} from 0.1 M H_2SO_4 into CCl_4 by HDBP in the presence of TBP, came to the conclusion that the observed synergistic effect is predominantly due to the extraction of the monosubstituted product $UO_2A_2(HA)B$.

The present work has been undertaken to study the nature of the extracted uranyl species and the distribution equilibria of U(VI) between 0.1 M H_2SO_4 and hexane or CCl_4 when HDBP—TBP or HDBP—TOPO are used as combined extractants so as to throw some light on the nature of the synergistic effect in U(VI) extraction. As compared with Ref. 2 more reagents have been used in the present work. It has taken advantage of the availability of the results of studies on the equilibria of HDBP + TBP and of HDBP + TOPO under the same extraction conditions.[19] Thus it has been possible to evaluate the equilibrium concentrations of the various $(HA)_pB_q$ species. The preliminary results of this work have been reported earlier.[23,24]

EXPERIMENTAL

Reagents. The quality and method of purification of the HDBP, TBP, TOPO, hexane, carbon tetrachloride, and H_2SO_4 used have been described previously.[19]

The α-emitter ^{233}U was purchased in the form of $^{233}UO_2(NO_3)_2$ in 1 M HNO_3 solution from AERE, Harwell, England. A solution of $^{233}U(VI)$ in 0.1 M H_2SO_4 was made by adding appropriate amounts of sulfuric acid to the $^{233}UO_2(NO_3)_2$ nitric acid solution, evaporating it nearly to dryness and diluting the residue to 0.1 M H_2SO_4. In the extraction experiments, the initial concentration of U(VI) in the aqueous phase was less than 9×10^{-6} M and may be considered as negligible compared with the total concentrations of HA or B.

Distribution experiments. Equal volumes of aqueous and organic phases (5 ml each) in a glass-stoppered centrifuge tube were equilibrated by tilting the tubes in a rotating rack for at least 2 h. The equilibrated phases were separated by centrifugation. The distribution ratio D was mostly determined using the double extraction technique in the

following way: 2 ml of the aqueous phase was taken (with a pipette) and equilibrated with an equal volume of 0.25 M HDBP solution in hexane, which extracted practically all the $^{233}U(VI)$ activity from the aqueous phase. To determine the distribution ratio D the α-activities in 0.20 ml of the organic solutions were compared. The α-active samples were prepared by first evaporating the organic solutions in the air and then heating and decomposing the organic compounds in the sample by means of a magnetic induction generator (ZETA I H). The α-activity was measured with an α-scintillation detector (Tracerlab P12A) connected with a Tracerlab SC-70 Compu/Matic V or a SC-81 Versa/Matic II scaler. The aqueous phase was always 0.10 M H_2SO_4 and all experiments were carried out in rooms thermostated at 25°C.

SYMBOLS AND EQUILIBRIUM CONSTANTS

HA = dibutylphosphoric acid $(n\text{-}C_4H_9O)_2P(=O)OH$, (HDBP), or other dialkylphosphoric acid

B = tributylphosphate $(n\text{-}C_4H_9O)_3P{=}O$, (TBP), or trioctylphosphine oxide $(n\text{-}C_8H_{17})_3P{=}O$, (TOPO)

$[\ ]$ = equilibrium concentration in the aqueous phase

$[\ ]_{org}$ = equilibrium concentration in the organic phase

C_A = initial total concentration of HA in the organic phase

C_B = initial total concentration of B in the organic phase

K_a = $[H^+][A^-][HA]^{-1}$ stoichiometric acid dissociation constant

φ = $1 + K_a[H^+]^{-1}$

a = $[HA]\varphi$

b = $[B]_{org}$ concentration of free B in the organic phase

I_{aq} = α-activity of ^{233}U in the aqueous phase, cpm

I_{org} = α-activity of ^{233}U in the organic phase, cpm

K_{pq} = $[(HA)_pB_q]_{org}[HA]_{org}^{-p}[B]_{org}^{-q}$ formation constant of $(HA)_pB_q$ complexes in the organic phase

K_{2aq} = $[H_2A_2][HA]^{-2}$ dimerization constant in the aqueous phase

K_{1pq} = $[UO_2A_2(HA)_{p-2}B_q]_{org}[H^+]^2/[UO_2^{2+}][HA]^p[B]_{org}^q$

K_{10q} = $[UO_2SO_4B_q]_{org}/[UO_2^{2+}][SO_4^{2-}][B]_{org}^q$ formation constant of extractable uranyl species

β_{1pq} = $K_{1pq}[H^+]^{-2}$

β_{10q} = $K_{10q}[SO_4^{2-}]$

D = $[U]_{org}/[U] = I_{org}/I_{aq}$ net distribution ratio of U(VI)

DATA

The primary data are given in Table 1 as log D, log C_A, and log [HA], in Tables 2 and 3 as C_B, log D, log C_A, log [HA], and log $[B]_{org}$. The data are represented in Fig. 1 as log D *versus* log C_A and in Figs. 2, 5, 6, 8 in diagrams, showing log D *versus* log [HA], for various constant values of C_B.

CHEMICAL MODEL

The aqueous phase is assumed to contain UO_2^{2+} ions and the HDBP species HA, A^-, and H_2A_2 and has the same $[H^+] = h$ in all experiments. From the value of acid constant at infinite dilution $K_a^\circ = 1.01 \times 10^{-2}$ (*cf.* Ref. 20) and the activity factors given by Kielland,[21] we calculated for 0.10 M H_2SO_4 the constant $K = [H^+][SO_4^{2-}][HSO_4^-]^{-1} = 2.894 \times 10^{-2}$M, $[H^+] = 0.1195$ M and $[SO_4^{2-}] = 83.62$ mM. For the acid constant of HDBP the value $K_a = 10^{-0.979}$ M (*cf.* Ref. 2) is used. Even if these values are slightly in error, this appears only as a constant factor in the equilibrium constants and cannot effect the conclusions regarding the species present.

Table 1. The distribution of $^{233}U(VI)$ between solutions of HDBP in hexane or carbon tetrachloride and 0.1 M H_2SO_4 at 25°C. Data given as log D, log C_A, log [HA].

Hexane

−2.821, −3.008, −3.324; −1.862, −2.707, −3.056; −1.086, −2.485, −2.869; −0.424, −2.281, −2.709; + 0.348, −2.008, −2.511; + 2.878, −0.707, −1.873; + 2.655, −0.929, −1.953; + 3.047, −0.583, −1.831.

Carbon tetrachloride

−3.472, −3.503, −3.970; −2.411, −3.105, −3.691; −2.212, −3.094, −3.684; −1.478, −2.794, −3.491; −1.428, −2.838, −3.519; −1.037, −2.628, −3.390; −0.634, −2.492, −3.309; −0.565, −2.503, −3.316; −0.542, −2.406, −3.259; −0.239, −2.327, −3.214; + 0.513, −2.026, −3.045; + 0.319, −2.219, −3.153; + 0.770, −1.918, −2.986; + 0.984, −1.804, −2.924; + 1.373, −1.628, −2.830; + 1.411, −1.617, −2.824; + 1.661, −1.492, −2.758; + 1.701, −1.503, −2.764; + 2.040, −1.316, −2.666; + 2.244, −1.191, −2.601; + 2.809, −0.890, −2.445.

Table 2. The distribution of $^{233}U(VI)$ between solutions of HDBP in hexane and 0.1 M H_2SO_4 for different constant concentrations of TBP or TOPO at 25°C. Data given as log D, log C_A, log [HA], log $[B]_{org}$.

B = TBP

$C_B = 0.020$ M

−2.170, −3.136, −3.476, −1.700; −1.205, −2.835, −3.205, −1.701; −0.233, −2.550, −2.964, −1.704; + 0.222, −2.379, −2.828, −1.707; + 1.080, −2.122, −2.637, −1.714; + 1.791, −1.834, −2.443, −1.729; + 2.142, −1.550, −2.271, −1.756.

$C_B = 0.040$ M

−3.463, −3.680, −4.024, −1.398; −2.446, −3.282, −3.643, −1.399; −1.408, −3.368, −2.981, −1.400; − 0.421, −2.680, −3.107, −1.401; −0.104, −2.601, −3.042, −1.402; + 0.773, −2.282, −2.793, −1.407; + 1.652, −1.981, −2.579, −1.417; + 2.131, −1.680, −2.385, −1.436; + 2.242, −1.601, −2.337, −1.443.

$C_B = 9.977 \times 10^{-2}$ M

−1.850, −3.136, −3.599, −1.002; −1.492, −2.982, −3.460, −1.003; −0.877, −2.835, −3.332, −1.003; −0.377, −2.680, −3.202, −1.004; + 0.017, −2.550, −3.096, −1.005; + 0.315, −2.504, −3.059, −1.006; + 0.936, −2.282, −2.890, −1.009; + 1.263, −2.136, −2.784, −1.012; + 1.972, −1.834, −2.577, −1.022; + 2.550, −1.550, −2.396, −1.040.

$C_B = 0.200$ M

−2.197, −3.203, −3.804, −0.701; −1.329, −2.902, −3.530, −0.702; −0.442, −2.619, −3.286, −0.703; + 0.382, −2.379, −3.092, −0.705; + 0.888, −2.203, −2.958, −0.708; + 1.391, −2.027, −2.828, −0.711; + 1.674, −1.902, −2.742, −0.715; + 2.371, −1.691, −2.553, −0.726.

C_B = 0.499 M
−2.792, −3.282, −4.247, −0.303; −2.163, −2.981, −3.956, −0.303; −1.630, −2.805, −3.788, −0.304; −1.262, −2.680, −3.671, −0.304; −0.676, −2.504, −3.511, −0.305; −0.018, −2.282, −3.316, −0.307; + 0.488, −2.078, −3.145, −0.310; + 0.932, −1.981, −3.067, −0.312; + 1.434, −1.805, −2.929, −0.316; + 1.700, −1.680, −2.836, −0.319; + 2.078, −1.504, −2.708, −0.326.

C_B = 0.987 M
−2.021, −2.898, −4.288, −0.007; −1.665, −2.597, −3.993, −0.008; −1.227, −2.421, −3.822, −0.008; −0.606, −2.199, −3.610, −0.010; + 0.027, −1.995, −3.419, −0.012; + 0.542, −1.819, −3.259, −0.015; + 1.030, −1.643, −3.104, −0.020; + 1.747, −1.421, −2.916, −0.028; + 2.180, −1.199, −2.737, −0.039.

C_B = 1.452 M
−2.482, −2.898, −4.567, 0.161; −1.643, −2.421, −4.093, 0.160; −1.038, −2.199, −3.874, 0.159; −0.266, −1.898, −3.580, 0.156; + 0.674, −1.597, −3.293, 0.150; + 1.747, −1.199, −2.930, 0.134.

C_B = 1.974 M
−2.396, −2.898, −4.802, 0.295; −1.942, −2.597, −4.502, 0.294; −1.910, −2.421, −4.326, 0.294; −1.565, −2.296, −4.201, 0.293; −1.240, −2.120, −4.026, 0.292; −0.085, −1.597, −3.508, 0.286; + 0.281, −1.421, −3.335, 0.281.

B = TOPO

$C_B = 4.562 \times 10^{-3}$ M
−1.074, −3.898, −4.517, −2.347; −0.445, −3.500, −4.119, −2.357; + 0.878, −2.793, −3.411, −2.422; + 1.640, −2.395, −3.015, −2.532; + 2.389, −1.793, −2.462, −2.903; + 2.659, −0.792, −1.910, −3.617.

$C_B = 5.472 \times 10^{-2}$ M
+ 0.080, −3.120, −4.583, −1.268; + 0.537, −2.819, −4.280, −1.273; + 1.060, −2.518, −3.975, −1.285; + 2.168, −1.819, −3.244, −1.379; + 2.589, −1.518, −2.899, −1.506.

C_B = 0.100 M
+ 0.358, −2.898, −4.611, −1.004; + 0.835, −2.619, −4.331, −1.009; + 1.502, −2.199, −3.905, −1.025; + 2.021, −1.898, −3.594, −1.053; + 2.457, −1.619, −3.297, −1.103.

Table 3. The distribution of ^{233}U(VI) between solutions of HDBP in carbon tetrachloride and 0.1 M H_2SO_4 for different constant concentrations of TBP or TOPO at 25°C. Data given as log D, log C_A, log [HA], log $[B]_{org}$.

B = Tributylphosphate (TBP)

C_B = 0.204 M
−2.603, −3.424, −4.244, −0.690; −2.291, −3.327, −4.157, −0.690; −0.565, −2.724, −3.660, −0.692; + 0.341, −2.424, −3.441, −0.693; + 0.658, −2.327, −3.374, −0.694; + 1.288, −2.026, −3.176, −0.697; + 1.960, −1.724, −2.991, −0.702; + 2.352, −1.424, −2.815, −0.710.

C_B = 0.409 M
−3.208, −3.548, −4.562, −0.389; −1.736, −3.026, −4.074, −0.390; −0.499, −2.724, −3.813, −0.390; −0.278, −2.548, −3.668, −0.391; + 1.053, −2.026, −3.279, −0.294.

B = Trioctylphosphine oxide (TOPO)

$C_B = 4.677 \times 10^{-4}$ M
−2.535, −4.498, −4.896, −3.336; −2.015, −4.197, −4.613, −3.340; −1.804, −3.647, −4.137, −3.361; −1.458, −3.497, −4.012, −3.370; −1.292, −3.352, −3.899, −3.381; −0.681, −3.099, −3.716, −3.406; −0.398, −2.798, −3.513, −3.446; + 0.395, −2.497, −3.325, −3.498; + 1.967, −1.354, −2.687, −3.814; + 2.473, −0.953, −2.468, −3.972.

$C_B = 4.677 \times 10^{-3}$ M
−0.385, −3.099, −3.955, −2.376; + 0.332, −2.798, −3.687, −2.411; + 0.685, −3.497, −3.440, −2.464; + 1.656, −2.199, −3.221, −2.534; + 2.466, −1.354, −2.702, −2.804; + 2.404, −1.497, −2.783, −2.752; + 2.554, −0.953, −2.485, −2.959; + 2.807, −1.195, −2.615, −2.863.

$C_B = 2.932 \times 10^{-2}$ M
−1.214, −4.327, −5.819, −1.533; −1.247, −4.026, −5.518, −1.534; −0.983, −3.724, −5.216, −1.535; −0.507, −3.327, −4.815, −1.539; −0.004, −3.026, −4.510, −1.546; + 0.496, −2.724, −4.201, −1.559; + 1.325, −2.327, −3.782, −1.599; +1.966, −2.026, −3.455, −1.663.
$C_B = 5.865 \times 10^{-2}$ M
−0.772, −4.327, −6.107, −1.232; −0.678, −3.987, −5.766, −1.233; −0.680, −3.724, −5.504, −1.233; −0.676, −3.696, −5.475, −1.233; −0.474, −3.548, −5.327, −1.234; −0.323, −3.327, −5.104, −1.235; + 0.240, −2.026, −4.800, −1.239; + 0.615, −2.724, −4.494, −1.245; + 0.987, −2.424, −4.182, −1.259; + 1.418, −2.327, −4.080, −1.266; + 1.879, −2.026, −3.752, −1.302.

By the (m,p,q) complex in the organic phase we mean a complex of the general formula

$$(UO_2)_m(HA)_pB_q(H^+)_x(SO_4)_y$$

Since $[SO_4^{2-}]$ and $[H^+]$ are constant in the medium we cannot decide the values for x and y independently. However, we make the reasonable assumption that the extractable complexes are uncharged and since $[UO_2^{2+}]$ is always less than 10^{-5} M, that $m = 1$. Thus the $(1,p,q)$ complex is likely to be $UO_2A_2(HA)_{p-2}B_q$ and the $(1,0,q)$ complex is $UO_2SO_4B_q$.

In the calculations we may always neglect the amount of HA or B that has reacted with the UO_2^{2+} ions.

The concentration of $(1,p,q)$ complex is given as:

$$[UO_2A_2(HA)_{p-2}B_q]_{org} = C_{1pq} = \beta_{1pq}[UO_2^{2+}][HA]^p[B]_{org}^q \quad (1)$$

and that of (1,0,q) complex as:

$$[UO_2SO_4B_q]_{org} = C_{10q} = \beta_{10q}[UO_2^{2+}][B]_{org}^q \quad (2)$$

Using (1) and (2) we may express the distribution ratio as:

$$D_{calc} = \frac{\sum([UO_2A_2(HA)_{p-2}B_q]_{org} + [UO_2SO_4B_q]_{org})}{[UO_2^{2+}]}$$

$$= \sum\beta_{1pq}[HA]^p[B]_{org}^q \quad (3)$$

Given the values of [HA], $[B]_{org}$, and β_{1pq} the value of D_{calc} may be calculated.

COMPUTER ANALYSIS OF THE DATA

The equilibrium concentrations [HA] and $[B]_{org}$ were evaluated using the equilibrium constants for the formation of $(HA)_pB_q$-species, $(0,p,q)$ with the present notation, which have been determined previously (Table 5 of Ref. 19).

The data for the U(VI) extraction by HDBP in the presence of TBP or TOPO were treated by means of a new version of LETAGROPVRID computer program,[1] which calculated the set of values of the constants k_1, $k_2 \ldots k_N$ for the formation of the $UO_2A_2(HA)_{p-2}B_q$ complexes which will minimize the error-square sum:

$$U = \sum(\log D_{calc} - \log D_{exp})^2$$

Table 4. The extraction of U(VI) by HDBP into hexane or CCl_4 in the presence of TBP or TOPO. The total concentration of U(VI) was less than 10^{-5} M. Equilibrium constants [a] for formation of sets of extractable U(VI) complexes which were found to give the minimum error-square sum $U = \sum(\log D_{calc} - \log D_{exp})^2$.

System	
UO_2^{2+} – 0.10 M H_2SO_4 – HDBP – hexane	$UO_2^{2+}(aq) + 4HA(aq) \rightleftharpoons UO_2A_2(HA)_2(org) + 2H^+(aq)$ $\log K = 8.56 \pm 0.07$
UO_2^{2+} – 0.10 M H_2SO_4 – HDBP – TBP – hexane	$UO_2^{2+}(aq) + 4HA(aq) + B(org) \rightleftharpoons UO_2A_2(HA)_2B(org) + 2H^+(aq)$ $\log K = 11.38 \pm 0.06$
	$UO_2^{2+}(aq) + 3HA(aq) + B(org) \rightleftharpoons UO_2A_2(HA)B(org) + 2H^+(aq)$ $\log K = 7.88 \pm 0.25$
	$UO_2^{2+}(aq) + 2HA(aq) + 2B(org) \rightleftharpoons UO_2A_2B_2(org) + 2H^+(aq)$ $\log K = 4.30 \pm 0.19$
	$UO_2^{2+}(aq) + SO_4^{2-}(aq) + 2B(org) \rightleftharpoons UO_2SO_4B_2(org)$ $\log K = -2.05$ (max. -1.75)
UO_2^{2+} – 0.10 M H_2SO_4 – HDBP – TOPO – hexane	$UO_2^{2+}(aq) + 2HA(aq) + B(org) \rightleftharpoons UO_2A_2B(org) + 2H^+(aq)$ $\log K = 8.21 \pm 0.18$
	$UO_2^{2+}(aq) + 2HA(aq) + 2B(org) \rightleftharpoons UO_2A_2B_2(org) + 2H^+(aq)$ $\log K = 9.02$ (max. 9.39)
	$UO_2^{2+}(aq) + SO_4^{2-}(aq) + B(org) \rightleftharpoons UO_2SO_4B(org)$ $\log K = 2.17$ (max. 2.45)
UO_2^{2+} – 0.10 M H_2SO_4 – HDBP – CCl_4	$UO_2^{2+}(aq) + 4HA(aq) \rightleftharpoons UO_2A_2(HA)_2(org) + 2H^+(aq)$ $\log K = 10.77 \pm 0.11$
UO_2^{2+} – 0.10 M H_2SO_4 – HDBP – TBP – CCl_4	$UO_2^{2+}(aq) + 4HA(aq) + B(org) \rightleftharpoons UO_2A_2(HA)_2B(org) + 2H^+(aq)$ $\log K = 12.64 \pm 0.28$
	$UO_2^{2+}(aq) + 3HA(aq) + B(org) \rightleftharpoons UO_2A_2(HA)B(org) + 2H^+(aq)$ $\log K = 8.91$ (max. 9.11)
UO_2^{2+} – 0.10 M H_2SO_4 – HDBP – TOPO – CCl_4	$UO_2^{2+}(aq) + 3HA(aq) + B(org) \rightleftharpoons UO_2A_2(HA)B(org) + 2H^+(aq)$ $\log K = 11.28$ (max. 11.62)
	$UO_2^{2}(^+aq) + 2HA(aq) + B(org) \rightleftharpoons UO_2A_2B(org) + 2H^+(aq)$ $\log K = 8.06$ (max. 8.30)
	$UO_2^{2+}(aq) + 2HA(aq) + 2B(org) \rightleftharpoons UO_2A_2B_2(org) + 2H^+(aq)$ $\log K = 10.11 \pm 0.22$
	$UO_2^{2+}(aq) + SO_4^{2-}(aq) + B(org) \rightleftharpoons UO_2SO_4B(org)$ $\log K = 1.55 \pm 0.21$

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

Table 5. The equilibrium constants for the extraction of U(VI) with different dialkylphosphates and extraction systems:

$$UO_2^{2+}(aq) + 2H_2A_2(org) \rightleftharpoons UO_2A_2(HA)_2(org) + 2H^+(aq)$$

Extraction system	log K	Ref.
HDBP–Toluene/(HNO_3–NO_3^-)	4.56	Hardy [13]
HDBP–$CHCl_3$/1 M (H,Na)ClO_4	3.58	Dyrssen and Krašovec [15]
HDBP–Hexane/1 M (H,Na)ClO_4	4.50	—»—
HDOP–Hexane/2 M (H,Na)ClO_4	4.60	Baes *et al.*[12]
HDOP–Kerosene/HCl	4.53	Blake *et al.*[18]
HDBP–CCl_4/0.1 M H_2SO_4	3.84(3.45) [a]	Dyrssen and Kuča [2]
HDBP–CCl_4/0.1 M H_2SO_4	3.47	This work
HDBP–Hexane/0.1 M H_2SO_4	3.96	This work
Di-β-naphthylphosphate $CHCl_3$/1 M (H,Na)ClO_4	5.24	Krašovec and Klofutar [14]
Dibenzylphosphate $CHCl_3$/1 M (H,Na)ClO_4	4.88	—»—
Di-(p-Cl-phenyl)phosphate $CHCl_3$/1 M (H,Na)ClO_4	5.34	—»—
Di(p-tolyl)phosphate $CHCl_3$/1 M (H,Na)ClO_4	4.60	—»—
Diphenylphosphate $CHCl_3$/1 M (H, Na)ClO_4	4.87	—»—

[a] Recalculated value (*cf.* Table 7, mechanism III).

The input data to the computer were:

1) I_{aq} (^{233}U activity in the aqueous phase in cpm)
2) I_{org} (^{233}U activity in the organic phase in cpm)
3) [HA] concentration of free HA in the aqueous phase
4) $[B]_{org}$ concentration of free B in the organic phase

RESULTS AND DISCUSSION

CONCLUSIONS ABOUT THE EXTRACTABLE URANYL COMPLEXES WITH HDBP AND TBP

Hexane

Fig. 1 shows the distribution of U(VI) between 0.1 M H_2SO_4 and HDBP-hexane solutions as a function of C_A, the initial total concentration of HDBP in the organic phase, at different constant total concentration of TBP: $C_B = 0$ (no TBP present), 0.020, 0.040, 0.100, 0.200, 0.499, 0.987, 1.452, and 1.974 M. As indicated by these extraction curves the addition of TBP gives rise to a synergistic effect on the extraction of U(VI). This effect, however, seems to reach an optimum value at $C_B \sim 0.10$ M, beyond which the extraction decreases with increasing C_B, and at $C_B \geq 1$ M even an antagonistic effect on the extraction of U(VI) is seen to take place.

In Table 6 a summary is given of the values of U_{min} and of the equilibrium constants found for various possible sets of extractable uranyl species. The results of the computer analysis indicate that a combination of the extractable uranyl species (1,4,0) = $UO_2A_2(HA)_2$, (1,4,1) = $UO_2A_2(HA)_2B$, (1,3,1) = $UO_2A_2(HA)B$, (1,2,2) = $UO_2A_2B_2$ and (1,0,2) = $UO_2SO_4B_2$, (mech-

Table 6. Equilibrium constants [a] β_{1pq} of U(VI)–HDBP–TBP complex formation for various assumptions of extractable uranyl species in hexane, which minimize the error-square sum $U = \sum_{1}^{75} (\log D_{calc} - \log D_{exp})^2$

Mechanism	(1,4,0)	(1,4,1)	(1,3,1)	(1,2,1)	(1,2,2)	(1,0,1)	(1,0,2)	U_{min}	$\sigma(y)$
I	10.40 ± 0.26	13.46 ± 0.10					−2.26 max. −2.06	4.164	0.241
II	10.40 ± 0.26		10.34 ± 0.10				−2.76 max. −2.47	3.929	0.234
III	10.45 ± 0.26		10.34 ± 0.10	max. 6.17			−2.77 max. −2.46	3.929	0.234
IV	10.45 ± 0.26		10.33 ± 0.11		5.11 max. 6.14		−2.81 max. −2.40	3.923	0.235
V	11.11 max. 11.49			6.88 max. 7.10			max. −1.91	2.277	0.558
VI	10.40 ± 0.15	13.32 ± 0.08		6.21 ± 0.16			−2.90 max. −2.63	1.444	0.143
VII	10.40 ± 0.15	13.23 ± 0.16	9.68 max. 10.06	5.99 max. 6.30			−2.79 max. −2.53	1.350	0.139
VIII	10.40 ± 0.12	13.33 ± 0.06		5.80 max. 6.05			−3.25 max. −2.89	0.943	0.116
IX	10.40 ± 0.13	13.19 ± 0.12	9.77 ± 0.25	max. 5.92	6.12 ± 0.21		−3.11 max. −2.80	0.809	0.120
X	10.40 ± 0.11	13.23 ± 0.10	9.72 ± 0.23		6.14 ± 0.18		−3.13 max. −2.83	0.796	0.107
XI	10.40 ± 0.11	13.23 ± 0.10	9.71 ± 0.26		6.14 ± 0.18	−3.27 max. −2.58	−3.35 max. −2.71	0.792	0.107

[a] 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.

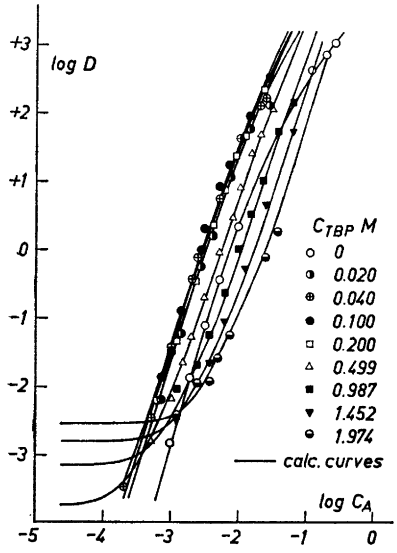

Fig. 1. The distribution of U(VI) between HDBP—TBP—hexane and 0.1 M H_2SO_4 solution as a function of C_A at different constant C_B: 0 (○), 0.020 (◑), 0.040 (⊕), 0.100 (●), 0.200 (□), 0.499 (△), 0.987 (■), 1.452 (▼), 1.974 M (◒). The distribution data are given in Tables 1 and 2. The lines have been calculated assuming the set of HDBP—TBP species in Table 5 of Ref. 19 and the set of extractable uranium species in Table 4.

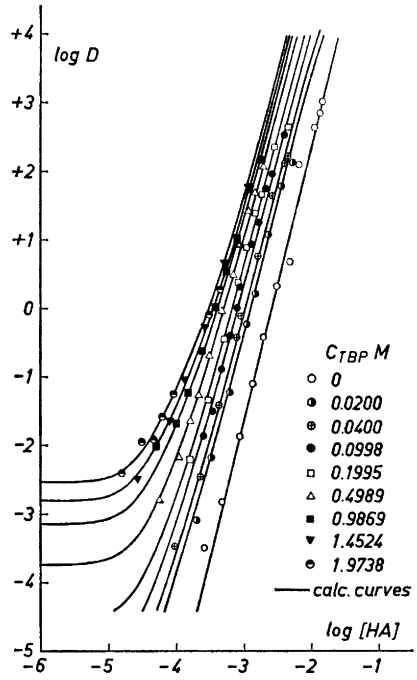

Fig. 2. The distribution of U(VI) between 0.10 M H_2SO_4 and hexane as a function of [HA] at different constant concentrations of TBP in the organic phase: 0(○), 0.020 (◑), 0.040 (⊕), 0.100 (●), 0.200 (□), 0.499 (△), 0.987 (■), 1.452 (▼), 1.974 M (◒). The distribution data are given in Tables 1 and 2. The curves have been calculated assuming the HDBP—TBP species in Table 5 of Ref. 19 and the set of extractable uranyl species in Table 4.

anism X) seems to give the best error-square sum compared with the other combinations tried. Adding (1,2,1) = UO_2A_2B gave no improvement to U. Addition of (1,0,1) = UO_2SO_4B gave a slight improvement to U (mechanism XI) but made the constants for the formation of (1,0,1) and (1,0,2) complexes very uncertain ($\sigma(\beta) > \beta$), and was thus rejected.

Using the equilibrium constant in Table 4 one may calculate the following equilibrium constants for addition and substitution reaction:

$$UO_2A_2(HA)_2(org) + B(org) \rightleftharpoons UO_2A_2(HA)_2B(org)$$
$$K = K_{141}K_{140}^{-1} = 10^{2.82}$$

$$UO_2A_2(HA)_2(org) + B(org) \rightleftharpoons UO_2A_2(HA)B(org) + HA(org)$$
$$K = K_{131}K_dK_{140}^{-1} = 10^{-2.86}$$

$$UO_2A_2(HA)_2(org) + 2B(org) \rightleftharpoons UO_2A_2B_2(org) + 2HA(org)$$
$$K = K_{122}K_d^2K_{140}^{-1} = 10^{-8.62}$$

where $K_d = [HA]_{org}[HA]^{-1}$.

Fig. 2 shows the distribution of U(VI) between 0.10 M H_2SO_4 and hexane for various [HA] and different constant concentrations of TBP in the organic phase. The lines are calculated by assuming the equilibrium constants in Table 4. As can be seen, these calculated curves fit the experimental points satisfactorily. Fig. 3 gives the mole percentage of the different uranyl species extracted at a constant $C_A = 5.624 \times 10^{-3}$ M, as a function of C_B. Low values of C_B seem to promote the extraction of the addition-type uranyl complex, $UO_2A_2(HA)_2B$, while higher concentrations of tributylphosphate favor the extraction of the substitution-type uranyl species, $UO_2A_2(HA)B$ and $UO_2A_2B_2$. At still higher TBP concentrations, $UO_2SO_4B_2$ becomes the predominant complex extracted. The competition in complex formation between the different $(HA)_pB_q$ complexes and uranyl species extracted will influence the extent of synergistic or antagonistic effects in the uranium extraction. Fig. 4 shows calculated curves for the system U(VI)—0.10 M H_2SO_4—HDBP—TBP—hexane, representing the percentage uranium extracted as a function of the total

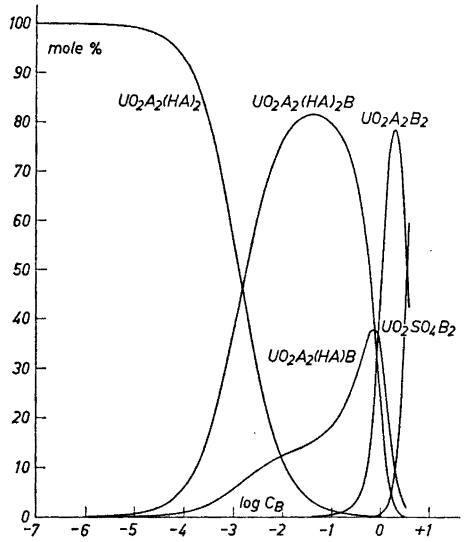

Fig. 3. The mole percentage of different extractable uranyl species in the two-phase systems HDBP—TBP—hexane/0.1 M H_2SO_4 as a function of C_B, at $C_A = 5.624 \times 10^{-3}$ M.

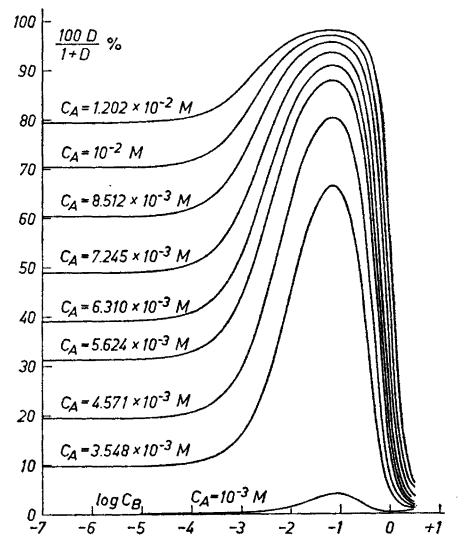

Fig. 4. Calculated curves for metal extraction in the system U(VI)—0.10 M H_2SO_4—HDBP—TBP—hexane as a function of the total concentration of TBP and different constant values of C_A. The curves have been calculated assuming the HDBP—TBP species in Table 5 of Ref. 19 and the set of extractable uranyl species in Table 4.

concentration of TBP at different constant values of C_A. The curves show the regions where synergistic effect or antagonistic effect in the uranium extraction may be expected. Addition of TBP at $C_B \approx 0.1$ M seems to give the optimum synergistic effect for all values of HA concentration considered ($C_A = 10^{-3}$—0.012 M).

Carbon tetrachloride

The extraction of UO_2^{2+} by HDBP into CCl_4 was studied at $C_B = 0$ (no TBP present), 0.204 M, and 0.409 M. The results of the computer analysis given in Table 7 indicate that the assumption of the extraction of the uranyl species (1,4,0) = $UO_2A_2(HA)_2$, (1,4,1) = $UO_2A_2(HA)_2B$ and (1,3,1) = $UO_2A_2(HA)B$ gives a lower error-square sum U than either the combination (1,4,0) + (1,4,1) or (1,4,0) + (1,3,1). Addition of other possible extractable complexes does not improve the error-square sum U.

The distribution of U(VI) between 0.10 M H_2SO_4 and carbon tetrachloride as a function of [HA] at different constant values of C_B is shown in Fig. 5. The curves have been calculated assuming the formation of $(HA)_pB_q$ species between HDBP—TBP with the equilibrium constants listed in Ref. 19 and Table 4. They are seen to fit the experimental points well. The results support

Table 7. Equilibrium constants [a] β_{1pq} of U(VI)—HDBP—TBP complex formation for various assumptions of extractable uranyl species in carbon tetrachloride which minimize the error square sum $U = \sum_1^{38} (\log D_{calc} - \log D_{exp})^2$ Values in parenthesis calculated from Dyrssen-Kuča data [2] (53 experimental points).

Mechanism	(1,4,0)	(1,4,1)	(1,3,1)	U_{min}	$\sigma(y)$
I	12.63 ± 0.13	14.82 ± 0.15		1.381	0.196
	(12.59 ± 0.20)	(14.32 ± 0.21)		(4.263)	(0.289)
II	12.63 ± 0.13		11.12 ± 0.16	1.429	0.199
	(12.62 ± 0.16)		(10.83 ± 0.17)	(2.857)	(0.237)
III	12.63 ± 0.09	14.48 ± 0.25	10.75 max. 10.96	0.612	0.132
	(12.60 ± 0.16)	(13.58 max. 14.10)	(10.72 max. 10.96)	(2.758)	(0.235)

[a] 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.

the conclusions made previously, when hexane was used as organic solvent, that both addition-type, $UO_2A_2(HA)_2B$, and substitution-type, $UO_2A_2(HA)B$, uranyl species may contribute to the synergistic effect in uranium extraction.

Recalculation of Dyrssen-Kuča extraction data. The extraction of U(VI) by HDBP into CCl_4 in the presence of TBP has been studied previously by Dyrssen and Kuča.[2] From their data these authors draw the conclusion that

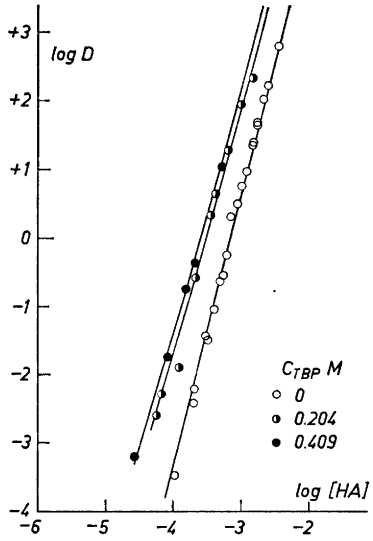

Fig. 5. The distribution of U(VI) between 0.10 M H_2SO_4 and carbon tetrachloride as a function of [HA] at different constant concentrations of TBP in the organic phase: 0 (○), 0.204 (◑), 0.409 M (●). The distribution data are given in Tables 1 and 3. The curves have been calculated assuming the set of HDBP—TBP species in Table 5 of Ref. 19 and the extraction of the uranyl species $UO_2A_2(HA)_2$, $UO_2A_2(HA)_2B$, and $UO_2A_2(HA)B$ with the equilibrium constants listed in Table 4.

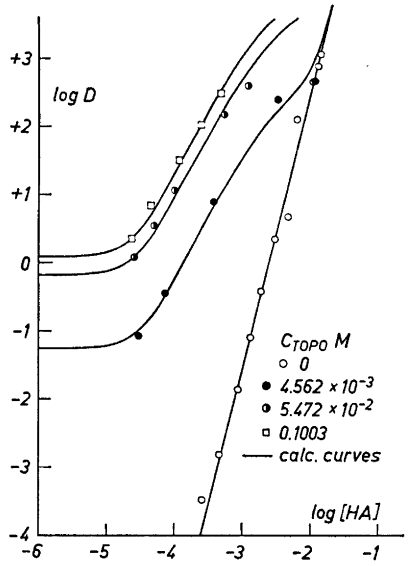

Fig. 6. The distribution of U(VI) between 0.10 M H_2SO_4 and hexane as a function of [HA] at different constant concentrations of TOPO in the organic phase: 0 (○), 4.562×10^{-3} M (●), 5.472×10^{-2} M (◑), and 0.100 M (□). The distribution data are given in Tables 1 and 4. The curves have been calculated assuming the set of HDBP—TOPO species in Table 5 of Ref. 19 and the set of extractable uranyl species given in Table 4.

the synergistic effect is mainly due to the extraction of the uranyl mixed complex of the mono-substitution-type (1,3,1) = $UO_2A_2(HA)B$. The calculations were based on the assumption of $(HA)_pB_q$ species and equilibrium constants found in the two-phase systems CCl_4/0.1 M HNO_3,[22] thus no account was taken of the presence of H_2A_2B in the organic phase and of HDBP dimers in the aqueous phase, as was found in the system CCl_4/0.10 M H_2SO_4 studied previously.[19]

Recalculation of Dyrssen-Kuča data assuming $(HA)_pB_q$ species and the equilibrium constants found for the CCl_4/0.10 M H_2SO_4 system indicates that the addition of the extractable uranyl species (1,4,1) and (1,3,1) to the (1,4,0) complex gives a better U value than does addition of (1,4,1) or (1,3,1) alone (see Table 7).

CONCLUSIONS ABOUT THE EXTRACTABLE URANYL COMPLEXES WITH HDBP AND TOPO

Trioctylphosphine oxide, TOPO, which is more basic in character than tributylphosphate was found previously [19] to form more stable complexes with HDBP, *e.g.* $K_{11} = [HAB]_{org}[HA]_{org}^{-1}[B]_{org}^{-1}$ in hexane was found to be $10^{4.88}$ for HDBP—TOPO, compared with $10^{2.94}$ for HDBP—TBP.

To study the effect of a more basic P=O group on the formation of extractable uranyl mixed-ligand complex, the extraction of U(VI) from 0.10 M H_2SO_4 by HDBP into hexane or CCl_4 was studied in the presence of TOPO.

Hexane. Fig. 6 shows the distribution of U(VI) between 0.10 M H_2SO_4 and hexane as a function of HA; $C_B = 0$ (no TOPO present), 4.562×10^{-3} M, 5.472×10^{-2} M, and 0.100 M. The values of HA have been calculated assuming HDBP—TOPO species and equilibrium constants listed in Ref. 19. LETAGROP analysis of the distribution data indicates that the set of extractable U(VI) complexes which gives the best value of the error-square sum U is the combination $(1,4,0) = UO_2A_2(HA)_2$, $(1,2,1) = UO_2A_2B$, $(1,2,2) = UO_2A_2B_2$ and $(1,0,1) = UO_2SO_4B$, with equilibrium constants listed in Table 4. In Table 8 the different possible sets of extractable uranyl species which minimize the error-square sum U are summarized. The addition of (1,4,1), (1,3,1) to the set of uranyl complexes mentioned above does not improve the value of the error-square sum. Although the addition of (1,0,2) leads to a slightly better U-value, the constant calculated for this species has a standard deviation which exceeds the magnitude of the constant itself.

In Fig. 6 the lines are calculated assuming the extraction of the uranyl species (1,4,0), (1,2,1), (1,2,2), and (1,0,1).

The results indicate that TOPO with a more basic character than TBP, seems to promote the formation of extractable uranyl mixed-ligand complexes of the substitution-type rather than the complexes of the addition-type, *e.g.* (1,4,1) as was found previously with TBP. The substitution reaction may be described by the following equilibrium reaction in the organic phase:

$$UO_2A_2(HA)_2(org) + B(org) \rightleftharpoons UO_2A_2B(org) + 2HA(org)$$
$$K = K_{121}K_{140}^{-1}K_d^2 = 10^{-4.71}$$

$$UO_2A_2(HA)_2(org) + 2B(org) \rightleftharpoons UO_2A_2B_2(org) + 2HA(org)$$
$$K = K_{122}K_{140}^{-1}K_d^2 = 10^{-3.90}$$

Fig. 7 shows the calculated uranium extraction curve, given as percentage uranium extracted as a function of TOPO concentration in the organic phase at different constant values of C_A. Comparing the curves in Fig. 4 with those in Fig. 7 one can see clearly the greater effect of TOPO compared with TBP in causing synergism in uranium extraction by HDBP.

Carbon tetrachloride. The extraction of U(VI) by HDBP at the presence of TOPO was also studied with carbon tetrachloride as the organic solvent. In Fig. 8 the distribution of U(VI) between 0.10 M H_2SO_4 and CCl_4 as a function of [HA] is given at $C_B = 0$ (no TOPO present), 4.677×10^{-4} M, 4.677×10^{-3} M, 2.932×10^{-2} M, and 5.865×10^{-2} M. A summary of the results of LETAGROP analysis for different assumptions of possible sets of extractable uranyl—HDBP—TOPO species is given in Table 9. The results of the calcula-

Table 8. Equilibrium constants [a] β_{1pq} of U(VI)–HDBP–TOPO complex formation for various assumptions of extractable uranyl species in hexane which minimize the error-square sum $U = \sum_{1}^{24} (\log D_{calc} - \log D_{exp})^2$.

Mechanism	(1,4,0)	(1,4,1)	(1,3,1)	(1,2,1)	(1,2,2)	(1,0,1)	(1,0,2)	U_{min}	$\sigma(y)$
I	10.38 ± 0.10		9.42 max. 12.25	10.06 ± 0.19	10.86 max. 11.15	1.09 max. 1.30		0.558	0.099
II	10.38 ± 0.14	8.90 max. 12.14	8.55 max. 9.99	10.06 ± 0.08	10.85 max. 11.19	1.09 max. 1.70		0.317	0.129
III	10.38 ± 0.13			10.07 ± 0.18	10.79 max. 11.23	0.91 max. 1.40	1.93 max. 2.59	0.279	0.121
IV	10.38 ± 0.12			10.05 ± 0.17	10.87 max. 11.24	1.09 max. 1.38		0.289	0.120
V	10.38 ± 0.13	9.56 max. 10.94		10.05 ± 0.18	10.87 max. 11.25	1.09 max. 1.39		0.289	0.123

[a] 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.

Table 9. Equilibrium constants [a] β_{1pq} for different possible sets of extractable uranyl complexes in the system U(VI)–0.10 M H_2SO_4–HDBP–TOPO–CCl_4, which minimize the error-square sum $U = \sum_{1}^{59} (\log D_{calc} - \log D_{exp})^2$.

(1,4,0)	(1,4,1)	(1,3,1)	(1,2,1)	(1,2,2)	(1,0,1)	(1,0,2)	U_{min}	$\sigma(y)$
12.60 ± 0.25	8.48 max. 10.72	13.90 max. 14.12			0.85 max. 1.16		8.027	0.381
12.60 ± 0.24		13.91 max. 14.13			0.83 max. 1.13		8.014	0.378
12.74 ± 0.23				12.38 max. 12.61	0.59 max. 0.91		7.699	0.371
12.74 ± 0.25	12.31 max. 13.56			12.38 max. 12.62	0.59 max. 0.92		7.698	0.374
12.61 ± 0.15	11.06 max. 11.79		10.38 ± 0.16		−0.07 max. 0.74	1.74 max. 2.21	3.090	0.239
12.61 ± 0.15			10.39 ± 0.16		−0.11 max. 0.81	1.76 max. 2.29	3.090	0.237
12.60 ± 0.14	9.96 max. 13.84	13.55 ± 0.21		12.03 ± 0.22	0.57 ± 0.24		2.264	0.205
12.60 ± 0.13		13.55 ± 0.21		12.03 ± 0.22	0.57 ± 0.24		2.264	0.203
12.63 ± 0.12			10.13 ± 0.20	11.92 max. 12.13	0.34 max. 0.76	1.16 max. 1.95	1.820	0.184
12.61 ± 0.11		13.13 max. 13.47	9.91 max. 10.15	11.96 ± 0.22	0.47 ± 0.21		1.471	0.165

[a] 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.

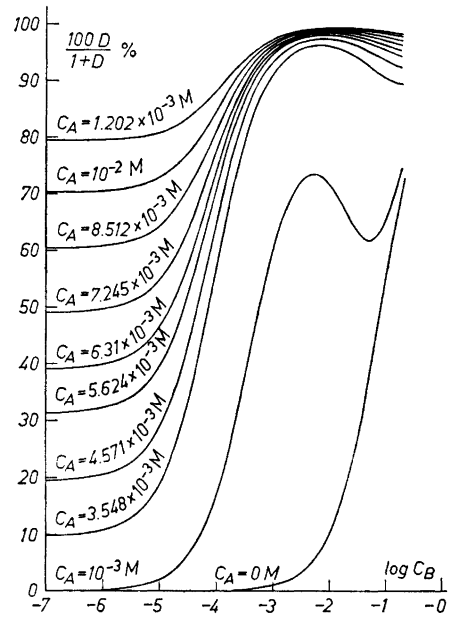

Fig. 7. Calculated curves for metal extraction in the system U(VI)—0.10 M H_2SO_4—HDBP—TOPO—hexane as a function of TOPO concentration in hexane and different constant values of C_A. The curves have been calculated assuming the set of $(HA)_pB_q$ species in Table 5 of Ref. 19 and the extractable uranyl species: $UO_2A_2(HA)_2$, UO_2A_2B, $UO_2A_2B_2$, and UO_2SO_4B and equilibrium constants given in Table 4.

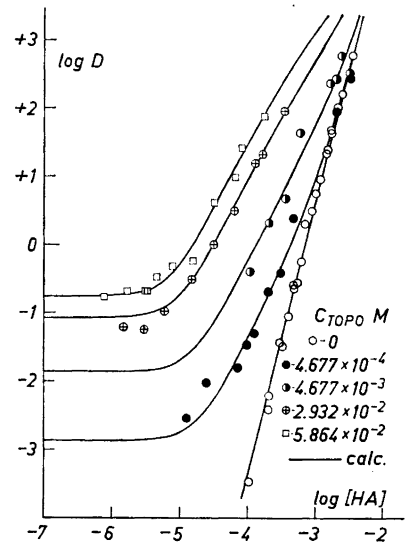

Fig. 8. The distribution of U(VI) between 0.10 M H_2SO_4 and carbon tetrachloride as a function of [HA] at different constant concentrations of TOPO in the organic phase: 0 (○), 4.677×10^{-4} M (●), 4.677×10^{-3} M (◐), 2.932×10^{-2} M (⊕), 5.865×10^{-2} M (□). The distribution data are given in Tables 1 and 3. The curves have been calculated assuming the set of HDBP—TBP species in Table 5 of Ref. 19 and the extraction of uranyl species $UO_2A_2(HA)_2$, $UO_2A_2(HA)B$, UO_2A_2B, $UO_2A_2B_2$, UO_2SO_4B, and $UO_2SO_4B_2$ with equilibrium constants listed in Table 4.

tions indicate that the available data can best be described by assuming the extraction of the uranyl species (1,4,0) = $UO_2A_2(HA)_2$, (1,3,1) = $UO_2A_2(HA)B$, (1,2,1) = UO_2A_2B, (1,2,2) = $UO_2A_2B_2$, and (1,0,1) = UO_2SO_4B. The addition of the addition-type of uranyl species (1,4,1) or (1,0,2) does not improve the error-square sum U.

The results thus agree with those obtained before, namely that when hexane was used as the organic solvent and under the extraction conditions studied TOPO seems to prefer to form substitution-type uranyl—HDBP—TOPO species.

COMPARISON OF THE VARIOUS SYNERGISTIC EFFECTS OBSERVED

To compare the power in producing synergistic effects in metal extraction of neutral extractants, like TBP and TOPO, one may define the synergistic enchancement by the expression

$$\eta = \frac{D_{AB}}{D_A + D_B} \tag{4}$$

$$\text{in which } D_{AB} = \frac{\sum[UO_2A_2(HA)_{p-2}B_q]_{org}}{[UO_2^{2+}]}$$

$$= \sum\beta_{1pq}[HA]^p[B]_{org}^q \tag{5}$$

$$D_A = \frac{[UO_2A_2(HA)_2]_{org}}{[UO_2^{2+}]} = \beta_{140}[HA]^4 \tag{6}$$

$$D_B = \frac{\sum[UO_2SO_4B_q]_{org}}{[UO_2^{2+}]} = \sum\beta_{10q}[B]_{org}^q \tag{7}$$

Inserting (5), (6), and (7) into (4):

$$= \frac{\sum\beta_{1pq}[HA]^p[B]_{org}^q}{\beta_{140}[HA]^4 + \sum\beta_{10q}[B]_{org}^q} \tag{8}$$

Given the values of β_{1pq} the value of η may be calculated for given values of [HA] and $[B]_{org}$. The synergistic effect caused by the different synergic reagents may thus be compared from the values of η for given extraction conditions, *e.g.* for maximum synergistic effect, or in the case when given species $(1,p,q)$ are predominantly extracted. In Table 10 the synergistic effect in the extraction of uranium by HDBP in the presence of TBP and TOPO is compared at $[HA] = 10^{-3}$ M and $[B]_{org} = 0.1$ M.

Table 10. The synergistic effect in the extraction of U(VI) by HDBP in the presence of TBP and TOPO for $[HA] = 10^{-3}$ M and $[B]_{org} = 0.1$ M.

Extraction system	Extractable uranyl complexes	$\eta = \frac{D_{AB}}{D_A + D_B}$
UO_2^{2+} – 0.1 M H_2SO_4 – HDBP – TBP – hexane	(1,4,0), (1,4,1) (1,3,1), (1,2,2) (1,0,2)	89
UO_2^{2+} – 0.1 M H_2SO_4 – HDBP – TBP – CCl_4	(1,4,0), (1,4,1), (1,3,1)	9
UO_2^{2+} – 0.1 M H_2SO_4 – HDBP – TOPO – hexane	(1,4,0), (1,2,1), (1,2,2), (1,0,1)	1490
UO_2^{2+} – 0.1 M H_2SO_4 – HDBP – TOPO – CCl_4	(1,4,0), (1,3,1) (1,2,1), (1,2,2), (1,0,1)	2580

Acknowledgement. The author is very much obliged to Professor David Dyrssen, Göteborg University, for having suggested the investigation and for his advice and valuable discussions during the course of the work. He is very grateful to Professor Lars Gunnar Sillén for valuable criticism and advice. Discussions with Dr. Björn Warnqvist during the course of computer treatment of the data are gratefully acknowledged. The work has been supported by the *Swedish Natural Science Research Council* (NFR) and *Anslaget för Främjandet av ogradueradе forskares vetenskapliga verksamhet,* KTH, Stockholm. Dr Derek Lewis has revised the English.

REFERENCES

1. Ingri, N. and Sillén, L. G. *Arkiv Kemi* **23** (1964) 97.
2. Dyrssen, D. and Kuča, L. *Acta Chem. Scand.* **14** (1960) 1945.
3. Blake, Jr., C. A., Baes, Jr., C. F., Brown, K. B., Coleman, C. F. and White, J. C. *2nd Intern. Conf. Peaceful Uses Atomic Energy*, Paper 1550, Geneva 1958; ORNL-2172, Oak Ridge 1956.
4. Kennedy, J. AERE/C/M 369, Harwell 1958.
5. Kennedy, J., Burford, F. A. and Sommer, P. G. *J. Inorg. Nucl. Chem.* **14** (1960) 114.
6. Kennedy, J., Sommer, P. G. and Deane, A. M. *Chem. Ind. (London)* **1960** 443.
7. Baes, Jr., C. F. *Nucl. Sci. Eng.* **16** (1963) 405.
8. Sato, T. *J. Inorg. Nucl. Chem.* **26** (1964) 311.
9. Zangen, M. *J. Inorg. Nucl. Chem.* **25** (1963) 581.
10. Hahn, H. T. and Van der Vall, E. M. *J. Inorg. Nucl. Chem.* **26** (1964) 191.
11. Irving, H. M. N. *Proc. Intern. Conf. Solvent Extraction Chem.* (ICSEC) Gothenburg, North-Holland, Amsterdam 1967, p. 91.
12. Baes, C. F., Zingaro, R. A. and Coleman, C. F. *J. Phys. Chem.* **62** (1958) 129.
13. Hardy, C. J. *J. Inorg. Nucl. Chem.* **21** (1961) 348.
14. Krašovec, F. and Klofutar, C. *J. Inorg. Nucl. Chem.* **27** (1965) 2443.
15. Dyrssen, D. and Krašovec, F. *Acta Chem. Scand.* **13** (1959) 561.
16. Sato, T. *J. Inorg. Nucl. Chem.* **24** (1962) 699.
17. Sato, T. *Naturwiss.* **50** (1963) 19.
18. Blake, Jr., C. A., Horner, D. E. and Schmitt, J. M. Report ORNL-2259 (1959).
19. Liem, D. H. *Acta Chem. Scand.* **22** (1968) 753.
20. Sillén, L. G. and Martell, A. E. *Stability Constants of Metal-ion Complexes 1964, Spec. Publ.* No. 17, The Chemical Society, London.
21. Kielland, J. *J. Am. Chem. Soc.* **2** (1937) 1675.
22. Dyrssen, D. and Liem, D. H. *Acta Chem. Scand.* **14** (1960) 1091.
23. Liem, D. H. and Dyrssen, D. *Acta Chem. Scand.* **20** (1966) 272.
24. Liem, D. H. *Proc. Intern. Conf. Solvent Extraction Chem.* (ICSEC) Gothenburg, North-Holland, Amsterdam 1967, p. 264.

Received September 25, 1967.