Inorganica Chimica Acta, 110 (1985) 69–76

The Solvent Extraction of Metal Ions from Aqueous Solutions containing NNN′N′-Ethylenediaminetetraacetic and Related Acids.
Part 1. Uranium(IV)

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Received March 1, 1985

Abstract

The uranium(IV) complexes $[U(EDTA)(H_2O)_2]$, $[U(HOEDTA)]^+$, and $[U(DTPA)]^-$ are well-formed in the pH range 2–3 ($[DTPA]^{5-}$ = diethylenetriaminepentaacetate; $[HOEDTA]^{3-}$ = N-(2-hydroxyethyl)ethylenediaminetriacetate). Of these, only $[U(DTPA)]^-$ is extracted from an aqueous phase at pH 2 by the perchlorate salt of the primary amine, Primene JM-T. As the aqueous phase pH was raised, extraction occurred in all three cases and hydrolysed species may be extracted from EDTA and HOEDTA solutions but $[U(DTPA)]^-$ resists hydrolysis. The addition of sulphate had a marked effect on the extraction of U(IV) from EDTA and HOEDTA through the formation of $[U(EDTA)(SO_4)(H_2O)]^{2-}$ and $[U(HOEDTA)(SO_4)(H_2O)_n]^-$. The equilibrium constant, log β_1, for:

$$[(U(EDTA)(H_2O)_2] + [SO_4]^{2-} \rightleftharpoons [U(EDTA)(SO_4)(H_2O)]^{2-} + H_2O$$

was found to be 2.43 ± 0.04 ($I = 1$ mol dm^{-3}, $NaClO_4$; pH 2.0; 20 °C) from spectrophotometric data.

With tri-n-octylphosphine oxide (TOPO) electronic spectroscopy showed that the same U(IV) complex was extracted at pH 2 for Cs_2UCl_6, U(IV)/HOEDTA, and U(IV)/DTPA and the aminepolycarboxylates were aqueous phase masking agents but with $[U(EDTA)(H_2O)_2]$ oxidation gave a uranyl(VI) organic phase species.

Uranium(IV) is strongly extracted from aqueous solutions of HOEDTA at pH 2 or 3 by bis(2-ethylhexyl)phosphoric acid (HBEHP) but less so from EDTA and DTPA. Since U(IV) is completely extracted from Cs_2UCl_6 it could be that the aminepolycarboxylates were aqueous phase masking agents although spectral evidence did not support this.

Introduction

There have been a few reports on metal ion extraction from aqueous solutions of aminepolycarboxylic acids (complexones) into organic phases containing long chain amines. Primary (including Primene JM-T), secondary, and tertiary amines and a quaternary salt have been used [1, 2] in xylene to extract ions such as Am(III) and Eu(III) from EDTA solutions and extraction of the same elements [3] from HOEDTA and DTPA by the quarternary salt Aliquat 336-S has been described. The amines were converted to the salts of the complexones either by a pre-equilibration [1, 2, 3] or concomitantly [1, 3] with metal ion extraction and in either case it was assumed that the chelates, *e.g.* $[Eu(EDTA)]^-$, are extracted when coordinating aqueous phase inorganic anions were absent. Conversely, if a trivalent lanthanide is introduced [4] as the sulphate then extraction from dilute sulphuric acid into long chain, primary amine sulphates proceeds via sulphato-complexes $[Ln(SO_4)_2]^-$ with the aminepolycarboxylic acids acting as aqueous phase masking agents when some selectivity between neighbouring pairs of lanthanides was achieved. In all these experiments, the aqueous phase acidity was low, *e.g.* pH 2, in order to allow the ionisation of the organic acids and to favour the formation of the chelates. If the metal ion concentration is low it is exceedingly difficult to demonstrate extraction via the chelate, *e.g.*, $[Eu(EDTA)]^-$, except by the use of amine and complexone dependence experiments or by showing that the metal ion does not extract under the same conditions but in the absence of the complexone. Experience has shown [5] that it is desirable to confirm the nature of the extracted species by use of an independent technique. We know of no extraction experiments with U(IV) and an aqueous phase aminepolycarboxylic acid.

In the present study, we extracted U(IV) from aqueous phases containing aminepolycarboxylic acids into Primene JM-T, TOPO, and HBEHP. The distribution ratio D_u was measured for a variety of conditions including the addition of the complexing anion,

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0020-1693/85/$3.30

sulphate, for extraction into Primene JM-T. Unless otherwise stated, the concentration of U(IV) equalled that of the complexone. Electronic and IR spectroscopy was used to help elucidate the nature of the extracted species. Throughout the abbreviations EDTA, DTPA, and HOEDTA refer to non-specific forms of the acids. For specific cases charges are included.

Experimental

Materials

Primene JM-T was a gift from Rohm and Haas (UK) Ltd. and used as supplied. *Anal.* The major constituent is stated as 1,1,3,3,5,5,7,7,9,9-decamethyldecylamine, RMM = 297 daltons, requires: C, 80.8; H, 14.5; N, 4.7%. For Primene JM-T found: C, 81.0; H, 14.6; N, 4.5%. RMM, found from non-aqueous titration with perchloric acid in chlorobenzene, 324. In all weighings with Primene JM-T a RMM of 324 was assumed. All other materials including diluents were of the highest obtainable grade. Cs_2UCl_6 and $[U(EDTA)_2 \cdot 2H_2O]$ were prepared by standard methods. *Anal.* $[U(EDTA)_2 \cdot 2H_2O]$ requires: C, 21.4; H, 2.9; N, 5.0%. Found: C, 21.3; H, 2.1; N, 4.7%.

Extraction Experiments

All extraction experiments were repeated at least twice and two samples for analysis were taken from each equilibrium aqueous phase. The reproducibility of the D_u values was 10% or better. D_u was determined by measurements on the initial and equilibrium aqueous phases only. Before determination [6] with 4-(2-pyridylazo)resorcinol (PAR), uranium(IV) was oxidised to uranium(VI) with excess potassium persulphate. The initial concentrations of U were determined in the presence of the same aqueous phase components as used in the extractions.

Solutions of Primene JM-T were prepared by weighing aliquots of the amine into graduated flasks which were than made up to the mark with the diluent. Primene JM-T was converted to its salt by shaking an organic phase with an equal volume of an appropriate mineral acid aqueous phase. Mechanical agitation for 30 min was used in all extraction experiments since preliminary work showed that equilibrium was achieved in this time. For uranium extractions, equal phase volumes (usually 5 cm^3) were always used. The phases separated cleanly on standing or after centrifugation. The pH of the initial aqueous phases was adjusted with perchloric acid or sodium or ammonium hydroxide; pH was measured with calibrated Philips PW 9418 or 9409 meters.

Solutions of TOPO and HBEHP were also made up by weight in graduated flasks.

Spectral Measurements

Infrared Experiments

The organic phase was warmed to remove solvent xylene and the spectrum of the residue was recorded as a liquid film between the KBr plates on a Perkin Elmer 577 spectrophotometer.

Electronic Spectra

Primene JM-T perchlorate is much more soluble in hexane than xylene and hexane was usually used as the diluent. In a typical experiment Cs_2UCl_6 (0.01 mol dm^{-3}) was dissolved in an aqueous phase at the appropriate pH containing an equal concentration of the aminepolycarboxylic acid. Primene JM-T perchlorate (0.25 mol cm^{-3}) was prepared in hexane. The organic phase spectrum was recorded using 10 mm or 40 mm matched quartz cells (solvent blank) and a calibrated Unicam 8-100 spectrophotometer. The wavelength reproducibility was within the recommended limits (0.5 nm).

Results and Discussion

Uranium(IV) forms the complexes [7] $[U(EDTA)(H_2O)_2]$, $[U(DTPA)]^-$, and $[U(HOEDTA)(H_2O)_n]^+$ at low pH although the formation constant of the last is not known. These species are presumably eight-coordinate and some are known to form adducts with a secondary ligand. Examples are $[U(EDTA)(H_2O)(SO_4)]^{2-}$ [8] and for Th(IV) $[Th(DTPA)(tiron)]^{5-}$ ([9], tiron = tetra-anion of 1,2-dihydroxybenzene-3,5-disulphonic acid). The adducts are likely to have coordination numbers greater than eight in some cases.

The variation in the degree of formation of the species (calculated from literature constants) $[UCl]^{3+}$, [U(EDTA)], $[U(HOEDTA)]^+$, and $[U(DTPA)]^-$ with pH is given in Table I. Hydrolysis of the hydrated U(IV) ion sets in between pH 2 and 3 but is avoided [7] by the addition of $Na_2H_2EDTA \cdot 2H_2O$, $H_3HOEDTA$, or H_5DTPA.

1. Extraction of U(IV) from Aminepolycarboxylate Solution by Primene JM-T Perchlorate (Solvent Xylene)

Extraction of U(IV) into Primene JM-T perchlorate is not to be expected in the pH range 2–3 from solutions of Cs_2UCl_6, U(IV)/EDTA, and U(IV)/HOEDTA and none was found (Table II). On raising the pH above 3.5 for both $[U(EDTA)(H_2O)_2]$ and $[U(HOEDTA)(H_2O)_n]^+$ hydrolysis commences [7]. For EDTA, $[U(OH)(EDTA)]^-$ and $[U(OH)(EDTA)]_2^{2-}$ are well-characterised [7] as initial hydrolysis products. Table II shows the variation of D_u as the equilibrium pH was raised. For extraction from EDTA, plots of log D_u against log[Primene

TABLE I. Species Distribution (%) in Uranium(IV) Solutions Containing Aminepolycarboxylic Acids[a].

	pH	1	2	3
$[EDTA]^{4-}$	U^{4+}	0.6	0.01	$<1 \times 10^{-3}$
$\log_{10} K = 25.8$[b]	[U(EDTA)]	99.4	99.99	>99.99
$[HOEDTA]^{3-}$	U^{4+}	29.5	1.2	0.1
$\log_{10} K = 19$[c]	$[U(HOEDTA)]^+$	70.5	98.8	99.9
$[DTPA]^{5-}$	U^{4+}	4.6	0.02	$<1 \times 10^{-3}$
$\log_{10} K = 28.76$[d]	$[U(DTPA)]^-$	95.4	99.98	>99.99
Cs_2UCl_6	$[UCl]^{3+}$	8.7	–	–

[a]Total U = total aminepolycarboxylic acid, pK_a values [10]. [b][11]. [c]Estimate, for Th(IV) $\log_{10} K = 18.5$ [12]. [d][13], [Th(H·DTPA)] is reported [14] but no similar species for U(IV); $\log_{10} K$ $[UCl]^{3+} = 0.30$ [15], total Cl = 1×10^{-2} mol dm^{-3}.

TABLE II. Extraction Data for U(IV); Variation of D_u with pH.

Series 1. Primene JM-T perchlorate[a] (Cs_2UCl_6, pH 2, $D_u = 0.00$)																
	$U(EDTA)(H_2O)_2$				$H_3HOEDTA$				H_5DTPA							
pH	2.90	3.15	3.35	3.60	1.99	2.26	2.64	3.44	0.62	1.20	2.00	3.00				
D_u	0.00	0.11	0.25	0.31	0.00	0.00	0.08	0.10	0.05	0.13	0.46	0.72				
Series 2. Primene JM-T perchlorate[a]; total sulphate 0.05 mol dm^{-3}																
	Cs_2UCl_6				$[U(EDTA)(SO_4)]^{2-}$				$H_3HOEDTA$				H_5DTPA			
pH	1.86	2.30	2.81	3.62	0.55	2.00	2.50	3.50	1.99	2.41	3.07	3.94	1.90	2.88	3.54	4.15
D_u	3.27	2.52	1.89	1.25	0.41	1.51	6.55	7.24	∞[b]	84	17	9.2	0.71	0.88	0.90	0.96
Series 3. TOPO (0.2 mol dm^{-3}; hexane)																
	Cs_2UCl_6				$H_3HOEDTA$				$[U(EDTA)(H_2O)_2]$				H_5DTPA			
pH	1.35	2.28	2.51		1.92	2.29	2.49		1.83	2.06	2.50		1.78	2.16	2.45	
D_u	∞[b]	12.3	9.0		∞[b]	5.5	4.5		0.2	0.3	0.5		0.8	2.2	2.5	
Series 4. HBEHP (mol dm^{-3}); toluene; pH 2																
HBEHP	Cs_2UCl_6				$H_3HOEDTA$				$[U(EDTA)(H_2O)_2]$				H_5DTPA			
0.05	∞[b]				∞[b]				4.52				1.22			
0.01	∞[b]				1.31				0.43				0.12			

[a]Primene JM-T, 0.033 mol dm^{-3}; U(IV) = organic acid = 5.00×10^{-4} mol dm^{-3}. [b]No detectable aqueous phase U at equilibrium.

JM-T] at equilibrium pH 4.15 and 4.50 were straight lines of slope 1.66 and 1.63 respectively (Table III, Series 1a). We presume that hydrolysed species containing either $[EDTA]^{4-}$ or $[HOEDTA]^{3-}$ are extracted. With H_5DTPA, the anion $[U(DTPA)]^-$ is well-formed and extraction (Table II) was observed even at an equilibrium pH of 0.62 and D_u increased to 0.82 at an equilibrium pH of 4.65 and then decreased slightly at higher pH. The ion $[U(DTPA)]^-$ is stable [7] to hydrolysis below pH 6. The Primene JM-T dependence plot obtained at pH 1.96 had a slope of 1.04 (Table III, Series 1b) indicating $[U(DTPA)]^-$ as the extracted species.

2. *Formation of $[U(EDTA)(H_2O)(SO_4)]^{2-}$ from $[U(EDTA)(H_2O)_2]$*

This ion has been identified from ^1H NMR experiments [8] in sulphate solution of low pH and is resistant to hydrolysis. At pH 2 we assumed that no free U(IV) was present (Table I) and that $[HSO_4]^-$ forms no complex with $[U(EDTA)(H_2O)_2]$ so that the relevant equilibria and mass balance equations are as shown below (H = H^+, HS = $[HSO_4]^-$, S = $[SO_4]^{2-}$, UE = $[U(EDTA)(H_2O)_2]$, UES = $[U(EDTA)(H_2O)(SO_4)]^{2-}$, S_T = total sulphate, U_T = total U(IV) = total EDTA):

$$H + S \rightleftharpoons HS \qquad K_H (I = 1) \qquad (1)$$

TABLE III. Primene JM-T Concentration Dependencies[a].

Series 1. Primene JM-T perchlorate (JM-T, mol dm^{-3}); xylene

(a) [(U(EDTA)(H$_2$O)$_2$]

JM-T	0.033	0.030	0.028	0.025	0.020	
D_u	0.37	0.31	0.28	0.23	0.16	pH 4.15
D_u	0.36	0.30	0.27	0.23	0.16	pH 4.50

(b) [U(DTPA)]$^-$

D_u	0.24	0.22	0.20	0.18	0.14	pH 2.00

Series 2. Primene JM-T perchlorate (JM-T, mol dm^{-3}); xylene

Extraction from sulphate media

(a) [U(EDTA)(H$_2$O)$_2$]; I = 1.00 (NaClO$_4$); total sulphate = 0.05; pH 2.00

JM-T	0.033	0.030	0.028	0.025	0.020
D_u	0.040	0.033	0.029	0.022	0.014

(b) Cs$_2$UCl$_6$; total sulphate = 0.01; pH 2.00

JM-T	0.033	0.030	0.028	0.025	0.020	0.015	0.010
D_u	2.44	2.24	2.06	1.74	1.47	1.16	0.88

(c) H$_3$HOEDTA; I = 1.00 (NaClO$_4$); total sulphate = 0.05; pH 2.00

JM-T	0.033	0.030	0.028	0.025	0.020
D_u	0.20	0.18	0.16	0.15	0.12

(d) H$_5$DTPA; total sulphate = 0.05; pH 2.00

JM-T	0.033	0.030	0.028	0.025	0.020
D_u	0.98	0.88	0.83	0.74	0.60

[a] U(IV) = organic acid = 5 × 10^{-4} mol dm^{-3}.

$$\mathrm{UE} + \mathrm{S} \rightleftharpoons \mathrm{UES} \qquad \beta_1 \qquad (2)$$

$$([\mathrm{U(EDTA)(H_2O)_2}] + [\mathrm{SO_4}]^{2-} \rightleftharpoons [\mathrm{U(EDTA)(SO_4)(H_2O)}]^{2-} + \mathrm{H_2O})$$

$$\mathrm{S_T} = \mathrm{S} + \mathrm{HS} + \mathrm{UES} \qquad (3)$$

$$\mathrm{U_T} = \mathrm{UE} + \mathrm{UES} \qquad (4)$$

These equations may be combined to give:

$$[(1 + K_\mathrm{H}\mathrm{H})\beta_1]\mathrm{S}^2 - [\mathrm{S_T}\beta_1 - 1 - K_\mathrm{H}\mathrm{H} - \beta_1\mathrm{U_T}]\mathrm{S} - \mathrm{S_T} = 0 \qquad (5)$$

Thus at a given pH, an approximate value of β_1 can be used to find S, the equilibrium free sulphate ion concentration, for any solution composition. Analysis of spectrophotometric data to give a refined value of β_1 through the program SQUAD [16, 17] requires as input:

$$\mathrm{S_T}^1 = \mathrm{S} + \mathrm{UES} \qquad (6)$$

Using the first approximate values of S eqns. (1) and (3) were used to find $\mathrm{S_T}^1$. SQUAD found the best-fit β_1 from the input $\mathrm{U_T}$, $\mathrm{S_T}^1$, an estimate of β_1, and spectrophotometric absorbance data. Seven solutions with $\mathrm{U_T}$ = 5.00 × 10^{-4} mol dm^{-3} and $\mathrm{S_T}$ in the range 6.25 × 10^{-4} – 2.50 × 10^{-2} mol dm^{-3} at pH 2 and I = 1 mol dm^{-3} (NaClO$_4$) were measured at 4 nm intervals between 230 and 262 nm to give the required absorbance input. SQUAD then refined β_1 and calculated the extinction coefficients of UE and UES at each wavelength. The new value of β_1 was then used to find new values of $\mathrm{S_T}^1$ and the process repeated until successive values of log β_1 differed by less than 0.01 log unit. In order to check the standard of refinement the extinction coefficients (ϵ) of UE were measured at the same wavelengths in the absence of sulphate at pH 2 and I = 1.0 mol dm^{-3}. The results are given in Table IV.

There is a remarkable degree of agreement between the calculated and experimental values of ϵ, UE which would seem to fully justify the assumptions made in the analysis. Under these conditions the degree of formation of UES (% of $\mathrm{U_T}$) varied between 12.2% ($\mathrm{S_T}$ = 6.25 × 10^{-4}) to 85.8% ($\mathrm{S_T}$ = 2.50 × 10^{-2} mol dm^{-3}). Calculation then showed that under these conditions [SO$_4$]$^{2-}$ would not replace [EDTA]$^{4-}$ in the coordination sphere of U(IV).

$$\mathrm{U^{4+}} + [\mathrm{SO_4}]^{2-} \rightleftharpoons [\mathrm{U(SO_4)}]^{2+} \qquad \log K_1 = 3.42\ [18] \qquad (7)$$

TABLE IV. Formation Constant of $[U(EDTA)(SO_4)(H_2O)]^{2-}$. $I = 1$ mol dm^{-3} ($NaClO_4$), pH ≈ 2, $K_H = 12.59$ dm^3 mol^{-1} [21], $\log_{10}\beta_1 = 2.43$ (±0.04); 20 °C.

λ (nm)	ε (calc.) UE[a,b]	ε (exp.) UE	ε (calc.) UES[b]
230	1655	1656	1778
234	1489	1490	1610
238	1316	1318	1438
242	1150	1150	1271
246	979	980	1099
250	811	812	932
254	644	644	765
258	477	476	596
262	310	312	433

[a] ε, dm^3 mol^{-1} cm^{-1}. [b] Estimated standard deviation from SQUAD, ±3.

$$[U(SO_4)]^{2+} + [SO_4]^{2-} \rightleftharpoons [U(SO_4)_2] \qquad \log K_2 = 2.40\ [18] \qquad (8)$$

$$[Th(SO_4)_2] + [SO_4]^{2-} \rightleftharpoons [Th(SO_4)_3]^{2-} \qquad \log K_3{}^1 = 0.76\ [19] \qquad (9)$$

Notwithstanding the excellent agreement in the values of ε(UE), the refined value of $\log \beta_1$ was higher than anticipated by about an order of magnitude. Sulphate must replace one or possibly two water molecules and $[U(EDTA)(H_2O)_2]$ is uncharged and hindered so that a value more like $\log K_3{}^1$ (above) seemed likely. The high calculated value of $\log \beta_1$, may explain the resistance of $[U(EDTA)(H_2O)(SO_4)]^{2-}$ to hydrolysis since the important hydrolysis constants of $[U(EDTA)(H_2O)_2]$ are also relatively high (water molecules omitted):

$$[U(EDTA)] + OH^- \rightleftharpoons [U(EDTA)(OH)]^- \qquad \log K_{H1} = 9.28\ [7] \qquad (10)$$

$$2[U(EDTA)(OH)]^- \rightleftharpoons [U(EDTA)(OH)]_2{}^{2-} \qquad \log K_{H2} = 2.9\ [7] \qquad (11)$$

3. Extraction of U(IV) from Solutions Containing Sulphate by Primene JM-T Perchlorate (Solvent Xylene)

(i) $[U(EDTA)(H_2O)_2]$

The addition of sulphate, which suppresses hydrolysis through the formation [8] of $[U(EDTA)(H_2O)(SO_4)]^{2-}$, caused a remarkable increase in D_u for extraction into Primene JM-T perchlorate (Table II). The slope of the Primene JM-T dependence plot (Table III, Series 2a) was 2.08. Under the prevailing conditions the sulphato-complex is better than 80% formed so that this result has increased reliability. By holding the U(IV) and Primene JM-T concentrations constant and varying total sulphate at a fixed pH, a plot of $\log D_u$ against $\log[SO_4{}^{2-}]$ should give at low sulphate concentrations, a slope equal to the number of sulphate ions present in the extracted complex and at higher sulphate a value of $\log D_u$ independent of the sulphate concentration [20]. Two such experiments were performed at pH 2 with Primene JM-T = 0.033 mol dm^{-3} and total sulphate in the range $2.00 \times 10^{-3} - 2.00 \times 10^{-1}$ mol dm^{-3}. The expected behaviour was observed (Table V). The slopes of the linear positions of the plots were 0.83 ($U_T = 1.00 \times 10^{-3}$ mol dm^{-3}) and 1.00 ($U_T = 5.00 \times 10^{-4}$ mol dm^{-3}). Since the ionic strength was low (K_H approaches 100 as $I \to 0$ [22], eqn. (5)), the slopes were calculated assuming that half the total sulphate was present as $[HSO_4]^-$ but variation in this had very little effect on the value of the slope. Exchange between $[ClO_4]^-$ and $[SO_4]^{2-}$ and $[HSO_4]^-$ was ignored (see below). The combined results indicate that $[U(EDTA)(H_2O)(SO_4)]^{2-}$ was the extracted species.

In principle, it is possible to find $\log \beta_1$ (eqn. (2)) from the extraction data [20] but because the degree of exchange between $[ClO_4]^-$ and the other inorganic anions is not known there is no justification for continuing the calculations. The organic phase electronic spectra indicated that no oxidation of U(IV) occurred.

TABLE V. Sulphate Concentration Dependence in Primene JM-T Perchlorate Extraction. Primene JM-T = 0.03 mol dm^{-3}; $[U(EDTA)(H_2O)]$ 1.00×10^{-3} (Series 1) and 5.00×10^{-4} mol dm^{-3} (Series 2); pH = 2.00.

Series 1. Total sulphate, $S_T{}^1$, mol dm^{-3}									
$S_T{}^1$	0.002	0.004	0.005	0.010	0.020	0.025	0.040	0.050	0.100
D_u	0.013	0.094	0.169	0.200	0.439	0.630	0.918	1.097	1.178
$S_T{}^1$	0.200								
D_u	1.186								
Series 2. Total sulphate, $S_T{}^1$, mol dm^{-3}									
$S_T{}^1$	0.005	0.010	0.020	0.025	0.040	0.050	0.100	0.200	
D_u	0.309	1.584	1.635	1.865	2.691	3.019	4.709	4.712	

(ii) Extraction of Cs_2UCl_6 from Aqueous Sulphate Solutions Alone

Calculation showed that a 1.00×10^{-2} mol dm^{-3} solution of Cs_2UCl_6 containing 5.00×10^{-2} mol dm^{-3} sulphate ion would consist (in terms of total uranium) of 0.1% free U(IV) ion, 11.3% $[U(SO_4)]^{2+}$, and 88.5% $[U(SO_4)_2]$ with very little $[UCl]^{3+}$ present. At pH 2 and a low ionic strength, the presence of $[HSO_4]^-$ would complicate the analysis but even so the sulphato-complexes would be well formed ($\log K_1$, U(IV) + $Cl^- \rightleftharpoons [UCl]^{3+}$, 0.30). Under these conditions U(IV) was extracted into Primene JM-T perchlorate (Table II) but the D_u values were in general lower than those observed in the presence of EDTA (Table II). The slope of the Primene JM-T dependance plot (Table III, Series 2b) was 1.04. The form of the extracted species is unknown but could be, for example, $[U(OH)(SO_4)_2]^-$. The solid $U(OH)_2SO_4$ is known [22] and $[Hf(OH)_2(SO_4)_2]^{2-}$ is said to be an organic phase species in Alamine 336 extraction [23]; $U(OH)(NO_3)_3 \cdot xTBP$ has also been identified [24].

The combined data help to confirm that $[U(EDTA)(SO_4)(H_2O)]^{2-}$ is the extracted species in the previous example.

(iii) $H_3HOEDTA$

The addition at pH 2 of 0.05 mol dm^{-3} sulphate to a solution of Cs_2UCl_6 and $H_3HOEDTA$ caused U(IV) to be completely extracted into Primene JM-T perchlorate (Table II). The slope of the Primene JM-T dependence plot was 1.06 (pH 2, Table III, Series 2c) which may suggest $[U(HOEDTA)(SO_4)]^-$ as the extracted species. Even though the D_u values were much greater than from sulphate alone, the situation is not as clear cut as for the EDTA system since a solution of pH 2 would contain some free U(IV) ion and the slope of the Primene JM-T dependence plot was the same as that found from sulphate alone. The balance of the evidence does suggest a HOEDTA species in the organic phase.

(iv) H_5DTPA

The addition of pH 2 of 0.05 mol dm^{-3} sulphate to a solution of Cs_2UCl_6 and H_5DTPA had little effect (Table II) on the D_u value. Since $[U(DTPA)]^-$ is fully formed and the slope of the Primene JM-T dependence plot (Table III, Series 2d) remained at 1 we assume no sulphato-adduct of $[U(DTPA)]^-$ is extracted into Primene JM-T perchlorate.

4. Spectroscopic Studies Relevant to the Primene JM-T Extractions

(a) Exchange of Sulphate for Organic Phase Perchlorate

For the Primene JM-T extractions, an alternative is to use the sulphate rather than the perchlorate salt in which case it might well have been possible to find β_1 (eqn. (2)) from the extraction data [20]. We avoided the use of the sulphate salt as it would appear that its presence in lanthanum [4] and possibly U(IV) [25] systems can favour the extraction of sulphato-complexes which do not contain the aminepolycarboxylate ion. On evaporation of diluent in each case, the organic phase perchlorate ion vibrational spectrum in the antisymmetric stretching region (centred at 1080 cm^{-1}) was largely unaffected on the extraction of $[U(EDTA)(SO_4)]^{2-}$ from sulphate (0.05 mol dm^{-3}) solution and the strong organic phase absorption found at 1172 cm^{-1} on equilibrating Primene JM-T with dilute sulphuric acid was absent. In the antisymmetric bending region centred near 640 cm^{-1} there was marginal evidence to suggest sulphate/perchlorate exchange on the extraction of $[U(EDTA)(SO_4)]^{2-}$ from sulphate solution as before. Gravimetric analysis on the initial and equilibrium sulphate-containing aqueous phases proved insufficiently precise to detect any differences. It appeared that exchange was surprisingly slight with Primene JM-T perchlorate (0.033 mol dm^{-3}) and total sulphate in the range $2 \times 10^{-3} - 1 \times 10^{-1}$ mol dm^{-3} but further work is required.

(b) The f–f Electronic Spectrum of Uranium(IV)

The f–f spectrum of uranium(IV) below 750 nm is characterised by fairly sharp transitions centred near 660, 550, 485, and 430 nm of which the first is the most intense. We measured the equilibrium organic and aqueous phase spectra used here in appropriate cases for Primene JM-T extraction and found them to contain U(IV). Nephelauxetic effects of a few percent have been observed on adding various complexing agents to a uranium(IV) sulphate solution [26]. The nephelauxetic factors of water and sulphate with U(IV) were found to be almost the same [27]. The instrument used in the present work had a wavelength reproducibility of 0.5 nm or better. For extraction into Primene JM-T perchlorate significant differences were found (Table VI) for the organic phase spectra obtained from: (i) U/EDTA/SO_4, (ii) U/HOEDTA/SO_4, and (iii) U/SO_4 which would seem to confirm that the extracted species were not the same in each case and the aminepolycarboxylate ions were not acting as aqueous phase masking agents. This argument is strengthened by observations in the TOPO systems (see below) where identical organic phase spectra were obtained for U(IV) extraction under various conditions but for HBEHP where we suspect an identical extraction mechanism in each case (see below) what appear to be significant differences were observed. It is thus difficult to draw conclusions but at least it was confirmed that no oxidation of U(IV) had occurred.

TABLE VI. Electronic Spectra (nm) of the Uranium(IV) Solutions[a].

(a) Extraction into Primene JM-T perchlorate					
	λ(max). Organic phase. Aqueous sulphate = 0.05 mol dm^{-3}				
Cs_2UCl_6	650	550	490	470	428
$H_3HOEDTA$	656	544	486	460	sh[b]
$[U(EDTA)(H_2O)_2]$	654	548	484	462	sh
	λ (max). Aqueous phase. Sulphate = 0.05 mol dm^{-3}. pH 2				
Cs_2UCl_6[c]	652	548	480	sh	428
$[U(EDTA)(H_2O)_2]$	660	552	488	sh	430
	λ (max). Aqueous phase. No sulphate. pH 2				
$[U(EDTA)(H_2O)_2]$	658	552	488	sh	430
$H_3HOEDTA$	658	550	486	sh	430
Cs_2UCl_6	646, 629, 548, 495, 482, 470, 430				
(b) Extraction into TOPO					
	λ (max). Organic phases (except[d] EDTA)				
	674, 646, 642(sh), 624(sh), 550, 539, 485, 450(sh), 437, 422				

[a] For details, see Experimental. [b] sh = shoulder. [c] U(IV) present as $[U(SO_4)_2]$, see text. [d] See text.

5. *Extraction of U(IV) from Aminepolycarboxylate Solution by Tri-n-octylphosphine Oxide (TOPO; Solvent Hexane)*

Table II gives the variation of D_u with pH from Cs_2UCl_6 alone and from U(IV) solutions of the three aminepolycarboxylates for extraction into TOPO; U(IV) is well-extracted in all four cases and particularly at low pH. Examination of the electronic spectra (Table VI) of the organic phases obtained from Cs_2UCl_6 alone, $H_3HOEDTA$/U(IV), and H_5DTPA/U(IV) showed them to be identical in peak positions and general appearance, in marked contrast to the examples quoted earlier for which the organic phase spectra were merely similar. It must be the case that: (i) the extracted species is the same in the three cases and cannot contain aminepolycarboxylate, (ii) HOEDTA and DTPA are acting as aqueous phase masking agents with DTPA the most successful, as expected, and (iii) the presence of organic phase TOPO serves to radically alter the aqueous phase species distribution involving HOEDTA, DTPA and U(IV). The nature of the organic phase species was not determined.

From solutions containing $[U(EDTA)(H_2O)_2]$ extraction into TOPO was observed (Table II) but here the organic phase contained only U(VI) as deduced from an examination of the organic phase spectrum (no absorption at 660 nm; typical uranyl(VI) absorption centred at 430 nm).

6. *Extraction of U(IV) from Aminepolycarboxylate Solution by Bis(2-ethylhexyl)phosphoric Acid (HBEHP; Solvent Toluene)*

HBEHP is known to function in metal ion extraction as the anion $[BEHP]^-$, the half-ionised dimer $[H(BEHP)_2]^-$, and the neutral molecule although the last is unlikely from solutions of low acidity. In the present study, the only well-characterised U(IV) cations in aqueous solution at pH 2 are $[U(H_2O)_8]^{4+}$ (from Cs_2UCl_6 and U(IV)/HOEDTA) and $[U(HOEDTA)\cdot nH_2O]^+$ with none reported for EDTA or DTPA. Cs_2UCl_6 (5.00×10^{-4} mol dm^{-3}) was completely extracted (Table II) by HBEHP (0.05 mol dm^{-3}) in the aqueous phase pH range 1.72 to 4.09. On adding $H_3HOEDTA$ (5.00×10^{-4} mol dm^{-3}) at pH 2 again U(IV) was completely extracted (HBEHP, 0.05 mol dm^{-3}). The presence of EDTA (D_u; 4.52) or DTPA (D_u; 1.22) at pH 2 reduced the value of D_u to give the order $Cs_2UCl_6 \simeq$ U(IV)/HOEDTA > U(IV)/EDTA > U(IV)/DTPA. The HBEHP dependence plot was non-linear from $H_3HOEDTA$. The same order was found for 0.010 mol dm^{-3} HBEHP ($H_3HOEDTA$ D_u = 1.31; H_4EDTA, 0.43; H_5DTPA 0.11). The combined evidence suggests (see also TOPO extraction) that the same (unknown) species is extracted in each case and the aminepolycarboxylates act as aqueous phase masking agents. If this were the case, identical organic phase spectra might be expected from the four systems as for TOPO extraction. Such behaviour was not found; peak positions were not identical (U(IV), initial 0.01 mol dm^{-3}; HBEHP 0.20 mol dm^{-3}; solvent xylene; pH 2; path length 40 mm: Cs_2UCl_6 660; U(IV)/HOEDTA 662; U(IV)/EDTA 650; U(IV)/DTPA 652 nm).

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