The chemistry of uranium
Part 43. The interaction between uranium(IV), Cl⁻, Br⁻ and monodentate amide ligands — a quantitative treatment

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Abstract

The reactions of UCl_4 with chloride, UBr_4 with bromide ions and UCl_4 with an amide ligand N, N-diethylpropionamide (DEPA) in acetone solution have been treated quantitatively, by applying spectrophotometric data and iterative computing methods. Sets of simultaneous equilibria were established for each system. Conditional equilibrium constants were obtained and species distribution curves produced.

Introduction

Although the chloro and bromo chemistry of uranium(IV) has been studied extensively with reference to solid complexes which were isolated from aqueous or non-aqueous solution [1–3], only a limited number of studies dealt with the quantitative treatment of solution equilibria in either of these media. Only the formation constants for the first two chloro complexes of uranium(IV) have been reported in aqueous solutions [4]. The weak complexing capability of chloride ions towards uranium(IV) in aqueous solution as well as difficulties in detecting complex formation due to the small spectral changes associated with such a system could serve as an explanation for this situation.

Earlier work performed in acetone solutions [5] indicated that significant spectral changes occur when a UCl_4 solution reacts with a soluble chloride in this solvent to form six-coordinated anionic chloro complexes. In a previous study by the present authors [6] these spectral changes were used for the calculation of conditional formation constants for UCl_4, UCl_5^- and UCl_6^{2-} by a simulation method. During this study characterization of the individual species was not applied. The subsequent characterization of solid uranium tetrachloride and bromide complexes of the types UCl_5L^- [7], $UCl_3L_3^+$ [7], UX_4L_2 [8] and $UX_2L_4^{2+}$ [9] (X = Cl and Br) through X-ray structural and electronic spectral analysis reached a stage where the knowledge obtained through the characterization of

solid species could now be applied towards similar studies in solution.

The object of this work was to obtain the formation constants for the various equilibrium species involved in these systems in acetone solutions and the concomitant species distribution curves. It was realized that the quantitative description of the reaction between uranium(IV) and chloride and bromide ions, respectively, would have to be refined as far as possible before the more complicated $U/X^-/L$ systems could be tackled in a systematic manner. In this paper we therefore report results obtained from a reinvestigation of the U/Cl^- system and the first results for the U/Br^- system. This is followed by the study of the U/Cl/DEPA system where DEPA = N,N-diethylpropionamide. This system is of interest since both UCl_4DEPA_2 and $[UCl_3L_4]^+[UCl_5DEPA]^-$ could be isolated. A crystal structural analysis [7] was also done on the latter compound.

Experimental

Spectrophotometric methods

Both solid reflectance and solution spectra were recorded on a Shimadzu UV 3100 spectrophotometer. Spectral data were obtained by introducing 3 cm³ of a 0.01 M acetone solution of UCl_4 into a 1.0 cm quartz cuvette with a teflon stopper. A concentrated solution of the ligand containing 0.25 mole equiv. was introduced successively using a 100 μl syringe. Spectra from 350 to 2200 nm were recorded at 20 °C before the first and after each addition. The absorbance values as-

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sociated with the spectra were corrected for dilution after each recording and before storing.

Spectrophotometric and potentiometric titrations were performed simultaneously in a double jacketed titration vessel at 20 °C. The cap of the reaction vessel allowed for an inlet and outlet tube, an indicator and reference electrode and the burette tip to be placed into the solution. The solution in the reaction vessel was pumped through the cuvette in the Beckman 198404 constant temperature cuvette holder by an ISCO WIZ peristaltic pump. The ligand solution was added to the reaction mixture using a Metrohm 645 Multi-Dosimat and the potential of the electrode measured by a Metrohm 632 pH-meter. The indicator electrode was a Metrohm EA 246 Ag/AgCl electrode with an internal solution of 10% NBu_4ClO_4 in acetone. The reference electrode was a Metrohm double junction electrode with a 2×10^{-4} mol dm^{-3} acetone solution of LiCl as inner solution. The outer solution was a 20% solution of NBu_4ClO_4 in acetone.

The software package Spectracalc by Galactic Industries Corporation was used for the Gaussian analysis.

Chemicals

UCl_4 and UBr_4MeCN_4 as well as their acetone solutions were prepared as previously reported [10] N,N-Diethylpropionamide (DEPA) and N,N'-dimethyl-N,N'-diphenyl urea (DDU) were obtained from Tokyo Kasei Kogyo Co., Ltd. N,N-Dimethylacetamide (DMA) (Hopkins and Williams) and N,N,N,N-tetraethyl urea (TEU) (Eastman and Kodak) were used as supplied. UCl_4DEPA_2 and $[UCl_3L_4]^+[UCl_5DEPA]^-$ were prepared as previously described [7].

Qualitative speciation using spectral results of UX_4/X^- systems

The general method which was followed for the speciation study in solution involved a comparison of the solid reflectance spectrum of the compound with that of the compound dissolved in methylene dichloride. If these two spectra closely resembled one another then the solution spectrum was used to characterize the species in terms of ϵ_m and λ_{max}. The following species could be treated in this way.

UX_6^{2-}

The spectrum of UCl_6^{2-} has been well characterized both in the solid state [11–13] and in acetonitrile [14, 15] and nitromethane [16] solutions. Its non-aqueous solution spectra in the above-mentioned solvents as well as in acetone and methylene dichloride solutions are very similar. All of these have a triplet at ~2000 nm. ($[PPh_3et]_2UCl_6$ has maxima at 1969, 1993 and 2024 in CH_3CN solution, and at 1970, 1995 and 2025 in acetone solution). Its solid reflectance spectrum has a

doublet with peaks at 1965 and 2025 nm. The situation is very similar with the bromo analogue, viz. a doublet with peaks at 2042 and 2081 nm for the solid reflectance spectrum and very similar triplets for the solution spectra (2046, 2061 and 2082 nm for acetonitrile and 2047, 2063 and 2084 nm for acetone solutions, respectively).

$[UX_5S]^-$ ($S = acetone$)

Although all efforts to prepare a solid compound of this anion with a simple large cation failed for both $X = Cl$ and $X = Br$ [5] an autoionized solid $[UCl_3DEPA_4][UCl_5DEPA]$ was recently isolated and characterized [7]. A typical six coordinated somewhat broad band with a maximum at 1990 nm in its solid state spectrum was ascribed to the presence of this anion [7]. The published procedure was repeated by us and the centre of the band was found to be at 1975 nm. The spectra of CH_3CN solutions 0.01 M in UCl_4 and which contained UCl_4, $Nbut_4Cl$ and an amide ligand in the mole ratio 1:1:1 were subsequently recorded for each of a number of amide ligands. Their absorption maxima were all found to be in the same region, viz. 1972 (DEPA) and 1968 (DMA and TEU) nm. Low absorptivity values in the 1150 nm region (in these mixtures) indicated the absence of higher coordinated species. The corresponding spectra hardly differed when acetone or methylene dichloride were used as solvents. In the light of the above a single maximum at 1975 nm in the spectrum of a similar acetone solution containing only UCl_4 and Cl^- in a 1:1 mole ratio can confidently be ascribed to the presence of $[UCl_5S]^-$. Very similar results were obtained with the corresponding bromo analogues. Single band maxima were obtained at 2010 (DMA), 2017 (TEU) and 2034 (acetone alone) nm in acetone solutions.

UX_4S_2

A number of UCl_4L_2 complexes of weak amide ligands have band maxima in the vicinity of 1950 nm, e.g. 1955 (DDU) [17] and 1950 (DEPA) nm in both their solid reflectance and solution spectra. A band maximum in this region of the spectrum of the acetone solution of UCl_4 can therefore be assumed to be characteristic of UCl_4S_2. A similar maximum at ~1970 nm can be expected for the bromo analogue. (A maximum at 1970 nm was found for UBr_4DDU_2 [17].)

UX_4S_4 and $UX_3S_4^+$

It is known that a major band with maximum at ~1150 nm is typical of seven coordinated species, e.g. $[UCl(TMPO)_6]Cl_3$ [10] (TMPO = trimethylphosphine oxide), and eight coordinated species e.g. UCl_4NMA_4 [1] (NMA = N-methylacetamide), for chloro complexes of uranium(IV). The bromo analogues are similar to the above chloro complexes.

Results of the titration of UCl₄

Results of the titration of UCl$_4$

The spectra obtained at the various stages of the spectrophotometric titrations (Fig. 1) can now be analyzed with reference to major species involved.

Spectrum of an acetone solution of UCl$_4$ containing no additional Cl$^-$: absorptions at B and I (Fig. 1) can be ascribed to chloro species having coordination numbers greater than six, e.g. UCl$_3$S$_4$$^+$ or UCl$_4$S$_4$. Shoulders at C ($\sim$1950 nm) and D ($\sim$1975) suggest the presence of UCl$_4$S$_2$ and UCl$_5$S$^-$, respectively.

UCl$_4$:Cl$^-$ mole ratio region 1:0 to 1:1
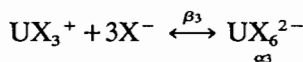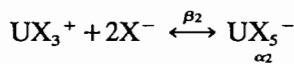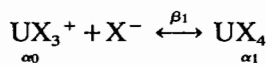
UCl$_4$:Cl$^-$ mole ratio region 1:0 to 1:1

A drastic decrease in the concentration of the higher coordinated species is indicated by the decrease in the absorption at B and I, respectively. The increase in the shoulder D to form the maximum E ($\sim$1975 nm) at a mole ratio of 1:1 indicates the presence of major amounts of UCl$_5$S$^-$. Another interesting feature in this region is the presence of an isosbestic point at K which seems to suggest that the main reaction in this region is the formation of UCl$_5$S$^-$ from the higher coordinated species. A sharp band maximum at A ($\sim$1100 nm), which is associated with this anion, also appears in this region.

Mole ratio region 1:1 to 1:2

Mole ratio region 1:1 to 1:2

The spectral changes in this region suggest that the main reaction is associated with the change from UCl$_5$S$^-$ to UCl$_6$$^{2-}$ as evidenced by the gradual change of the major maximum at E to the three band maxima at F, G and H which are typical of UCl$_6$$^{2-}$. The isosbestic point at J and the absence of higher coordinated species as indicated by an absence of absorption at $\sim$1150 nm support this argument.

Quantitative treatment of the U(IV)/X$^-$ system

Quantitative treatment of the U(IV)/X$^-$ system

The following equilibria were now postulated in the light of the above to describe the system for X = Cl:

$$UX_3^+ + X^- \underset{\alpha_0}{\overset{\beta_1}{\longleftrightarrow}} UX_4 \; \underset{\alpha_1}{}$$

$$UX_3^+ + 2X^- \underset{\alpha_0}{\overset{\beta_2}{\longleftrightarrow}} UX_5^- \; \underset{\alpha_2}{}$$

$$UX_3^+ + 3X^- \underset{\alpha_0}{\overset{\beta_3}{\longleftrightarrow}} UX_6^{2-} \; \underset{\alpha_3}{}$$

A computer program was written to handle the experimentally obtained UCl$_4$:Cl$^-$ mole ratio versus absorption values at each of a number of wave numbers.

The method applied to the calculations can be summarized as follows. Estimates were made for the β values of the equilibria and for the molar absorptivities of the various species. The β values, the total metal concentration and the total added chloride ion concentrations were then used to calculate the free chloride ion concentration for each experimental point (mole ratio) in the titration. The mole fraction of each species at each point in the titration was then calculated, using the free chloride ion concentration. These mole fraction values were then used, in conjunction with the total uranium concentration and the estimates of the molar absorptivities to calculate the absorbance contribution of each species at each point in the titration. The calculated absorbance values at each mole ratio were then added and compared to the corresponding experimental absorbance values. Convergence of the data was obtained by a least-squares iterative method. The final results were inspected with reference to the molar absorptivity values of those species which had previously been characterized. These values were then modified, if necessary, and fixed in the final iteration process.

The values of the formation constants thus obtained were $\beta_1 = 1.0 \times 10^8$, $\beta_2 = 5.3 \times 10^{15}$ and $\beta_3 = 1.0 \times 10^{21}$ ($K_1 = 1 \times 10^8$, $K_2 = 5.3 \times 10^7$ and $K_3 = 1.9 \times 10^5$). It is difficult to determine these values accurately in the light of the covariance of the ϵ_m values and the constants. The fact that the ϵ_m values of species which could be characterized could be fixed, however, increased the confidence level of the β values as compared to the purely numerical treatment. The representations in Fig. 2 indicate to what extent the data of the titration curves could be simulated at two different wavelengths. Very similar simulations could be obtained at the other wavelengths.

The results obtained for the molar absorptivity values (in cm^{-1} mol^{-1} dm^{-3}) of the various species at the wavelengths under consideration for this system are given in Table 1.

The species distribution curves are presented in Fig. 3. The linear formation of UCl$_5$S$^-$ over the mole ratio region 1:0 to 1:1 as characterized by the major bands at 1975 nm ($\epsilon_m = 32.6$) and 1099 nm ($\epsilon_m = 28.4$) (Table 1) to reach its maximum concentration sharply at a mole ratio of 1:1 is also supported by results obtained
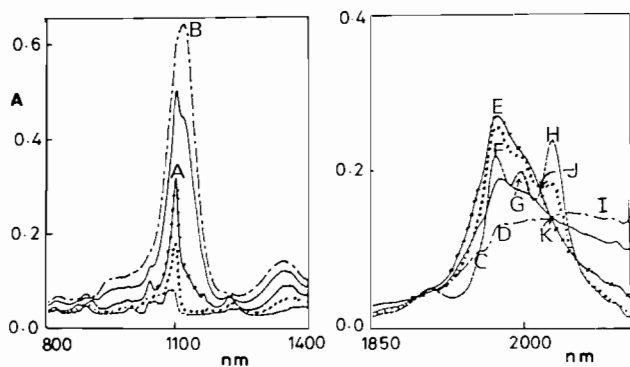

Fig. 1. Results of a spectrophotometric titration of 0.01 M UCl$_4$ with Nbut$_4$Cl in acetone solution. – – – U:Cl mole ratio 1:4; —— U:Cl mole ratio 1:4.5; – · – U:Cl mole ratio 1:5; · · · · · U:Cl mole ratio 1:5.5; – · · – U:Cl mole ratio 1:2.
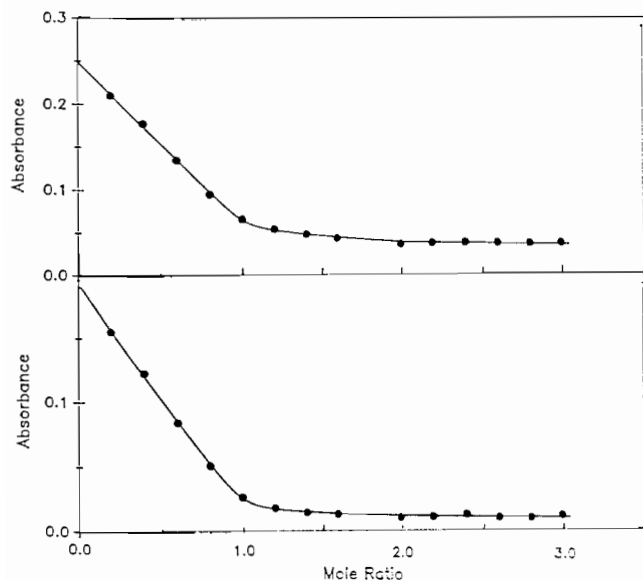
Fig. 2. Comparison of the simulated (smooth curves) and experimental (dots) data for the spectrophotometric titration of 0.01 M UCl$_4$ with Nbut$_4$Cl at 1080 (top curve) and 1154 (bottom curve) nm, respectively.

TABLE 1. Calculated molar absorptivities for species involved in the U(IV)/Cl$^-$ system

Wavelength (nm)	Molar absorptivities			
	ϵ_m^0 (UCl$_3^+$)	ϵ_m^1 (UCl$_4$)	ϵ_m^2 (UCl$_5^-$)	ϵ_m^3 (UCl$_6^{2-}$)
660	103	52.3	4.8	6.9
1080	83.0	49.7	11.0	8.8
1099	92.1	93.5	28.4	7.1
1117	170	87.8	3.4	3.5
1154	75.6	34.0	3.4	3.0
1975	12.8	2.3	32.6	24.9
2015	17.9	14.1	24.1	24.2
2027	34.1	10.7	18.0	31.5

from earlier conductometric titration curves [5] which gave a sharp break at this point. Gaussian analyses performed on the 2000 nm region of the spectrum of such solutions indicate a major band maximum at 1975 nm thus also suggesting the presence of a major quantity of UCl$_5$S$^-$. The systematic decrease in the concentration of the higher coordinated uranium(IV) chloro species to almost zero at a mole ratio of 1:1 is in agreement with earlier data obtained from enthalpimetric titrations of UCl$_4$ versus Cl$^-$ which indicated that heat is absorbed in the reaction over this region thus suggesting that the reaction is entropy driven. Heat is, however, evolved from 1:1 to 1:2 mole ratios [5] which agrees with the reaction in which one acetone molecule is replaced by a Cl$^-$. The presence of a small amount of UCl$_4$S$_2$ at

a mole ratio of 1:1 is suggested by a small band at $\sim$1950 nm in the Gaussian analysis of the spectrum.

A similar systematic change of essentially UCl$_5$S$^-$ to UCl$_6^{2-}$ in the 1:1 to 1:2 mole ratio region is again supported by breaks in the conductometric titration curve at mole ratios of 1:1 and 1:2 [5], a linear curve in between as well as the presence of an 'isosbestic point' at J (Fig. 1) and similar ϵ_m values of the two species at 2015 nm in Table 1.

A limitation of the present model is that it cannot differentiate between the different neutral UCl$_4$ species. The ϵ_m values given in Table 1 for UCl$_4$ must therefore be regarded as average values of the different species. A Gaussian analysis of the spectrum of a UCl$_4$ solution in acetone in the 2000 nm (5000 cm^{-1}) region indicated a band at 1950 nm which can be assigned to UCl$_4$S$_2$. If a similar ϵ_m value to that of UCl$_4$DEPA$_2$ is assumed for this species its approximate concentration can be calculated to be 18%. This would mean that about 24% of the uranium is present as UCl$_4$S$_x$ ($x=3$ or 4) if the value of 42% for total UCl$_4$ species obtained from the species distribution is taken to be correct. A band at 1975 nm in the same spectrum could be assigned to UCl$_5$S$^-$. A similar calculation yields 27% for the latter. It is in fair agreement with a value of 29% obtained from the species distribution calculation.

Sharp breaks in conductometric and enthalpimetric titration curves at a mole ratio of 1:2 as well as the fact that the spectrum changes only marginally after a mole ratio of 1:2 even with large excess of Cl$^-$, all agree with high % of UCl$_6^{2-}$ found at 1:2 in the species distribution curve.

The UBr$_4$/Br$^-$/acetone system

The behaviour of this system is similar to its chloro analogue. The band maxima in the spectrum of the corresponding bromo complexes in general experience a shift to higher wavelengths. Whereas the Ag/AgCl electrode could be used in the initial part of the titration to monitor the free Cl$^-$ concentration this was not possible in the case of the bromo system in the light of the unreliability of the Ag/AgBr electrode under the experimental conditions. (AgBr starts to dissolve as AgBr$_2^-$ already at relatively low Br$^-$ concentrations in acetone as solvent.)

The results of the spectrophotometric titration are represented in Fig. 4. The constants obtained by using the same equilibria and program as for the chloro system are $\beta_0=8\times10^5$, $\beta_1=4\times10^{12}$ and $\beta_2=2.8\times10^{16}$ ($K_1=8\times10^5$, $K_2=5\times10^6$ and $K_3=7\times10^4$). The representations in Fig. 5 illustrate to what extent the simulation could be achieved when compared to the experimental data for two wavelengths. The molar absorptivities are given in Table 2 and the species distribution curves in Fig. 6.
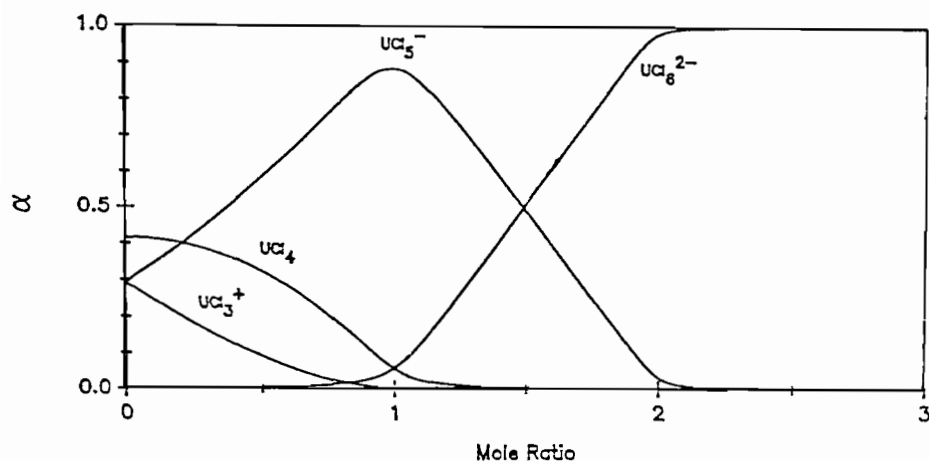
Fig. 3. Species distribution curves for the reaction of 0.01 M UCl$_4$ with Nbut$_4$Cl in the UCl$_4$:Nbut$_4$Cl mole ratio region 1:0 to 1:3.
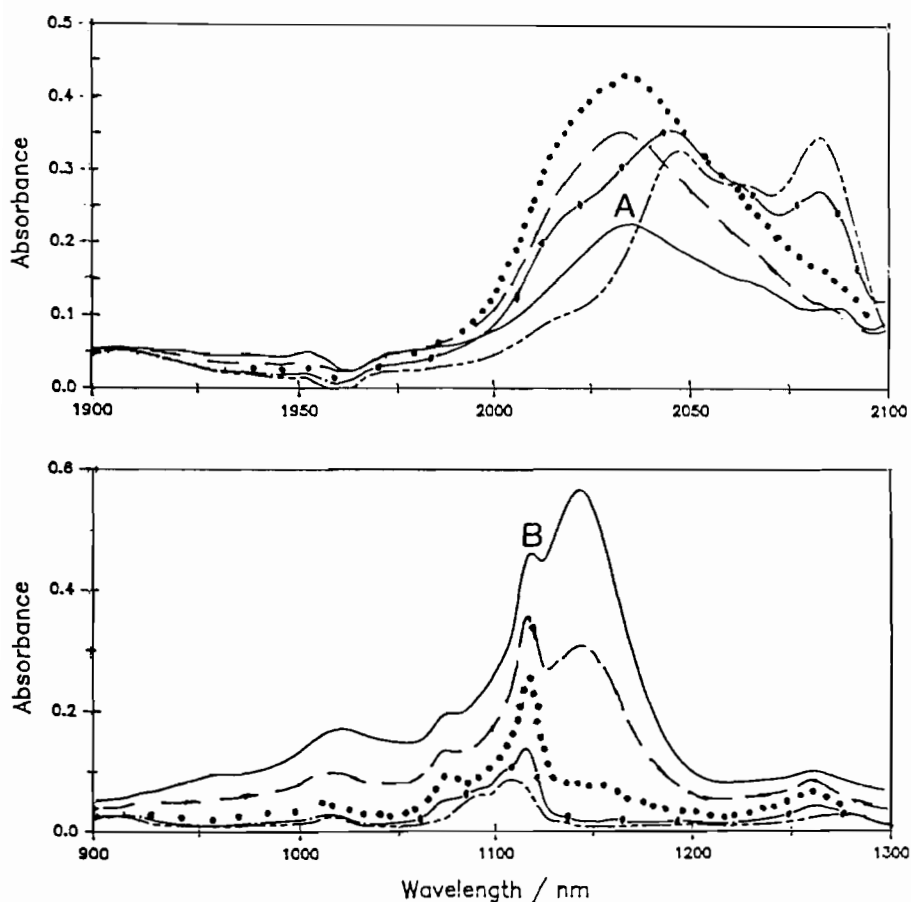

Fig. 4. Results of the spectrophotometric titration of 0.01 M UBr$_4$ with Nbut$_4$Br in acetone solution. —— U:Br mole ratio 1:4; – – – U:Br mole ratio 1:4.5; · · · · · U:Br mole ratio 1:5; – · – U:Br mole ratio 1:5.5; – —— – U:Br mole ratio 1:6.

Discussion

When the species distribution curves of the two halide systems are compared it is clear that there are more ions present in the 0.01 M solution of UBr$_4$ (84% of uranium(IV)) than in a similar UCl$_4$ solution (58%).

This is in agreement with conductivity measurements reported earlier [18] where λ_{200} had the values 45 and 25 S cm^2, respectively. Although the corresponding bromide ion concentration will be higher than that of the chloride as illustrated by the curves in Fig. 7 (Br$^-$ is a slightly weaker ligand than Cl$^-$ towards ura-

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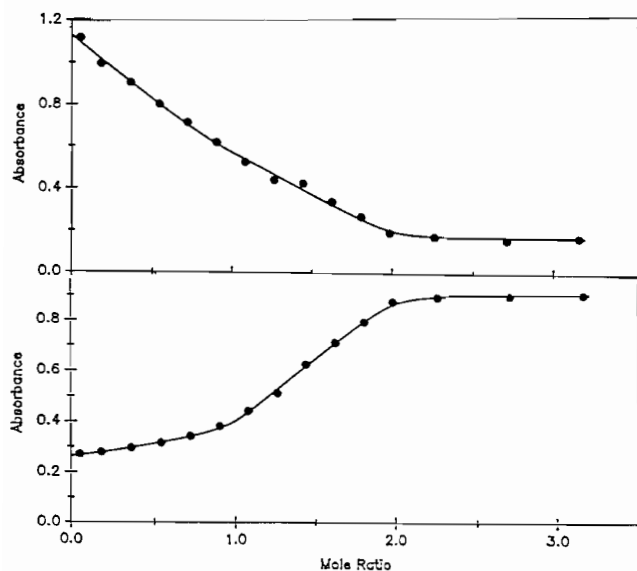

Fig. 5. Comparison of the simulated (smooth curves) and experimental (dots) data for the spectrophotometric titration of 0.01 M UBr$_4$ with Nbut$_4$Br at 1120 (top curve) and 2084 (bottom curve) nm, respectively.

TABLE 2. Calculated molar absorptivities for species involved in the U(IV)/Br$^-$ system

Wavelength (nm)	Molar absorptivities			
	ϵ_m^0 (UBr$_3^+$)	ϵ_m^1 (UBr$_4$)	ϵ_m^2 (UBr$_5^-$)	ϵ_m^3 (UBr$_6^{2-}$)
668	82.6	34.9	11.6	5.4
1012	39.2	12.7	7.1	1.8
1074	42.6	13.8	12.5	1.0
1120	102	41.9	32.1	10.0
1148	143	58.1	11.4	0.2
2034	7.6	18.4	60.4	16.5
2052	6.9	19.8	44.3	44.3
2084	12.8	1.3	21.8	50.5

Fig. 6. Species distribution curves for the reaction of 0.01 M UBr$_4$ with Nbut$_4$Br in the UBr$_4$:Nbut$_4$Br mole ratio region 1:0 to 1:3.

nium(IV)), the main contribution towards the conductivity comes from a greater % of autoionized species. Solvation of anions is relatively small in an aprotic
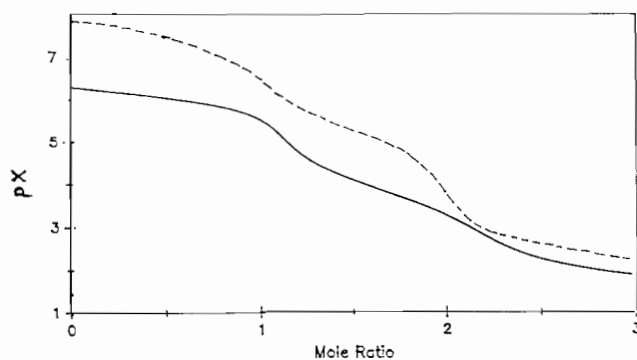

Fig. 7. Plot of the calculated log X$^-$ concentration during the titration of 0.01 M UX$_4$ with Nbut$_4$X in the UX$_4$:Nbut$_4$X mole ratio region 1:0 to 1:3 (X = Cl$^-$ for top curve and X = Br$^-$ for bottom one).

solvent like acetone, which results in the fact that anions are relatively strong donors in such media. The UBr$_5$S$^-$ species is well established in acetone solution and the results obtained from Gaussian analysis of the spectrum in the region of 2000 nm also enabled the determination of the concentration of this species at each of the mole ratios from 1:0 to 1:2. These are indicated in the curve in Fig. 6. The relatively more significant UBr$_5$S$^-$ bands, A at ~2030 nm and B at ~1120 nm regions in Fig. 6, also suggest a relatively bigger initial % of UBr$_5$S$^-$. The ϵ_m values in Table 2 are in agreement with these.

The rest of the species distribution diagram is very similar to that of the chloro system. The maximum concentration of UBr$_5$S$^-$ found at a mole ratio of 1:1 is somewhat higher mainly because the formation of UBr$_6^{2-}$ is lower at any specific mole ratio than in the case of the chloro analogue. The molar absorptivities of UBr$_5$S$^-$ and UBr$_6^{2-}$ are the same at 2052 nm. The maxima in these values are also higher for the bromo analogues.

The UCl$_4$/DEPA system

Although qualitative reaction schemes [10] have been proposed for the above type of system no quantitative treatment has been recorded so far. The successful treatment of the UCl$_4$/Cl system and the structural and spectral data which became available for solids containing important species in this system improved the chances for a satisfactory quantitative treatment. Since this is a more complicated mixed ligand system the chloride ion concentration cannot be calculated as in the UCl$_4$/Cl$^-$ system. It would be necessary to determine the Cl$^-$ concentration at each experimental point in order to numerically treat the system with an iterative procedure. As DEPA is a relatively weak oxygen donor ligand the chloride ion concentration will probably not become very high via ligand replacement unless a large excess of ligand is used. The potentiometric deter-

mination of chloride which could only be applied at the beginning of the titration of UCl_4 with Cl^- when the Cl^- concentration is low could therefore be more satisfactorily applied in this instance. A ~ 0.01 M acetone solution of UCl_4 was thus titrated with a concentrated solution of DEPA and followed spectrophotometrically and potentiometrically simultaneously. The results of these titrations are represented in Figs. 8 and 9, respectively.
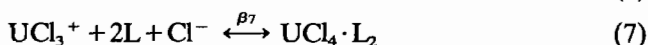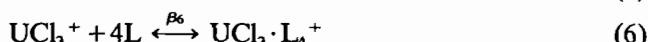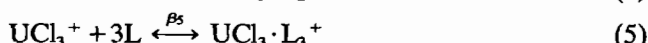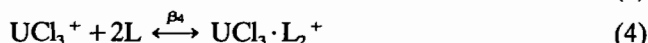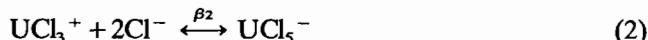
Qualitative treatment

From Fig. 8 it can be seen that a shoulder at ~ 1950 nm, ascribed to UCl_4S_2, gradually increases to a peak at 1952 nm which reaches its maximum at about a mole ratio of 1:2.5 thus indicating the formation of UCl_4DEPA_2. The presence of shoulder B at mole ratios 0.5, 1.0 and even slightly at 1.5 and 2 provides evidence for the presence of UCl_5S^-. Shoulders at E in the 1100 nm region also support this assumption. The peak F is typical of UCl_4L_2 species. The conductometric titration curve (Fig. 9) indicates an initial increase in conductivity which can be ascribed to enhanced autoionization. This is soon followed by a systematic reduction in conductivity due to molecule formation, i.e. UCl_4DEPA_2. After a mole ratio of 2.5 a gradual

increase in conductivity results owing to gradual ionization (see Fig. 9).

Quantitative treatment

The above information was now used as a basis for the description of the system in terms of the following set of equilibria:

$$UCl_3^+ + Cl^- \xrightarrow{\beta_1} UCl_4 \tag{1}$$

$$UCl_3^+ + 2Cl^- \xrightarrow{\beta_2} UCl_5^- \tag{2}$$

$$UCl_3^+ + L \xrightarrow{\beta_3} UCl_3 \cdot L^+ \tag{3}$$

$$UCl_3^+ + 2L \xrightarrow{\beta_4} UCl_3 \cdot L_2^+ \tag{4}$$

$$UCl_3^+ + 3L \xrightarrow{\beta_5} UCl_3 \cdot L_3^+ \tag{5}$$

$$UCl_3^+ + 4L \xrightarrow{\beta_6} UCl_3 \cdot L_4^+ \tag{6}$$

$$UCl_3^+ + 2L + Cl^- \xrightarrow{\beta_7} UCl_4 \cdot L_2 \tag{7}$$

The conditional stability constants obtained by simulation studies of the spectrophotometric titration of UCl_4 with DEPA are as follows: $\beta_1 = 1.0 \times 10^5$; $\beta_2 = 1.1 \times 10^{10}$; $\beta_3 = 9.7 \times 10^4$; $\beta_4 = 1.0 \times 10^7$; $\beta_5 = 3.1 \times 10^9$; $\beta_6 = 6.1 \times 10^{11}$; $\beta_7 = 3.0 \times 10^{12}$.

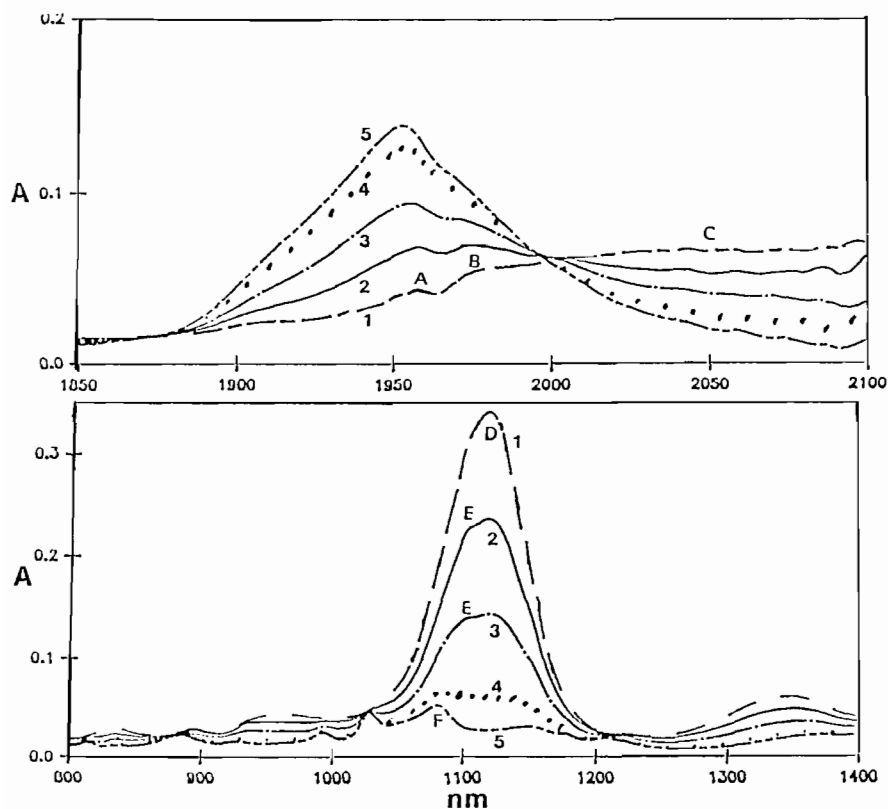The results of the simulations performed at 1080 and 1117 nm, respectively, are represented in Fig. 10.

Fig. 8. Results of a spectrophotometric titration of 0.00469 M UCl_4 with DEPA in acetone solution. Curve 1, UCl_4:DEPA mole ratio 1:0; curve 2, UCl_4:DEPA mole ratio 1:0.5; curve 3, UCl_4:DEPA mole ratio 1:1; curve 4, UCl_4:DEPA mole ratio 1:1.5; curve 5, UCl_4:DEPA mole ratio 1:2.
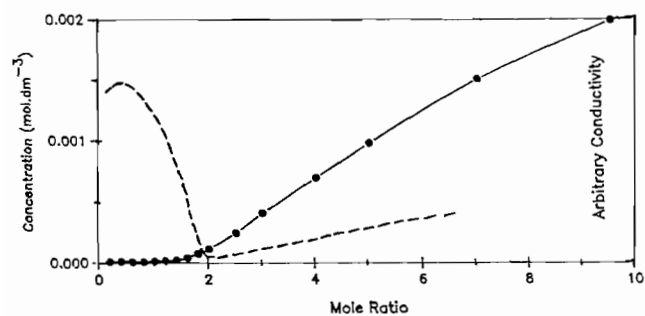
Fig. 9. Potentiometrically measured free Cl^- concentration at various UCl_4:DEPA mole ratios during the titration of 0.00469 M UCl_4 with DEPA in acetone solution (dots). The broken curve represents the conductivity changes under similar conditions (see right-hand side for ordinate axis).
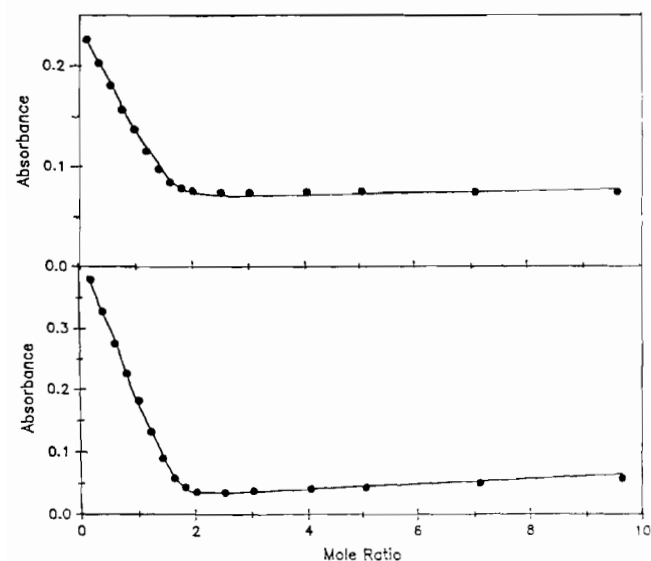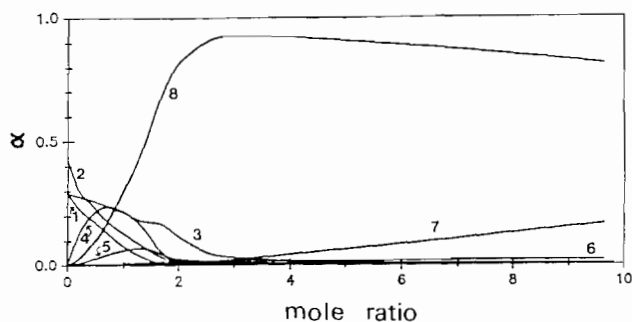

Fig. 11. Species distribution curves for the reaction of 0.00469 M UCl_4 with DEPA in the UCl_4:DEPA mole ratio region 1:0 to 1:10. Curve 1, UCl_3^+; curve 2, UCl_4; curve 3, UCl_5^-; curve 4, UCl_3DEPA^+; curve 5, $UCl_3(DEPA)_2^+$; curve 6, $UCl_3(DEPA)_3^+$; curve 7, $UCl_3(DEPA)_4^+$; curve 8, $(DEPA)_2$.

Fig. 10. Comparison of the simulated (smooth curves) and experimental (dots) data for the spectrophotometric titration of 0.00469 M UCl_4 with DEPA in the UCl_4:DEPA mole ratio region 1:0 to 1:10 at 1080 (top curve) and 1117 (bottom curve) nm, respectively.

Similar good fits could be obtained at the other wavelengths. A set of equations similar to the above with the exception that eqn. (6) was left out was also used for simulation studies. Satisfactory fits could not have been obtained in that way.

The molar absorptivity values calculated by the program fit in fairly well with those expected, e.g. an ϵ_m value of 62 was calculated for $UCl_3L_4^+$ and a value of 65 obtained for an 0.02 M acetone solution containing U, Cl, DEPA and ClO_4 at the mole ratio of 1:3:4:1. The other cationic species could not be isolated as such. If the molar absorptivity values at 1117 and 1154 nm are considered they seem to be all seven or eight coordinated species e.g. $UCl_3LS_3^+$, $UCl_3L_2S_2^+$ or $UCl_3L_3S^+$. Those of the six coordinated species UCl_5S^- and UCl_4L_2 are very close to the expected values at

all wavelengths studied. The species distribution curves are given in Fig. 11. These distribution curves clearly indicate the simultaneous nature of the equilibria and the complexity of the system. The species distribution curves indicate that the major initial reaction (up to a mole ratio of 0.5) consists of the formation of UCl_3L^+ (eqn. (3)) mainly at the expense of UCl_3^+ and UCl_4 since all these equilibria are interrelated. It is of interest to note that the initial increase in conductivity is also accompanied by the increase in concentration of UCl_3L^+ and that after a mole ratio of 0.5 the concentration of the neutral species UCl_4DEPA_2 becomes dominant. The reason for the relatively weak conductometric endpoint can be interpreted in terms of the presence of autoionized species up to a mole ratio of ~ 2.7. After this point ionization takes over very gradually. This is in agreement with the gradual increase in conductivity.

Acknowledgements

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