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A ^{31}P and ^{15}N NMR Study of the Synergistic Extraction of Uranyl Nitrate by Tributylphosphate and Di-2-ethylhexyl Phosphoric Acid

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Abstract

Low temperature ^{31}P and ^{15}N NMR spectroscopy was used to investigate the species forming in the organic layer following the extraction of uranium from nitric acid solutions with the synergistic mixture, TBP–DEHPA. It was found that the complex formed during extraction was a mixed nitrato complex $UO_2(NO_3)A\cdot TBP$. Although the existence of the complex $UO_2A_2\cdot x TBP$ may be demonstrated in model systems, the complex does not form under actual extraction conditions.

Introduction

In a recent paper, we have discussed the application of multi-nuclear NMR spectroscopy to investigate speciation during the extraction of uranium from nitric acid solutions with bis-2-ethylhexyl phosphoric acid (DEHPA) [1].

Since DEHPA is often used in conjunction with other organophosphorus extractants [2–4], we decided to extend our studies to the bis-2-ethylhexyl-phosphoric acid–tributylphosphate (DEHPA–TBP) synergistic solvent extraction system.

Extraction constant measurements in this system by Bykhovtsov *et al.* [5–7] had led them to postulate the existence of the species $UO_2A_2\cdot UO_2(NO_3)_2\cdot 2TBP$ ($A = (C_8H_{17}O)_2PO_2^-$).

In the light of our previous study, it seemed likely to us that by using ^{31}P and ^{15}N NMR spectroscopy to probe the organic phase, we might find direct spectroscopic evidence for such a species.

Experimental

UO_2A_2 was prepared by the method of Peppard and Ferraro [8]. $UO_2(NO_3)_2\cdot 2TBP$ was prepared by the method of Fleming and Lynton [9].

^{15}N labelled uranyl nitrate was prepared by dissolving UO_3 in a slight excess of 6 M $H^{15}NO_3$ (supplied by M.S.D. isotopes) and drying under vacuum.

Extractions were done by stirring together for 15 min, equal aliquots of a 0.5 M solution of the extractants in spectral grade hexane with a 1 M $UO_2(NO_3)_2$ solution in 3 M nitric acid.

^{31}P and ^{15}N spectra were run on a Brucker 90 FT spectrometer using C_6D_6 as a lock solvent. It was found that, in the case of the ^{15}N spectra, adding a relaxation agent such as chromium acetylacetonate decreased the time necessary to obtain a spectrum; but it did cause some signal broadening. ^{31}P chemical shifts are reported relative to 85% aqueous H_3PO_4 as zero. ^{15}N chemical shifts are reported relative to nitromethane as zero.

Results and Discussion

^{15}N and ^{31}P NMR spectra were obtained both for the solution obtained by extracting a 1 M solution of uranyl nitrate in 3 M nitric acid with an equimolar solution of DEHPA and TBP in hexane and for model systems in which a stoichiometric amount of one of the extractants was added to the isolated complex of uranium with the other extractant.

The spectra were run at low temperatures (240 K) in order to stop exchange. ^{31}P and ^{15}N chemical shifts are listed in Tables I and II.

I. DEHP–TBP–HNO_3

A solution of 0.5 M DEHPA and 0.5 M TBP in hexane equilibrated with 3 M HNO_3 gave ^{31}P peaks at −0.9 ppm and −2.1 ppm. DEHPA equilibrated alone with HNO_3 had a ^{31}P chemical shift of −0.3 ppm; while TBP alone equilibrated with HNO_3 had one of −2.5 ppm. Thus it appears that a TBP–DEHPA–HNO_3 complex forms in the mixed system.

II. $UO_2(NO_3)_2$*–*HNO_3*–TBP*

$UO_2(NO_3)_2\cdot 2TBP$ has a ^{31}P chemical shift of 0.5 ppm at ambient temperature; the shift increases

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TABLE I. ^{31}P Chemical Shifts

Compound	Solvent	T (K)	^{31}P (ppm)
0.1 M DEHPA	hexane	210	−0.33
0.1 M DEHPA	hexane (saturated with HNO_3)	210	−0.34
0.1 M $UO_2(DEHPA)_2$	hexane	210	5.80
		305	6.22
0.025 M $UO_2(DEHPA)_2$	hexane	305	6.15
TBP	hexane–C_6D_6 (1:4)	236	−0.50
		305	−0.67
TBP–HNO_3–xH_2O	hexane–C_6D_6 (1:4)	305	−2.45
$UO_2(NO_3)_2 \cdot 2TBP$	hexane–C_6D_6 (1:4)	230	0.82
		305	0.52

TABLE II. ^{15}N Chemical Shifts of some TBP and DEHPA Complexes

Compound	Solvent	T (K)	^{15}N (ppm)[a]
0.18 M $UO_2(^{15}NO_3)_2 \cdot 2TBP$	C_6D_6	250	8.34
1 M $TBP \cdot H^{15}NO_3 \cdot xH_2O$	C_6D_6	305	31.84
0.1 M $UO_2(^{15}NO_3)(A)(HA)$	hexane	185	10.83

[a] Measured relative to $Na^{15}NO_3$, but reported relative to nitromethane as zero, using ^{15}N ($Na^{15}NO_3$) = 3.53 ± 0.1 ppm.

slightly at lower temperatures. Adding excess TBP causes exchange averaging of the free and bound TBP signals [7].

Adding excess TBP to a solution of $UO_2(^{15}NO_3)_2 \cdot 2TBP$ in hexane caused no change in the ^{15}N spectra. However, adding a small amount of TBP saturated with nitric acid caused signal broadening at ambient temperatures. Nitrate exchange between $UO_2(^{15}NO_3)_2 \cdot 2TBP$ and TBP–HNO_3–H_2O could be slowed so that separate signals could be observed by cooling to 250 K. Shaking a solution of $UO_2(NO_3)_2 \cdot 2TBP$ in hexane with aqueous nitric acid alone does not lead to nitrate exchange. Excess TBP in the organic layer is necessary as a phase transfer agent before nitrate exchange can take place.

III. $UO_2(NO_3)_2 \cdot 2TBP$–DEHPA

Representative low temperature ^{31}P spectra are shown in Fig. 1. When DEHPA is added to a solution of $UO_2(NO_3)_2 \cdot 2TBP$ in a molar ratio of 1:1, the low temperature ^{31}P spectrum shows new peaks at 4.4 ppm, 2.9 ppm and −3.0 ppm, as well as a peak at 0.72 ppm due to the original complex. The peaks at 2.9 ppm, 3.0 ppm, and 0.72 ppm show exchange broadening at ambient temperatures while the peak at 4.4 ppm remains sharp. The former peaks thus may be assigned to TBP in three different sites; and the latter peak to DEHPA, complexed to uranium. Under the same conditions, the ^{15}N spectrum shows new ^{15}N signals at 10.3 ppm and 36.8 ppm, as well as a peak at 9.0 ppm arising from residual $UO_2(^{15}NO_3)_2 \cdot$

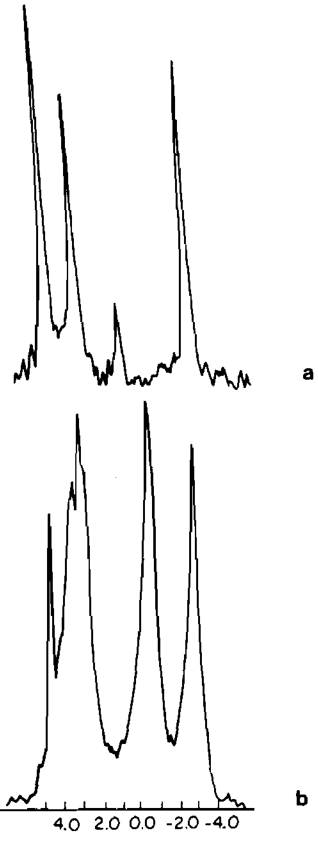

Fig. 1. ^{31}P spectra in hexane at 210 K of: (a) $UO_2(NO_3)_2 \cdot 2TBP + HA$; (b) $UO_2(NO_3)_2 \cdot 2TBP + 4HA$.

2TBP. When 1 M TBP is equilibrated with 6 M $H^{15}NO_3$, a ^{15}N peak is observed at 31.8 ppm at 210 K. By analogy, the peak at 36.8 ppm may thus be assigned to a $TBP{\cdot}HNO_3$ complex. The difference in chemical shift may be ascribed to the fact that the model system is anhydrous, whereas in extraction from aqueous solution, the extracted $TBP{\cdot}HNO_3$ carries along water of hydration [10, 11]. Moreover, the contribution of ionized forms $(Bu_3O)_3PO^+H{\cdots}NO_3^-$ is believed to depend both on the solvent and the amount of coextracted water [12].

When the $UO_2(NO_3)_2{\cdot}2TBP$:DEHPA ratio is 1:2, the peak due to $UO_2(NO_3)_2{\cdot}2TBP$ has disappeared from both the ^{31}P and ^{15}N spectrum. Two additional minor peaks, which undergo exchange broadening at ambient temperature, appear in the ^{31}P spectrum at −1.0 ppm and 3.2 ppm. By analogy with the HNO_3–TBP–DEHPA system, the peak at −1.0 ppm may be assigned to the $DEHPA{\cdot}TBP{\cdot}HNO_3$ complex. The exact stoichiometry of the complex is not known.

When the ratio reaches 1:4, the intensity of the ^{31}P peaks at 3.3 ppm has increased markedly; the peak at −1.0 ppm also increases in intensity and shifts to −0.65 ppm. At ambient temperatures, all ^{31}P peaks now show exchange broadening. No change is noted in the ^{15}N spectrum.

Shaking the 1:4 solution with water causes the ^{15}N peak at 36.8 ppm to disappear while the peak at 10.3 ppm remains. The peak at 36.8 ppm is thus most likely the DEHPA–HNO_3–TBP complex (TBP equilibrated alone with $H^{15}NO_3$ has a ^{15}N peak at 31.8 ppm).

Peak assignments in this system are listed in Tables III and IV. It appears that the spectra may be best explained in terms of the following equilibria:

$$UO_2(NO_3)_2{\cdot}2TBP + HA \rightleftharpoons UO_2(NO_3)(A){\cdot}TBP + HNO_3{\cdot}TBP \quad (1)$$

$$UO_2(NO_3)(A){\cdot}TBP + HA \rightleftharpoons UO_2A_2{\cdot}TBP + HNO_3{\cdot}TBP \quad (2)$$

$$yHA + HNO_3{\cdot}TBP \rightleftharpoons yHA{\cdot}HNO_3{\cdot}TBP \quad (3)$$

While no peak due to $UO_2A_2{\cdot}TBP$ is resolved in the spectrum of the 1:1 mixture, the presence of unreacted $UO_2(NO_3){\cdot}2TBP$ suggests some competition of eqn. (2). The peak due to $UO_2A_2{\cdot}TBP$ is probably still buried under the much stronger peak at 2.9 ppm. When the ratio of $UO_2(NO_3){\cdot}2TBP$:HA reaches 1:2, there appears to be a competition between eqns. (2) and (3).

While the formula of the mixed complex in eqn. (1) implies a 1:1 ratio of DEHPA anion and TBP, the intensity of the peaks suggest a slight deficiency of TPB. Similarly the exact stoichiometry of the DEHPA–TBP–HNO_3 adduct is not known.

TABLE III. Peak Assignments in the $UO_2(NO_3)_2{\cdot}2TBP$–DEHPA Model System – ^{15}N Spectra

Peak position[a] (ppm)	Assignment
9.0	$UO_2({*}NO_3)_2{\cdot}2TBP$
10.3	$UO_2({*}NO_3)A{\cdot}TBP$
36.8	$TBP{\cdot}H{*}NO_3{\cdot}xHA$

[a] At 240 K. All peaks undergo exchange broadening at ambient temperature.

TABLE IV. Peak Assignments in the $UO_2(NO_3)_2{\cdot}2TBP$–DEHPA Model System – ^{31}P Spectra

Peak position[a] (ppm)	Assignment
−3.0[b]	$TBP{*}{\cdot}HNO_3$
−2.9[b]	$TBP{*}{\cdot}HNO_3{\cdot}xHA$
−0.65[c]	$TBP{\cdot}HNO_3{\cdot}xHA{*}$
0.72[b]	$UO_2(NO_3)_2{\cdot}2TBP{*}$
2.9[c]	$UO_2(NO_3)A{\cdot}TBP{*}$
4.4[c]	$UO_2(NO_3)A{*}{\cdot}TBP$
3.2[c]	$UO_2A_2{*}{\cdot}TBP$[d]

[a] At 240 K. [b] Undergoes exchange broadening at ambient temperature. [c] Undergoes exchange broadening at ambient temperature when the ratio $HA{:}UO_2(NO_3)_2{\cdot}2TBP > 1.0$. [d] A second peak could not be resolved. There was considerable peak overlap of all species.

It is interesting to note that the nitrate can be removed from the $UO_2(NO_3)A{\cdot}HA$ complex but not from the $UO_2(NO_3)A{\cdot}TBP$ complex by washing [1].

IV. UO_2A_2–TBP

The ^{31}P spectra at 260 K of a solution of UO_2A_2–TBP in a 1:2 ratio shows peaks at −0.3 ppm, 3.9 ppm and 4.8 ppm of approximate intensity 1:1:2. The peaks at 4.8 ppm and 3.9 ppm undergo some exchange broadening at ambient temperatures. The spectrum can be explained in terms of the formation of a complex $UO_2A_2{\cdot}2TBP$. The peak at −0.3 ppm may be assigned to the bound TBP, by comparison of the chemical shift with that of $UO_2(NO_3)_2{\cdot}2TBP$ and by the fact that it increases in intensity and shifts to −0.5 ppm in the presence of excess TBP (1:4 mol ratio).

It is interesting that the DEHP anions are not equivalent in the ^{31}P spectra of the UO_2A_2–TBP complex whereas they are in the UO_2A_2 complex [1]. Possibly this may be due to the formation of a bridged complex (Fig. 2).

V. $UO_2(NO_3)_2$–HNO_3–DEHPA–TBP

When 1 M $UO_2(NO_3)_2$ was extracted from 3 M HNO_3 with a solution of 0.5 M DEHPA and 0.5 M TBP in hexane, the ^{31}P spectra at ambient temperature showed peaks at 4.2 ppm and 2.4 ppm. On

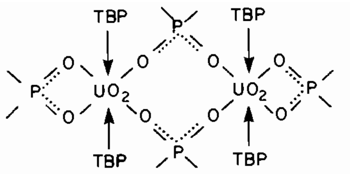

Fig. 2. Possible structure of the UO_2A_2–TBP complex.

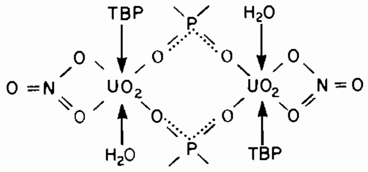

Fig. 3. Complex formed during extraction of $UO_2(NO_3)_2$ from 3 M HNO_3 with a solution of 0.5 M DEHPA and 0.5 M TBP in hexane.

cooling to 240 K, the peaks shifted to 4.4 ppm and 2.9 ppm but no new peaks appeared.

It is obvious that the ^{31}P peaks in the extract from 3 M HNO_3 correspond more closely to those appearing in the $UO_2(NO_3)_2 \cdot 2TBP$–DEHPA model rather than the UO_2A_2–TBP model.

Thus the complex formed during extraction is the mixed one $UO_2(NO_3)A \cdot TBP$ in which nitrate is bonded to uranium. In accordance with the stoichiometry deduced from the extraction data by Bykhovtsov *et al.* [5–7], the most likely structure for the complex is that shown in Fig. 3. The complex may also contain some coordinated water. Under the conditions of our experiment, no evidence was found for the competitive extraction of nitrate as nitric acid.

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References

1 A. E. Lemire, A. F. Janzen and K. Marat, *Inorg. Chim. Acta, 110*, 237 (1985).
2 Y. Marcus and A. S. Kertes, 'Ion Exchange and Solvent Extraction of Metal Complexes', Wiley-Interscience, New York, 1974, p. 521–551, p. 650–714.
3 B. Weaver in J. A. Murinsky and Y. Marcus (eds.), 'Ion Exchange and Solvent Extraction', Marcel Dekker, New York, 1979, p. 189.
4 J. Bock, P. Valint and H. Hayworth, *Chem. Eng. News*, 49 (1980).
5 V. L. Bykhovtsov and G. N. Melikhova, *Radiokhimiya., 11*, 619 (1969).
6 V. L. Bykhovstsov and T. Yu. Zimina, *Radiokhimiya., 12*, 686 (1970).
7 V. L. Bykhovtsov, *Radiokhimiya, 12*, 412 (1970).
8 D. F. Peppard and J. R. Ferraro, *J. Inorg. Nucl. Chem., 10*, 275 (1959).
9 J. E. Fleming and H. Lynton, *Chem. Ind.*, 1409 (1959).
10 W. E. Stewart and T. H. Siddall, III, in J. A. Murinsky and Y. Marcus (eds.), 'Ion Exchange and Solvent Extraction', Vol. 3, Marcel Dekker, New York, 1973, p. 83.
11 L. L. Burger, *Nucl. Sci. Eng., 16*, 428 (1963).
12 O. V. Andreeva, G. P. Savoskina and E. N. Sventitskii, *Zh. Neorg. Khim., 26*, 386 (1981).