

## A $^{31}\text{P}$ and $^{15}\text{N}$ NMR Study of the Extraction of Uranyl Nitrate by Di-2-ethylhexyl Phosphoric Acid

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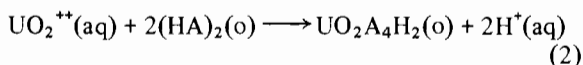
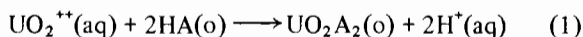
### Abstract

Low temperature  $^{31}\text{P}$  and  $^{15}\text{N}$  NMR spectroscopy was used to investigate the species forming in the organic layer following the extraction of uranium from nitric acid solutions with di-2-ethylhexyl phosphoric acid. It was found that uranium is extracted from neutral solutions as the 1:2 complex  $\text{UO}_2\text{A}_2$  regardless of what anion is present. For dilute nitric acid solutions, the uranium is extracted both as associated and mixed nitrate species. As the nitric acid concentration of the aqueous layer increases, the mixed nitrate complex,  $\text{UO}_2(\text{NO}_3)\text{A}\cdot\text{HA}$ , becomes predominant.

### Introduction

The extraction of uranium from aqueous acid by di-2-ethylhexyl phosphoric acid (DEHPA) both alone and in synergic mixtures with other organophosphorous extractants has been an object of study of several groups of workers [1–8]. Such studies, however, focussed primarily on measurements of extraction constants; and, while several models for the actual extracted species have been proposed, based on such data, little direct spectroscopic evidence has, of yet, been obtained.

Baes *et al.* [9] and Sato [1–4] studied the extraction of uranium from a variety of acids with DEHPA and concluded that, at low aqueous acid concentrations, an ion-exchange mechanism (eqns. (1) or (2)) was operative,

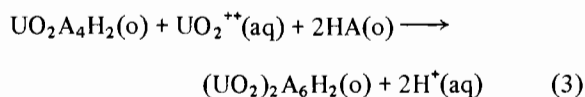


where  $\text{A} = (\text{C}_8\text{H}_{17}\text{O})_2\text{PO}_2^-$ .

Mechanism (1) was consistent with the 2:1 acid to uranium mole ratio found in the complex isolated

by Peppard *et al.* [5] from uranium saturated organic solutions.

Sato [1–4] also suggested, however, that the inclusion of a third mechanism (eqn. (3)) in which a polymeric complex is formed would lead to a better fit for the extraction data:



While a combination of mechanisms (2) and (3) appeared to provide a consistent rationalization of the extraction data for extractions from solutions of low aqueous acid concentration, they were not as satisfactory for extractions from solutions of high acid concentration.

In particular, anomalous results were obtained for the extraction of uranium from nitric acid [3].

While the partition coefficient for extraction of uranium from nitric acid initially shows a decrease with increasing aqueous acid concentration (as is the general case for most acids studied), it then begins to increase again above 3 M aqueous nitric acid concentration and shows a submaximum at approximately 6 M [3]. In addition, IR spectra of the organic layer following extraction from concentrated acid showed the presence of nitrate. This led Sato [3] to suggest that the submaximum was due to the formation of a solvate complex,  $\text{UO}_2(\text{NO}_3)_2\cdot 2\text{HA}$  and the competitive extraction of nitric acid by DEHPA ( $\text{HNO}_3\cdot 2\text{HA}$ ) at high aqueous acidities.

Nemodruk [6] later proposed that uranium was extracted as  $\text{UO}^{4+}$  from highly acidic solutions, but gave no direct evidence for the formation of  $\text{UO}^{4+}$  in solution. Vdovenko and Vavilov [7], on the other hand, disputed this mechanism and proposed instead the formation of a mixed complex,  $\text{UO}_2(\text{NO}_3)(\text{HA})_2\cdot 2\text{HA}$ .

In a recent study Rozen *et al.* [8, 10] suggested that in previous analyses of extraction data, the changes in activity coefficients of uranyl nitrate had been neglected and that this had led previous workers to incorrect formulations of the compositions of the species forming. From their own study under condi-

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TABLE I.  $^{31}\text{P}$  Chemical Shifts.

Compound	Solvent	T (K)	$^{31}\text{P}$ (ppm)
0.1 M DEHPA	hexane	210	-0.33
0.1 M DEHPA	hexane-saturated with $\text{HNO}_3$	210	-0.34
0.1 M $\text{UO}_2(\text{DEHPA})_2$	hexane	305	6.22
		210	5.80
0.025 M $\text{UO}_2(\text{DEHPA})_2$	hexane	305	6.15

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

Compound	Solvent	T (K)	$^{15}\text{N}$ (ppm) <sup>a</sup>
0.18 M $\text{UO}_2(^{15}\text{NO}_3)_2 \cdot 2\text{TBP}$	$\text{C}_6\text{D}_6$	250	8.34
1 M $\text{TBP} \cdot \text{H}^{15}\text{NO}_3$	$\text{C}_6\text{D}_6$	305	31.84
0.1 M $\text{UO}_2(^{15}\text{NO}_3)(\text{A})(\text{HA})$	hexane	185	10.83

<sup>a</sup>Measured relative to  $\text{Na}^{15}\text{NO}_3$ , but reported relative to nitromethane as zero, using  $^{15}\text{N}(\text{Na}^{15}\text{NO}_3) = 3.53 \pm 0.1$  ppm.

tions of constant ionic strength, they concluded that in weakly acidic media (up to 0.4 M), the extraction proceeded by the ion exchange mechanism (2) while at acidities  $>2.0$  M, the extraction took place by an exchange-solvate mechanism with the formation of a mixed complex  $\text{UO}_2(\text{NO}_3)(\text{HA})_2 \cdot 2\text{HA}$  in agreement with the suggestion of Vdovenko *et al.* [7].

As is obvious from the aforementioned studies, the actual speciation in the DEHPA extraction system is still not well resolved.

The potential of NMR spectroscopy to elucidate extraction mechanisms was originally pointed out in a review by Sidall and Stewart [11]; but as yet, only a limited number of workers have applied NMR in the study of such systems [12-14].

In this present study,  $^{31}\text{P}$  and  $^{15}\text{N}$  NMR spectroscopy has been used to investigate the species formed in the system  $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-DEHPA}$ .

## Experimental

$\text{UO}_2\text{A}_2$  was prepared by the method of Peppard and Ferraro [5].  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$  was prepared by the method of Fleming and Lynton [15].

$^{15}\text{N}$  labelled uranyl nitrate was prepared by dissolving  $\text{UO}_3$  in a slight excess of 6 M  $\text{H}^{15}\text{NO}_3$  (supplied by M.S.D. isotopes) and drying under vacuum.

Extractions were done by stirring together for 15 minutes, equal aliquots of a 0.1 M solution of the extractant in spectral grade hexane with a 1 M  $\text{UO}_2(\text{NO}_3)_2$  solution of varying acidity.

$^{31}\text{P}$  and  $^{15}\text{N}$  spectra were run on a Bruker 90 FT spectrometer using  $(\text{CD}_3)_2\text{CO}$  in a capillary as a lock solvent. It was found that, in the case of the  $^{15}\text{N}$  spectra, adding a relaxation agent such as chromium

acetylacetonate decreased the time necessary to obtain a spectrum; but it did cause some signal broadening.  $^{31}\text{P}$  chemical shifts are reported relative to 85% aq.  $\text{H}_3\text{PO}_4$  as zero.  $^{15}\text{N}$  chemical shifts are reported relative to nitromethane as zero.

The acid extracted into the DEHPA solutions was measured by extracting with water and titrating the extracted acid with 0.05 M sodium hydroxide.

## Results and Discussion

$^{31}\text{P}$  and  $^{15}\text{N}$  chemical shifts are summarized in Tables I and II.

### (a) $\text{UO}_2\text{X}_2\text{-HNO}_3\text{-DEHPA}$ ( $\text{X} = \text{Cl}^-, \text{NO}_3^-, \text{SO}_4^{2-}$ )

Extraction of 1 M solutions of uranyl nitrate and uranyl chloride and a saturated solution of uranyl sulfate in water gave a single species with a  $^{31}\text{P}$  chemical shift identical to that of the isolated  $\text{UO}_2\text{-A}_2$  complex. The signal remains sharp even at low temperatures. Our results, thus, indicate that under conditions of high organic loading, uranium is extracted from neutral solutions as the 1:2 complex,  $\text{UO}_2\text{A}_2$ , by DEHPA regardless of the anion present.

### (b) $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-DEHPA}$

In extraction from nitric acid solutions, however, the NMR results indicate a considerably more complex situation. While only a single  $^{31}\text{P}$  peak is observed at room temperature, the spectrum becomes more complicated when the temperature is lowered. Representative low temperature spectra are shown in Fig. 1. In extractions from nitric acid solutions in the concentration range 0-4 M, the low temperature  $^{31}\text{P}$  spectra suggests that there is a competition between a variety of species. In extractions from 4-

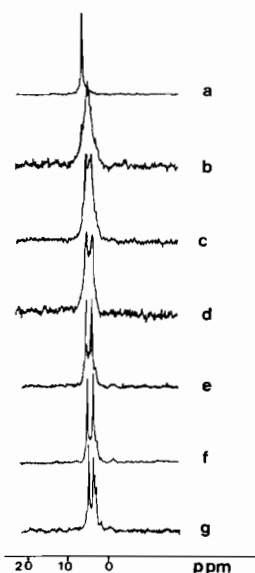


Fig. 1.  $^{31}\text{P}$  spectra at 210 K of the organic layer following extraction of uranyl nitrate with 0.1 M DEHPA in hexane from (a) water, (b) 2 M nitric acid, (c) 4 M nitric acid, (d) 6 M nitric acid, (e) 8 M nitric acid, (f) 12 M nitric acid, (g) 16 M nitric acid.

12 M nitric acid solutions, however, one species, that gives rise to two peaks of equal intensity at 3.8 ppm and 5.1 ppm in the low temperature  $^{31}\text{P}$  spectra (210 K), becomes predominant. At room temperature, these peaks coalesce because of rapid exchange of ligands between the two non-equivalent sites.

It was further noted that if the hexane extracts of the 6 M nitric acid solutions were back extracted with water, the water layer became acidic and the  $^{31}\text{P}$  spectra of the hexane layer reverted to the single peak at 6.4 ppm characteristic of  $\text{UO}_2\text{A}_2$ . Figure 2 shows a plot of the acid back extracted from the hexane layer as a function of initial aqueous phase acidity. The water wash showed no  $^{31}\text{P}$  signal.

Conversely, if the hexane was removed under vacuum from the extracts and the resultant oil redissolved in hexane, there was no change in the  $^{31}\text{P}$  spectra. Thus the acid appears to be present in the hexane extract in a non-volatile form.

In order to elucidate the nature of the acid extracts further, a solution of 1 M  $\text{UO}_2(^{15}\text{NO}_3)_2$  in 6 M  $\text{H}^{15}\text{NO}_3$  was extracted with 0.2 M DEHPA in hexane. At low temperatures (185 K), the hexane extract showed a  $^{15}\text{N}$  signal at 10.8 ppm. The signal position is consistent with nitrate bonded to uranium (*cf.*  $\text{UO}_2(^{15}\text{NO}_3)_2 \cdot 2\text{TBP}$  [8.3 ppm]). When the hexane extract was washed with water, the water extract gave a  $^{15}\text{N}$  signal consistent with dilute nitric acid.

#### (c) $\text{UO}_2\text{A}_2\text{-HA}$

A model system in which stoichiometric amounts of DEHPA were added to a 0.1 M solution of  $\text{UO}_2\text{A}_2$

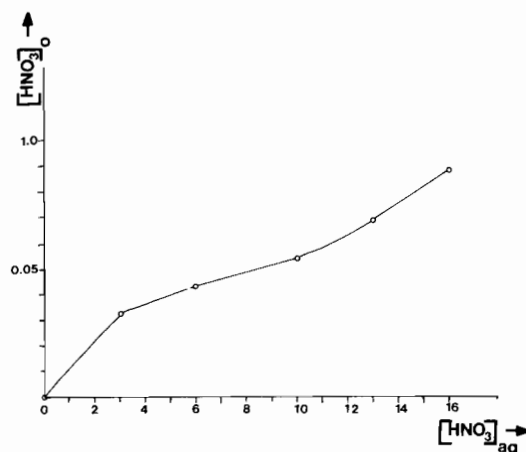


Fig. 2. Molarity of nitric acid in the organic layer as a function of initial molarity of nitric acid in the aqueous layer.

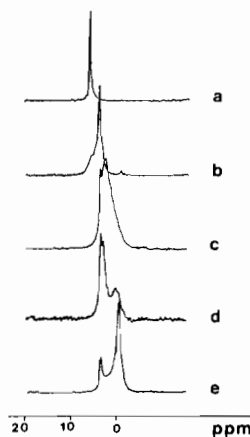


Fig. 3.  $^{31}\text{P}$  spectra in hexane at 210 K of: (a)  $\text{UO}_2\text{A}_2$  (0.1 M), (b)  $\text{UO}_2\text{A}_2 + \text{HA}$ , (c)  $\text{UO}_2\text{A}_2 + 4\text{HA}$ , (d)  $\text{UO}_2\text{A}_2 + 4\text{HA}$  (diluted to 0.025 M), (e)  $\text{UO}_2\text{A}_2 + 8\text{HA}$ .

in hexane was also studied for comparison. Representative low temperature spectra are shown in Fig. 3.

It is obvious that while there are a variety of species forming in this system, too, they are not the same species observed in the solvent extraction system.

The system is, however, interesting in itself, for it shows the formation of a mixture of complexes. In the system  $\text{UO}_2\text{A}_2 + 1 \text{HA}$ , the presence of  $\text{UO}_2\text{-A}_2$  is indicated by the shoulder at 5.2 ppm; but there is in addition a new peak at 3.6 ppm. When the  $\text{UO}_2\text{-A}_2\text{:HA}$  ratio reaches 1:2, the shoulder at 5.6 ppm has disappeared and only the peak at 3.6 ppm remains. It would therefore be tempting to assume that the peak at 3.6 ppm was the complex  $\text{UO}_2(\text{HA}_2)_2$ . However the shoulder at 5.6 ppm in the earlier spectrum is of lower intensity than would be expected if  $\text{UO}_2\text{-(HA}_2)_2$  were being formed stoichiometrically. Since the peak at 3.6 ppm is also relatively broad, it probably represents a mixture of associated forms

(dimers and higher oligomers). Association would also, of course, be facilitated by the low temperatures at which it was necessary to run the spectra in order to freeze out exchange.

Similarly the new peak appearing at 2.6 ppm when the  $\text{UO}_2\text{A}_2:\text{HA}$  ratio reaches 1:4 may be due to the formation of a solvate species  $\text{UO}_2(\text{HA}_2)_2 \cdot 2\text{HA}$ . There is also a shoulder at 0.34 ppm which becomes more prominent as the system is diluted with hexane. By comparison with the spectrum for the  $\text{UO}_2\text{A}_2 + 8 \text{ HA}$  system in which a strong peak for the free acid is observed, it seems reasonable to assign this shoulder to free DEHPA, still broadened by exchange. Thus the  $\text{UO}_2\text{A}_2:\text{HA}$  ratio must reach at least 1:4 before any free acid is observed.

The model system, then, demonstrates the possibility of several associated species; but the actual extraction system itself is even more complex. Neither the NMR spectra nor the extraction constant data alone give the whole picture; but in combination they permit certain conclusions to be drawn.

In the specific case of extraction from nitric acid in a concentration range of 0–4 M, the broadness of the NMR peaks suggest a variety of associated forms. However the shoulder at 5.6 ppm in the  $^{31}\text{P}$  spectrum of the 2 M extract (at 210 K) indicates that there is still some  $\text{UO}_2\text{A}_2$  present.

In extracts from nitric acid of concentration  $>4$  M, we believe the predominant species is a mixed complex,  $\text{UO}_2(\text{NO}_3)\text{A} \cdot \text{HA}$ , analogous to that proposed by Rozen [8, 10].

The fact that the  $^{31}\text{P}$  spectra shows two non-equivalent DEHPA molecules is also consistent with Rozen's formulation of the complex as an exchange-solvate one; the peaks at 5.1 ppm and 3.8 ppm may be assigned to bidentate and unidentate ligands, respectively. The solvate complex  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{HA}$  postulated by Sato [1–4] would be expected to show only one  $^{31}\text{P}$  peak. The  $^{15}\text{N}$  peak at 10.8 ppm is consistent with nitrate bonded to uranium rather than nitric acid H-bonded to free DEHPA.

One cannot, of course, distinguish on the basis of the NMR spectra alone between a monomeric structure (Fig. 4a) and an associated one such as that shown in Fig. 4b; since in both cases one would expect to see two non-equivalent  $^{31}\text{P}$  signals. Judging by the broadness of the NMR peaks, it seems likely that there is a mixture of closely related DEHPA-bridged associated species.

These NMR results thus represent the first direct spectroscopic evidence for the formation of the mixed species.

It may be noted that Rozen explained the extraction data in terms of a competition between the mixed complex  $\text{UO}_2(\text{NO}_3)(\text{HA}_2) \cdot 2\text{HA}$  and  $\text{UO}_2(\text{HA}_2)_2$ . However, certain of our observations lead us to believe that this is not quite the situation in our study.

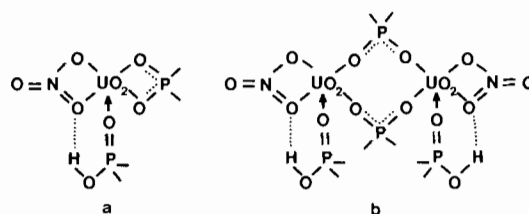


Fig. 4. Possible structures of the nitrate complex.

For example, washing the organic phase of the acid extracts with water causes the  $^{31}\text{P}$  spectrum to revert to that of  $\text{UO}_2\text{A}_2$  monomer while the  $^{15}\text{N}$  spectrum of the water wash shows the presence of nitric acid. If the species in the organic phase were those proposed by Rozen, one would expect that after the water wash, the  $^{31}\text{P}$  spectra would show either  $\text{UO}_2(\text{HA}_2)_2$  or  $\text{UO}_2\text{A}_2 + \text{HA}$  rather than  $\text{UO}_2\text{A}_2$  alone. The  $^{31}\text{P}$  spectra of the wash water also showed no DEHPA was extracted into the water. Finally, in the region 6–10 M, the amount of extracted  $\text{HNO}_3$  showed a levelling off to a ratio of  $\text{HNO}_3:\text{DEHPA}$  of 1:2 (Fig. 2).

We therefore believe that our results can be best rationalized in terms of the scheme shown in Fig. 5.

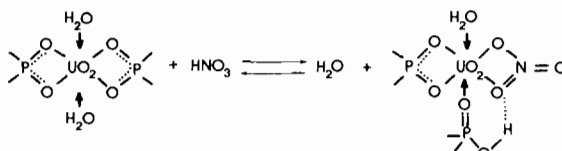


Fig. 5. Conversion of  $\text{UO}_2(\text{NO}_3)(\text{A}) \cdot \text{HA}$  to  $\text{UO}_2\text{A}_2$  upon washing with water.

Our conclusions do not negate Rozen's, however, since he was working with solutions of low uranium concentrations in which DEHPA would be present in excess, and we were working with uranium saturated organic solutions. Indeed, some limited studies we have made of solutions in which DEHPA is in excess do indeed show evidence for the presence of the  $\text{UO}_2(\text{HA}_2)_2$  species.

It should also be noted that Sato [3] suggested that at high aqueous nitric acid concentrations, the competitive extraction of  $\text{HNO}_3$  became more important. Rozen's work [8], however, showed that the extraction constant of nitric acid with DEHPA is considerably less than that of uranyl nitrate; and in accordance with this, we saw no evidence, even at the highest acid concentrations, for the  $\text{HNO}_3 \cdot 2\text{HA}$  complex.

It may also be noted that at very high nitric acid concentration ( $>12$  M), the amount of nitrate extracted into the organic layer is greater than that which can be accounted for by the complex  $\text{UO}_2-$

(NO<sub>3</sub>)A·HA. It therefore seems likely that there are other nitrate complexes forming in extractions from highly acidic solution. Since the <sup>31</sup>P spectra shows no peak corresponding to HA·HNO<sub>3</sub>, it is unlikely that the nitrate is being extracted as nitric acid. Unfortunately, the <sup>15</sup>N labelled nitric acid that we were using was only 6 M and hence we could not obtain any <sup>15</sup>N spectra at higher concentrations. There is also no extraction data available for this region; hence speculating as to the complexes being formed would be premature.

In conclusion, then, we believe our studies have shown that <sup>31</sup>P and <sup>15</sup>N multinuclear NMR spectroscopy may prove a useful tool, in conjunction with conventional extraction studies, in establishing speciation in solvent extraction systems. To date, the use of multinuclear NMR to study extraction systems has been extremely limited and in addition has been restricted to already isolated complexes [12, 13, 16]. This work is one of the first direct studies by NMR of the actual extracted phase and is also the first time <sup>15</sup>N NMR spectroscopy has been applied to the investigation of such systems. We are presently extending our studies to synergistic extraction systems.

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