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EXTRACTION OF TETRAVALENT AND HEXAVALENT ACTINIDE  
IONS BY TETRAHEPTYLAMMONIUM NITRATE

*by*

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### ABSTRACT

Extraction of Th(IV), Np(IV), Pu(IV), U(VI), Np(VI) and Pu(VI) by tetraheptylammonium nitrate in Solvesso-100 has been studied from nitric acid medium. Attempts were made to identify the complex species in the organic phase by studying the dependence of the distribution coefficient of the actinide on amine concentration and taking the absorption spectra of the organic phase containing actinide ions. A compound tetraheptylammonium trinitratodioxouranate(VI) has been isolated and characterised.

# EXTRACTION OF TETRAVALENT AND HEXAVALENT ACTINIDE IONS BY TETRAHEPTYLAMMONIUM NITRATE

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The extraction of metal ions by high molecular weight amines has become increasingly interesting in recent years. The tertiary and quaternary alkylamines offer several advantages for their use in the recovery of actinides from irradiated fuels. Relatively only a few data have been reported on the extraction of actinides, especially hexavalent ones by quaternary amines. Brown et al. <sup>(1)</sup> reported the extraction of Np(IV) by tetraheptylammonium nitrate and didodecyl-dimethyl-ammonium nitrate (DDAN). The extraction of Pu(IV) and U(VI) by tricaprilmethylammonium nitrate was studied by Koch <sup>(2)</sup> whereas Lopez-Monohero and Cohen <sup>(3)</sup> reported similar studies using dodecyldimethylbenzylammonium nitrate. Bao <sup>(4)</sup> has studied the extraction of Pu(IV) using different quaternary amines. In continuation of our earlier work <sup>(5,6)</sup> on the extraction of tetra- and hexavalent actinides by TTA and Aliquat-336, the extraction of tetra- and hexavalent actinides from aqueous nitric acid by tetraheptylammonium nitrate was studied, and the results obtained are reported in the present report.

## 1. EXPERIMENTAL

### 1.1 Materials

Tetraheptylammonium chloride obtained from Eastman Kodak Co., USA was used as such after converting it into nitrate form. Thorium-234 (U<sub>1</sub>) was separated from an old sample of nuclear pure uranium by I<sub>2</sub>F<sub>7</sub> precipitation and TTA extraction as described elsewhere <sup>(7)</sup>. Thorium-230 (containing 88% <sup>232</sup>Th) was obtained from Isotope Division, BARC. Other actinides were obtained and

purified as described earlier<sup>(6)</sup>. All other chemicals used were of A.R. grade.

### 1.2 Preparation of Tracers

Neptunium(IV), Np(VI) and Pu(VI) tracers were prepared and used as described earlier<sup>(6)</sup>. A stock solution of Pu(IV) was prepared by extraction of Pu(IV) from 1M nitric acid into 0.5M TTA in xylene followed by stripping of the extracted plutonium in 8M nitric acid. Sodium nitrite ( $\sim 0.03M$ ) was used as a holding reductant for Pu(IV) during its extraction by the amine.

### 1.3 Procedure

Experiments on the extraction of actinides by amine were carried out in the same way as described earlier<sup>(6)</sup>. 0.1M tetraheptylammonium nitrate (THAN) in Solvesso-100 was used as the organic phase. Initial aqueous concentrations of the actinide ions in the experiments were kept approximately as follows:

$^{237}\text{Np}$	= 2-3 $\mu\text{g/ml}$
Pu	= 6 $\mu\text{g/ml}$ in Pu(VI) experiments
Pu	= 30 $\mu\text{g/ml}$ in Pu(IV) experiments
$^{233}\text{U}$	= 58 $\mu\text{g/ml}$
Th	= 55 $\mu\text{g/ml}$

The dependence of the distribution coefficient on THAN concentration was investigated for each actinide using 1M nitric acid as the aqueous phase and varying concentration of THAN in the organic phase.

### 1.4 Analysis

Thorium-234 and  $^{239}\text{Np}$  present in both the phases at the end of the equilibration were determined by gamma ray counting using a well-type NaI(Tl) scintillation counter. The equilibrium concentration of  $^{230}\text{Th}$ ,  $^{233}\text{U}$  and plutonium in both the phases was measured by alpha liquid scintillation counter<sup>(8, 9)</sup>.

### 1.5 Isolation of Tetraheptylammonium Trinitrato-dioxouranate (VI)

About 25 ml of 0.12M THAN in benzene was contacted with an aqueous solution containing about 1M uranyl nitrate in 0.1M HNO<sub>3</sub> containing 5M of sodium nitrate. The uranium containing organic phase was kept under vacuum for about 3 hours at 65°C in a rotary evaporator to remove benzene. The compound thus isolated was a yellow syrupy liquid which was analysed subsequently. The analysis of C, H and N was done by microanalytical methods while uranium was analysed by decomposing the compound using a mixture of HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> and subsequently determining the uranium by redox method<sup>(10)</sup> after reducing it to U(IV) by Jones's reductor.

### 1.6 Absorption Spectra

Absorption spectra of Np(IV), Pu(IV), U(VI), Np(VI) and Pu(VI) extracted from 3M HNO<sub>3</sub> into 0.1M THAN were recorded on Cary-14 recording spectrophotometer. The absorption spectrum of the uranium THAN compound dissolved in benzene was also recorded. Infrared spectra of the uranium-THAN compound and its solution in benzene were recorded on Perkin-Elmer-237 infracord spectrophotometer.

### 1.7 Molecular Weight Determination

The molecular weight of the uranium-THAN compound was determined using Hitachi Perkin Elmer vapour pressure osmometer. Hexachlorocyclohexane in chloroform was used as the calibrating substance.

## 2. RESULTS AND DISCUSSION

### 2.1 Variation of $K_d$ with Nitric Acid Concentration

The distribution data, obtained for extraction of Th(IV), Np(IV) and Pu(IV) at varying concentrations of aqueous nitric acid, are given in Table 1. The upper limit of HNO<sub>3</sub> concentration used was limited to 5M as a third phase

formation was noticed during pre-equilibration of the amine with  $\text{HNO}_3$  having concentration higher than 6M. It is seen from these data that the extraction of all the tetravalent actinides reaches maximum at 1M  $\text{HNO}_3$  concentration and this observation is similar to that reported by Brown et al.<sup>(1)</sup> for the extraction of  $\text{Np(IV)}$  by THAN. It has been reported<sup>(2,6)</sup> that the extraction of tetravalent actinides by quaternary amines usually reaches maximum at 2-4M  $\text{HNO}_3$ . It is not clear why in the present case the extraction reaches maximum at about 1M  $\text{HNO}_3$ . Brown et al.<sup>(1)</sup> found that the extraction of  $\text{Np(IV)}$  by DDAN increases even upto 8M. Apparently, the structure of the quaternary amine, used for the extraction, is an important factor which decides the  $\text{HNO}_3$  concentration at which the maximum extraction takes place. More work is required to be done to know this effect.

It is also interesting to note that whereas the distribution coefficients of  $\text{Np(IV)}$  and  $\text{Pu(IV)}$  decrease with increasing concentration of  $\text{HNO}_3$  above 1M, the distribution coefficient of  $\text{Th(IV)}$  remains almost constant. This extraction behaviour of  $\text{Np(IV)}$  and  $\text{Pu(IV)}$  is reported<sup>(11)</sup> in other amine extraction studies along with the probable explanation for such decrease in their extraction. The extraction behaviour of  $\text{Th(IV)}$  observed in the present investigation however remains unexplained.

The present values of  $K_d$  for the extraction of  $\text{Np(IV)}$  are somewhat different from those reported under similar conditions by Brown et al.<sup>(1)</sup> This difference may be, at least partly, due to different diluents used in the two studies. The distribution coefficients of  $\text{Np(IV)}$  and  $\text{Pu(IV)}$  are very high, as seen from Table 1. Marcus and Kertes<sup>(12)</sup> have reported that symmetrical quaternary amines usually show higher extraction than unsymmetrical ones and the present data support this. It seems that the quaternary ammonium salt should not necessarily contain 1-methyl and 3-long chain aliphatic groups



to result in high extraction of tetravalent actinides as was reported by Muller<sup>(11)</sup>. Incidentally, the extraction of tetravalent actinides by THAN follows the order  $\text{Pu(IV)} > \text{Np(IV)} > \text{Th(IV)}$  which is similar to the order observed for their extraction<sup>(2,6)</sup> by Aliquat-336.

The distribution coefficient data obtained for the extraction of hexavalent actinides from varying concentrations of aqueous nitric acid into 0.1M THAN are shown in Fig.1. It is seen from this figure that the extraction of hexavalent actinides increases with the increasing  $\text{HNO}_3$  conc. The maximum could not be observed since the extraction studies could not be extended beyond 5M  $\text{HNO}_3$  for the reasons mentioned above. The extraction of hexavalent actinides by THAN follows the order  $\text{Np(VI)} \gtrsim \text{Pu(VI)} > \text{U(VI)}$  and is the same as reported for their extraction by Aliquat-336, TLA and TOA<sup>(6,11)</sup>.

## 2.2 Variation of $K_d$ with Amine Concentration

The distribution coefficient data obtained for the extraction of tetra- and hexavalent actinides from 3M nitric acid into THAN solution of varying concentration are shown in Figures 2 and 3. In the case of tetravalent actinides the log-log plots of  $K_d$  vs THAN concentration (Fig.2) are linear. The slope for Th(IV) and Pu(IV) lines is about 2 while that for Np(IV) is about 1.4. It can, therefore, be inferred that the species of tetravalent actinide extracted into THAN solution is  $\left[ (\text{C}_7\text{H}_{15})_4\text{N} \right]_2 \text{M}(\text{NO}_3)_6$  (M=Th, Np or Pu). For the extraction of hexavalent actinides the log-log plots of  $K_d$  vs THAN concentration (Fig.3) are also linear with a slope of about unity, thereby indicating that the species of hexavalent actinides extracted into THAN solution is  $(\text{C}_7\text{H}_{15})_4 \text{NNO}_2(\text{NO}_3)_3$ . This is similar to that reported earlier in the extraction of hexavalent actinides into Aliquat-336<sup>(6)</sup>.

### Absorption Spectra

The species of the actinides extracted into the amine phase is often identified from absorption spectra of the organic extracts of actinides. The absorption spectra of Np(IV) and Pu(IV) extracted into 0.1M THAN from 3M nitric acid are shown in Figure 4. The absorption spectra of Np(VI) and Pu(VI) obtained similarly are shown in Figure 5. The spectra in Figure 4 for Np(IV) and Pu(IV) show a close similarity with the spectra of  $\left[ (\text{C}_2\text{H}_5)_4\text{N} \right]_2 \text{Np}(\text{NO}_3)_6$  and  $\left[ (\text{C}_2\text{H}_5)_4\text{N} \right]_2 \text{Pu}(\text{NO}_3)_6$  respectively<sup>(13)</sup>. The absorption spectra of Np(VI) and Pu(VI) (Figure 5) also compare well with the spectra of  $(\text{C}_2\text{H}_5)_4\text{N} \text{NpO}_2(\text{NO}_3)_3$  and  $(\text{C}_2\text{H}_5)_4\text{N} \text{PuO}_2(\text{NO}_3)_3$  respectively<sup>(13)</sup>. It is therefore reasonable to conclude that tetravalent and hexavalent actinide ions are present in the THAN phase as hexanitrate and trinitrate complex species respectively.

### Tetraheptylammonium Trinitratodioxouranate

This compound was analysed chemically and results are given in Table 2. The molecular weight of this compound was determined using vapour pressure osmometer. The molecular weight extrapolated to zero concentration was found to be 810 (Figure 6). Both these data show the formula of the compound to be  $(\text{C}_7\text{H}_{15})_4\text{NUO}_2(\text{NO}_3)_3$ .

The absorption spectra of U-THAN compound dissolved in benzene and U(VI) extracted from nitric acid into THAN dissolved in benzene were recorded and are shown in Figure 7. The two spectra are similar and compare well with the spectrum of  $(\text{C}_2\text{H}_5)_4\text{NUO}_2(\text{NO}_3)_3$ <sup>(13)</sup>. It can therefore be inferred that  $\text{UO}_2(\text{NO}_3)_3^-$  is the species of uranium present in THAN solution.

The infrared spectra of THAN and uranium-THAN compound as well as their solutions were recorded and important bands are listed in Table 3. Similar spectra were reported by Koch<sup>(14)</sup> for U-Aliquat-336 nitrate compound and by comparison with the spectrum of Rb  $\text{UO}_2(\text{NO}_3)_3$ , he inferred that

$UO_2(NO_3)_3^-$  ion in U-Aliquat compound possesses similar structure as in the crystalline rubidium salt. The present spectrum was found to be similar to the spectrum reported by Koch for U-Aliquat-336 nitrate compound, thus indicating that U-THAN compound probably has a similar structure as that of U-Aliquat nitrate compound.

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#### REFERENCES

- (1) K.B. Brown, K.A. Allen, C.A. Blake, C.F. Coleman, A.T. Gresky and W. Weaver, ORNL-CP-60-1-119 (1960)
- (2) G. Koch, "Solvent Extraction Chemistry of Metals", Proc. Int. Conf., Harwell, Sept. 1965, Ed. H.A.C. McKay, J.L. Jenkine and A. Naylor, p.247, MacMillan, London, 1966
- (3) Lopez-Mencherero and A. Gehm, Eurochem. Symp. on AQ.Reprocess. Chem. for Irrad. Fuels, Brussels (1963), p. 147
- (4) R. Bac, "Long Chain Alkylammonium Nitrates as Extracting Agents for Pu(IV) Nitrate", Ph.D. Thesis, 1968
- (5) S.K. Patil, Rajendra Swarup, M.V. Ramaniah and N. Srinivasan, Radiochim. Acta, 18, 212 (1972)
- (6) Rajendra Swarup and S.K. Patil, J. Inorg. Nucl.Chem. 32, 1203 (1976)
- (7) S.K. Patil and V.V. Ramakrishna, Radiochim. Acta, 18, 190 (1972)
- (8) H. Ihle, M. Karayannis and A. Murrenhoff, p. 881, "Organic scintillators and liquid scintillation counting", Eds. D.L. Horrocks and Chin-Tzu Peng, Academic Press Inc., New York and London (1971)
- (9) M.J. McDowell, p.937, "Organic Scintillators and Liquid Scintillation Counting", Eds. D.L. Horrocks and Chin-Tzu Peng, Academic Press Inc., New York and London (1971)

- (10) Arthur I. Vogel, "Quantitative Inorganic Analysis", p.333, Longmans, Green & Co. Ltd. London (1961)
- (11) W. Muller, Act. Rev. 1, 71 (1967)
- (12) Y. Marcus and A.S. Kertes, "Ion-Exchange and Solvent Extraction of Metal Complexes", p. 752, Wiley-Interscience, London (1969)
- (13) W.E. Kedar, J.L. Ryan and A.S. Wilson, J. Inor. Nucl.Chem., 20, 131 (1961)
- (14) G. Koch, ANL-TRANS-312 (1966)

Table 1

VARIATION OF DISTRIBUTION COEFFICIENT OF  
TETRAVALENT ACTINIDES WITH NITRIC ACID

HNO <sub>3</sub> (M)	Distribution coefficient (Kd)				
	<sup>Th(IV)</sup> (a)      (b)		Np(IV)	Pu(IV)	Np(IV)*
0.5	38.3	48.7	157	276	-
0.75	-	-	575	4738	-
1.0	46.3	52.8	1616	5446	2800
2.0	50.5	52.3	1357	5175	1600
3.0	52.4	50.8	1141	-	-
4.0	52.3	54.8	1002	3722	750
5.0	55.5	50.8	843	2990	-

\*Ref. 1, values are approximate as they are read from the graph.

(a) Using <sup>234</sup>Th      (b) Using <sup>230</sup>Th

Table 2

ANALYSIS OF TETRAHEPYLAMMONIUM TRINITRATODIOXOURANATE (VI)

	Percent			
	U	C	H	N
Calc.	27.49	38.80	6.93	6.17
Found	25.9 ± 0.4 (3)	38.8 ± 0.8 (3)	6.88 ± 0.01 (2)	6.49 ± 0.2 (2)

Figures in bracket show number of determinations

Table 3

I.R. BANDS (FREQUENCY IN  $\text{cm}^{-1}$ )

THAN	THAN-U(VI) compound	THAN in benzene	THAN-U compound in benzen
1330(S)	730 (S)	1030 (S)	1030 (S)
1465(S)	935 (S)	1475 (S)	1150 (W)
2860(B)	1010 (S)	1538 (W)	1475 (S)
	1250 (M)		1538 (W)
	1525 (B)		1820 (S)

(S = Sharp, B = Broad, M = Medium, W = Weak)

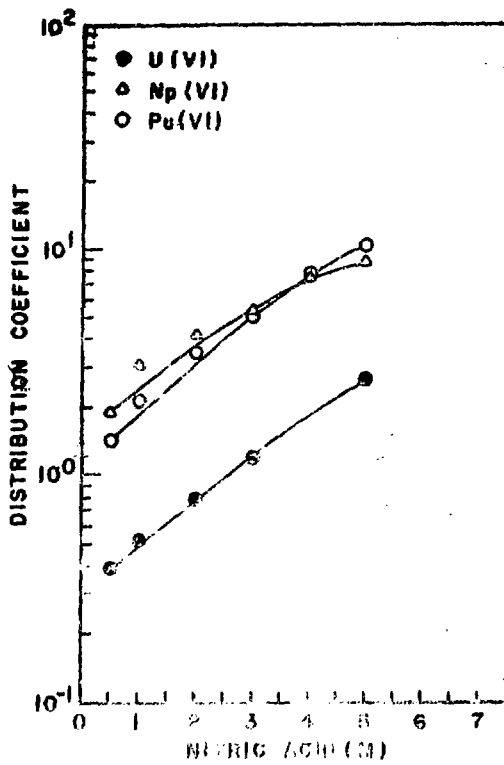


FIG-1. VARIATION OF DISTRIBUTION COEFFICIENT OF ACTINIDES (VI) WITH NITRIC ACID.

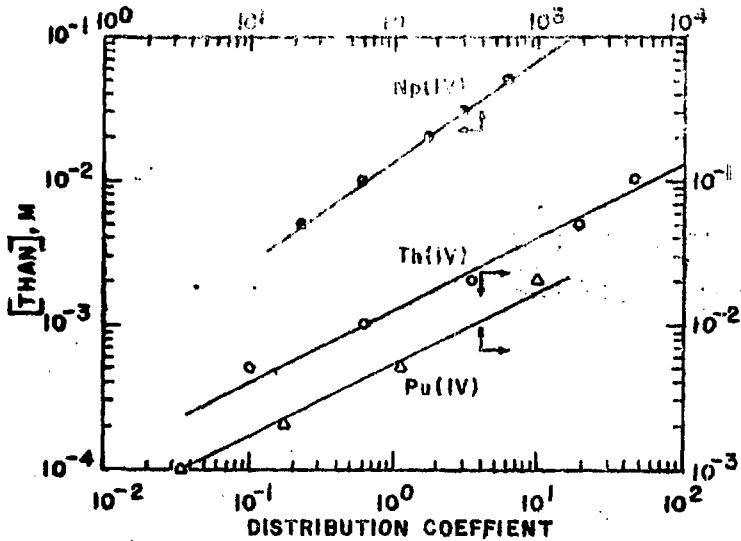


FIG-2. VARIATION OF DISTRIBUTION COEFFICIENT OF ACTINIDES WITH AMINE.

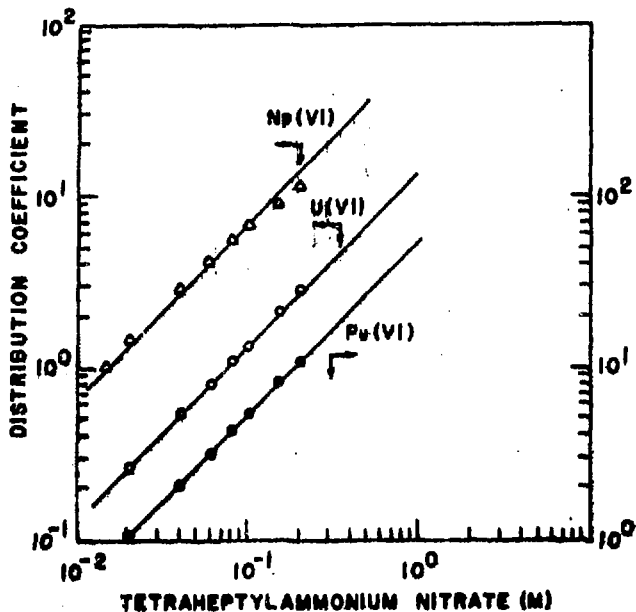


FIG.-3. VARIATION OF DISTRIBUTION COEFFICIENT OF ACTINIDES WITH AMINE.

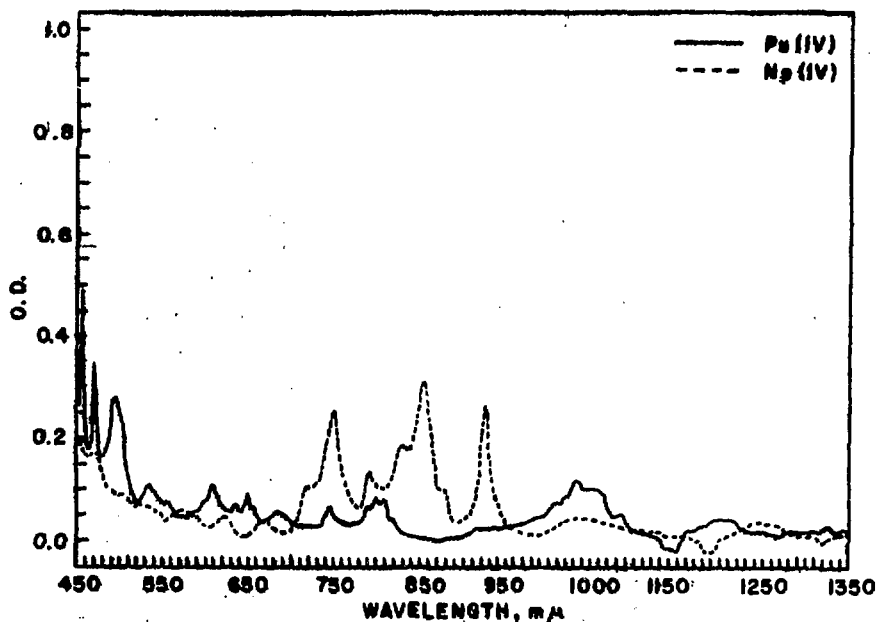


FIG.-4. ABSORPTION SPECTRA OF  $Pu(IV)$  &  $Np(IV)$  IN THF-BENZENE.  
 $Pu(IV) - 4.6 \times 10^{-3} M$        $Np(IV) - 5.9 \times 10^{-3} M$



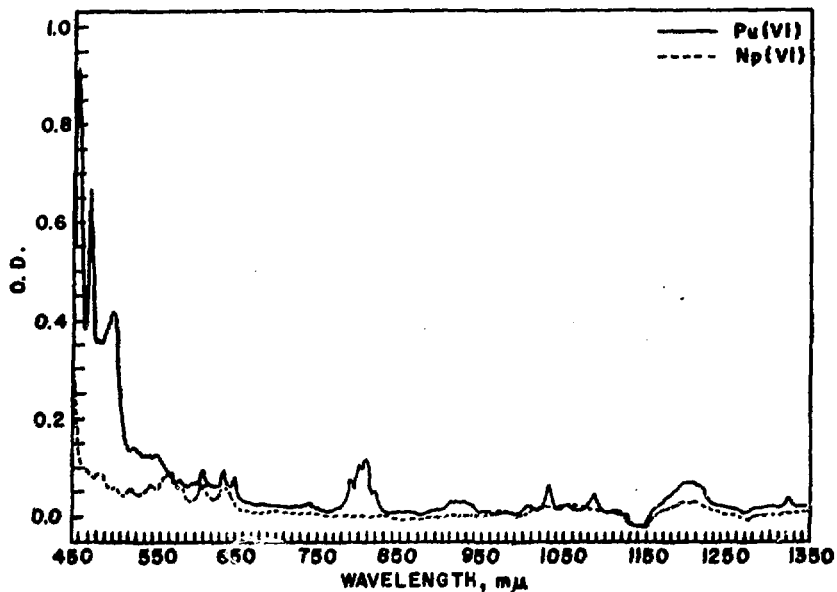


FIG.-5. ABSORPTION SPECTRA OF Pu(VI) & Np(VI) IN THAN-BENZENE  
 Pu(VI) -  $2.84 \times 10^{-3} M$  Np(VI) -  $4.67 \times 10^{-3} M$

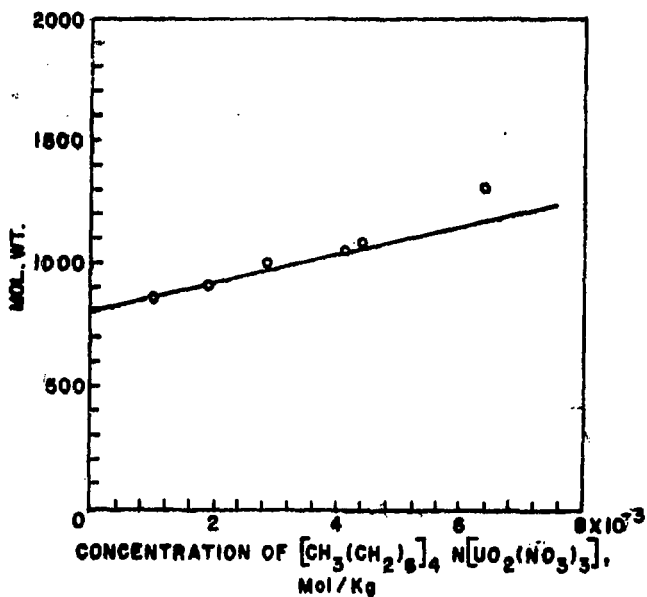


FIG.-6. VARIATION OF THE MOLECULAR WEIGHT OF  
 TETRAHEPTYLAMMONIUM-TRINITRATO-DIOXO-  
 URANATE (VI) WITH CONCENTRATION.

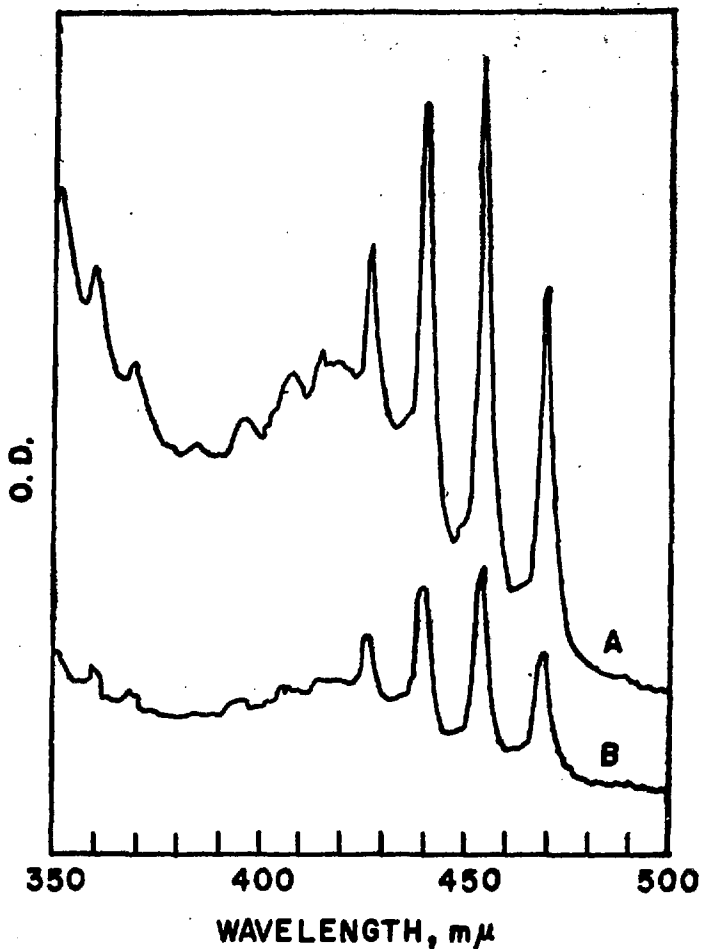


FIG.-7. ABSORPTION SPECTRA OF U(VI)

A - U(VI) IN THAN-BENZENE,  $[U] - 2 \times 10^{-2} M$

B - TETRAHEPTYLAMMONIUM-TRINITRATODIOXOURANATE (VI)  
IN BENZENE,  $[U] - 8.74 \times 10^{-3} M$

