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GOVERNMENT OF INDIA
परमाणु ऊर्जा आयोग
ATOMIC ENERGY COMMISSION

SPECTROPHOTOMETRIC STUDIES ON THE FORMATION OF
ADDUCTS INVOLVED IN SYNERGISTIC EXTRACTION OF
URANIUM (IV) BY MIXTURES OF HTTA AND NEUTRAL
DONORS

by

S. K. Patil and V. V. Ramakrishna
Radiochemistry Division

and

A. Ramanujam
Fuel Reprocessing Division

भाभा परमाणु अनुसंधान केन्द्र
BHABHA ATOMIC RESEARCH CENTRE
बंबई, भारत
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SYNERGISM
SOLVENTS
EQUILIBRIUM
CHEMICAL REACTION KINETICS
EXPERIMENTAL DATA
TPO

A B S T R A C T

Adduct formation between $U(TTA)_4$ and several neutral donor (S) was investigated by utilizing the changes in the absorption spectra of U(IV) resulting from the addition of neutral donors to a solution of $U(TTA)_4$. All the donors used in the present work form 1:1 adducts with $U(TTA)_4$. From the spectral changes, the equilibrium constants β_{AB} for the adduct formation reaction viz $U(TTA)_4 + S \rightleftharpoons U(TTA)_4 \cdot S$ were calculated for a few neutral donors. The $\log \beta_{AB}$ values obtained, in benzene medium, are : TOPO (6.23), TBPO (6.13), TPPO (4.72), DBBP (4.04), TBP (3.04) TIOTP (1.27) and MIEK (-0.10) and a value of 3.98 for TOPO in chloroform medium. The adduct formation was found to result in increasing the coordination number of U(IV) from 8 in $U(TTA)_4$ to 9 in the adducts it forms with the neutral donors.

Similar absorption spectral studies with $U(DETA)_4$ revealed that it forms much weaker adducts than the corresponding ones with $U(TTA)_4$.

The absorption spectra of the organic extracts of U(IV) from perchloric acid with mixtures of HPTA and a neutral donor were identical with the spectra of the adduct between $U(TTA)_4$ and the neutral donor. This suggested that the adduct species viz $U(TTA)_4 \cdot S$ is involved in the synergistic extraction of U(IV). The extraction constants relating to the synergistic extraction of U(IV), from aqueous perchloric acid into benzene solutions of HPTA and some of the neutral donors, were derived.

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INTRODUCTION

In the solvent extraction of metal ions from aqueous media into organic solvents containing a mixture of a β -diketone (HA) and a neutral donor (S), it has been observed⁽¹⁾ that the extraction is usually enhanced as compared to using either extractant alone. This enhancement in the extraction, usually known as synergism, is mainly due to the formation of adducts, in the organic medium, between the metal β -diketonate and the neutral donor. Such adducts, in the case of tetravalent actinides, were reported only for Th(IV)⁽²⁻⁴⁾. We have initiated a program on such studies and reported some results on the extraction of Np(IV)⁽⁵⁾ and Pu(IV)⁽⁶⁾. The most widely used, and perhaps the simplest, method⁽²⁻⁸⁾, for obtaining the formulae of the adducts and their formation constants involved is to measure the distribution ratio (K_d) of the metal ion, kept at tracer concentration, as a function of one of the variables, $[HA]_{(org)}$, $[H^+]_{(aq)}$ and $[S]_{(org)}$, keeping the other two constant. Such work

on the synergistic extraction of U(IV) was attempted by Irving and Edgington⁽⁹⁾ but they did not succeed due to the instability of the oxidation state of U(IV). We have observed such instability of U(IV) only when the mixture of HTTA (thenoyltrifluoroacetone) and TBP (tri-n-butylphosphate) containing U(IV) was in contact with an aqueous phase. U(TTA)₄ dissolved in benzene was found to be quite stable, even in the presence of neutral donors, when excess of HTTA was present. As the adduct formation, responsible for synergism, takes place in the organic phase and as U(IV) was found to be stable in that phase it was felt convenient to study the same by spectrophotometry. Adduct formation between Pu(TTA)₄ and TBP was recently investigated⁽⁶⁾ by the usual solvent extraction methods as well as by spectrophotometry and the results obtained by both methods were in good agreement with each other. In continuation of these studies, formation of adducts, between U(TTA)₄ and several natural donors was investigated by spectrophotometry and the results obtained are reported. Qualitative results obtained on formation of adducts between U(DEM)₄ (DEM - dibenzoylmethane) and several neutral donors are also included. The equilibrium constant for the extraction of U(IV) from perchloric acid into a benzene solution of HTTA was obtained by solvent extraction method. Using the data obtained, equilibrium constants involved in the synergistic extraction of U(IV), from perchloric acid into benzene solutions of HTTA and the neutral donors mentioned, were calculated.

EXPERIMENTAL

Materials

Uranous sulphate solution was prepared by reducing U(VI) in dilute sulphuric acid to U(IV) using Jones's reductor. HTTA and TOPO (tri-n-octyl phosphine oxide) were obtained from M/s. E. Merck, Germany. TBPO (tri-n-butylphosphine oxide), DBBP (dibutyl Butyl phosphonate) and TIOTP (tri-iso-octyl thiophosphate) were obtained from M/s. K & K Labs., USA. TPPO (tri-phenylphosphine oxide) was obtained from M/s. Fluka, Switzerland. TBP (tri-n-butyl phosphate) was obtained from M/s. Monsanto Chem. USA. MIBK (Methyl-iso-butylketone) was obtained from M/s. Glaxo Labs. India. All other chemicals used were of AR grade.

HTTA was kept in a vacuum desiccator, over P_2O_5 , and vacuum was applied for several hours. TOPO and TPPO were dried under vacuum. TBP was purified by the method given by Alcock et al⁽¹⁰⁾. MIBK was washed with dilute nitric acid containing ~ 0.01 M potassium dichromate followed by water and distilled. All other chemicals were used as obtained.

Preparation of $U(TTA)_4$

Alcoholic solutions of uranous sulphate and HTTA were mixed in stoichiometric quantities and $U(TTA)_4$ was precipitated by adding water. The precipitate was filtered, washed with a little alcohol, recrystallized from benzene and dried in a vacuum desiccator over P_2O_5 . The DTA curve and the m.p. of the compound ($250^\circ C$) obtained were in excellent agreement

with the reported data⁽¹¹⁾. The compound was analysed for its uranium content by dissolving a known weight of the compound in benzene, stripping the uranium into 8 M nitric acid from benzene, and analyzing the uranium by volumetry⁽¹²⁾. The uranium analysis was in agreement with that calculated from the formula weight of the compound. The compound $U(DEM)_4$ was also prepared by a similar procedure.

Stability of U(IV) in benzene solutions

Preliminary studies indicated that in a benzene solution of $U(HTTA)_4$, U(IV) was slowly oxidized to U(VI). This oxidation was more pronounced in the presence of any neutral donor that was added to the $U(HTTA)_4$ in benzene. However, if excess HTTA was present in the benzene solution, the U(IV) was found to be quite stable. A similar observation was made in other solvents also. With $U(DEM)_4$ the oxidation state of U(IV) was comparatively less stable, even in the presence of excess DEM.

Procedure for recording absorption spectra

Several solutions of $U(HTTA)_4$ in the required concentration range with 10 fold excess of HTTA and suitable concentrations of neutral donors under investigation were made so as to give varying ratios of $[S] / [U(IV)]$ with same concentration of U(IV), and their absorption spectra were recorded in the visible region using Cary-14 recording spectrophotometer employing 1.0, 5.0, or 10.0 cm path length cells and using the solvent as blank. HTTA, the neutral donors used and U(VI), if present in the solution were not found to absorb at the concentrations used, in the wavelength region studied. A scanning speed of 2.5 Å/sec

was used and the absorbance values at the required wavelengths were read from the record.

Procedure for measurement of the distribution ratios

For measuring the distribution of U(IV) equal volumes (10 ml) of a benzene solution containing desired concentration of HPTA and $U(TTA)_4$ ($\sim 10^{-3}$ M) and aqueous perchloric acid of required concentration (1 M or 2 M) were taken in a ground-glass stoppered tube and the phases were equilibrated for 30 min at 25°C. This time was reported⁽¹³⁾ to be sufficient for reaching equilibrium. At the end of the equilibration the concentration of U(IV) in the organic phase was estimated spectrophotometrically by measuring its absorbance directly at a suitable wavelength in the region 500-550 nm using a Beckmann DU-spectrophotometer employing 1.0 cm path length cells and benzene as blank. U(VI) was not expected to be present in the organic phase as any U(VI), formed by the oxidation of U(IV) to U(VI) during mixing of the phases, would be present only in the aqueous phase under the experimental conditions chosen. The concentration of U(IV) in the aqueous phase was measured⁽¹⁴⁾ by mixing an aliquot with a ferric chloride solution and then by measuring the concentration of resulting ferrous by developing colour with O-phenanthroline. Experiments were done in triplicate and the agreement in the distribution ratios was within 5%.

RESULTS

Beer's Law

The absorption spectra of $U(TTA)_4$ dissolved in benzene, at different concentrations of $U(TTA)_4$ are shown in Fig.1. It is seen from this figure

that the Beer's Law is obeyed, at different wavelengths, in the concentration range studied.

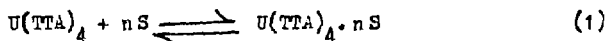
Effect of solvent on the absorption spectrum of $U(TTA)_4$

The absorption spectra of $U(TTA)_4$ dissolved in different "inert" solvents were recorded to know whether there is any interaction between $U(TTA)_4$ and the solvent. These are shown in Fig.2. An attempt was also made to record the spectra with cyclohexane, hexane and carbon tetrachloride as the solvents. However the solubility of $U(TTA)_4$ in them was too low to yield the solutions of $U(TTA)_4$ with high enough concentration to record their spectra even with 10 cm path length cells. The spectra given in Fig.2 are identical both with respect to position of absorption maxima and molar extinction coefficients indicating thereby negligible, if any, interaction of these solvents with $U(TTA)_4$.

On the contrary the spectra, shown in Fig.3, of $U(TTA)_4$ dissolved in solvents such as ketone, alcohol or ether differ with the solvents and also from those shown in Fig.2. It is therefore reasonable to infer that these solvents do interact with $U(TTA)_4$, presumably by coordination to the metal ion resulting in adduct formation.

Adduct Formation Equilibria

The formation of adducts between $U(TTA)_4$ and a neutral S can be represented by eq. (1) :



where n represents the number of S molecules associated with the adduct. As the addition of S to a solution of $U(TTA)_4$ in benzene resulted in appreciable changes in the absorption spectrum of $U(TTA)_4$ it was felt that the spectral changes could be conveniently used for studying the above equilibrium. The procedure adopted for the study is illustrated below with

DBBP as the neutral donor and the same procedure is applicable to other systems studied.

The absorption spectrum of $U(TTA)_4$ and the changes caused to it by addition of different amounts of DBBP are shown in Fig.4. Similar spectral changes were also noticed in the absorption band of $U(IV)$ around 1110 nm. However, only the visible region was used for studying the adduct formation equilibria in the present work. The presence of well defined isosbestic points in the spectra presented in Fig.4 clearly suggest that there are only two absorbing species in the system viz., $U(TTA)_4$ and $U(TTA)_4 \cdot n DBBP$, with only one value for n. The plots of the change in absorbance at any wavelength, other than the isosbestic points, with $[DBBP] / [U(IV)]$ are shown in Fig.4. When the extreme absorbance values were extrapolated the point of intersection was found when $[DBBP] : [U(IV)]$ was at 1:1 thereby suggesting the composition of the adduct to be $U(TTA)_4 \cdot DBBP$.

Thus, when a given absorption spectrum is due to a mixture of only two absorbing species the observed molar extinction coefficient, E, at a particular wavelength, can be given by the relation

$$EC = E_1 C_1 + E_2 C_2 \quad (2)$$

where, in the present case,

E_1 = molar extinction coefficient of $U(TTA)_4$

and E_2 = molar extinction coefficient of $U(TTA)_4 \cdot DBBP$

and C, the total $U(IV)$ concentration is given by

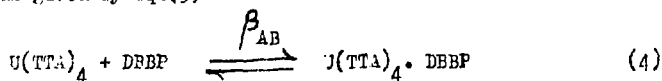
$$C = C_1 + C_2 \quad (3)$$

where

C_1 = concentration of $U(TTA)_4$

and C_2 = concentration of $U(TTA)_4 \cdot DBBP$

The equilibrium constant, β_{AB} , for the equilibrium represented by eq.(4) is given by eq.(5).



$$\beta_{AB} = \frac{[U(TTA)_4 \cdot DBBP]}{[U(TTA)_4][DBBP]} \quad (5)$$

By substituting C_1 and C_2 from eqs. (2) and (3) in eq.(5), eq.(6) follows :

$$\beta_{AB} = \frac{C_2}{C_1 [DBBP]_{(free)}} = \frac{(E_1 - E)}{(E - E_2)} \times \frac{1}{[DBBP]_{(free)}} \quad (6)$$

The equilibrium concentration of DBBP, $[DBBP]_{(free)}$, is given by eq.(7)

$$[DBBP]_{(free)} = [DBBP]_{(total)} - C_2 = [DBBP]_{(total)} \frac{C(E_1 - E)}{(E - E_2)} \quad (7)$$

Thus by knowing the values of C , $[DBBP]_{(total)}$, E_1 and E_2 it is possible to calculate the value of β_{AB} using eqs. (6) and (7) from the observed values of E .

Moderately Stable Adducts

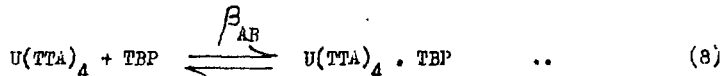
Using the procedure described above, the adduct formation constants using the neutral donors DBBP and TBP in benzene and TOPO in chloroform were calculated and the results are described below.

The absorption spectrum (Fig.4) of $U(TTA)_4$ obtained in the absence of DBBP was used to get E_1 values and the absorption spectrum of $U(IV)$ obtained when $[DBBP] / [U(IV)] \sim 8$ was used to get E_2 values as any further increase in the $[DBBP] / [U(IV)]$ ratio did not cause any observable change in the spectrum thereby suggesting the complete conversion of $U(TTA)_4$ to $U(TTA)_4 \cdot DBBP$ under these conditions. In the calculation of $[DBBP]_{(free)}$ (eq.(7)) the interaction between HTTA and DBBP was ignored as the interaction was expected to be much weaker as compared with the adduct formation constant. For the calculation of β_{AB} (eqs.(5) and (6)) the values of E obtained at $[DBBP] / [U(IV)] = 1.63$ were chosen since when the ratio was < 1 the free $[DBBP]$ was much less compared to its initial value and hence cannot be determined accurately and when the ratio was > 2 there is very little difference between the E and E_2 values (see Fig.5). The values of E_1 , E_2 and E obtained at different wavelengths and the values of β_{AB} calculated from them are given in Table 1. It is seen that the β_{AB} values, obtained from the data at different wavelengths, agree well with each other, the average value being 1.1×10^4 .

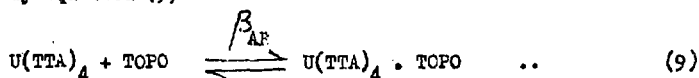
The absorption spectra of $U(TTA)_4$ in benzene and the changes due to the addition of varying concentration of TBP are shown in Fig.6. Similar spectra obtained by adding varying concentration of TOPO to a chloroform solution of $U(TTA)_4$ are shown in Fig. 7. In both the cases the presence of isosbestic points clearly indicate the presence of only two absorbing species. From the similarity of the spectra obtained with excess TBP or

TOPO with that obtained with excess DBBP, it is reasonable to infer that in both these cases 1:1 adducts are formed.

The values of the observed extinction coefficients for U(IV)-TBP system and those of β_{AB} calculated from these data are given in Table 2. The values of E_2 , the molar extinction coefficient for $U(TTA)_4 \cdot TBP$ were obtained from the spectra at $[TBP] / [U(IV)] = 40$ and 80 as the molar absorption was the same for both the spectra, at all wavelengths, indicating complete conversion of $U(TTA)_4$ to $U(TTA)_4 \cdot TBP$. An average value of $\beta_{AB} = 1.1 \times 10^3$ was obtained for the equilibrium represented by equation (8)



Similarly the values of the molar extinction coefficients for U(IV)-TOPO system in chloroform and of β_{AB} calculated from them are given in Table 3. The molar extinction coefficients E_2 of $U(TTA)_4 \cdot TOPO$ at different wavelengths were calculated from the spectra obtained at $[TOPO] / [U(IV)] = 14$ for similar reasons explained for TBP-U(IV) system. An average value of $\beta_{AB} = 9.6 \times 10^3$ was found for the equilibrium given by equation (9)

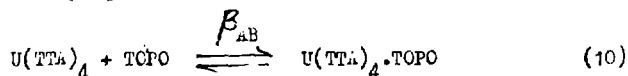


Strong Adducts

The absorption spectral changes observed when different amounts of TOPO were added to a benzene solution of $U(TTA)_4$ are shown in Fig.8.

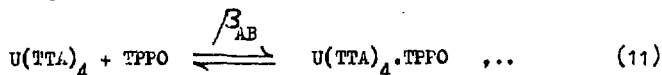
The isobestic points showing the presence of two absorbing species are quite well defined in this case also. The variation of the absorbance with $[TOPO] / [U(IV)]$ is shown in Fig.9 from which it is apparent that $U(TTA)_4$ forms a 1:1 adduct with TOPO. From the nature of Fig.9, it is clear that when $[TOPO]$ to $[U(IV)]$ ratio was < 1 , the TOPO added was almost completely consumed in the adduct formation which is complete when the ratio is equal to unity. This suggests that the β_{AB} value in this case is very high and it is not possible to calculate it accurately with the data given in Fig.8. In order to decrease the interaction between $U(TTA)_4$ and TOPO, when it would be possible to calculate β_{AB} , their interaction was studied at much lower concentrations of both the reactants. The absorption spectra of $U(TTA)_4$ (9.83×10^{-5} M) and the changes caused to it by addition of different amounts of TOPO are shown in Fig.10. The spectra remained unaltered when the $[TOPO] / [U(IV)]$ ratio was 2.54, 5.09 or 10.2 and hence the molar extinction coefficients E_2 , at different wavelengths were taken from any of these spectra. The values of E_1 , E_2 and E (at the ratio of 1.02) obtained at different wavelengths and the value of β_{AB} calculated from them are given in Table 4, It is seen that the β_{AB} values, obtained from the data at different wavelengths, agree well with each other, the average value being 1.72×10^6 . This value was further confirmed by obtaining all the data at another concentration of $U(IV)$. The data obtained at a $U(IV)$ concentration of 4.92×10^{-5} M are given in Table 5. The average value of $\beta_{AB} = 1.73 \times 10^6$ obtained from these data is in excellent agreement with that given above and hence

$\beta_{AB} = 1.7 \times 10^6$, the value for the equilibrium represented by eq. (1)

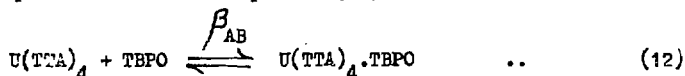


The absorption spectral changes recorded when different concentrations of TPPO or TBPO were added to a benzene solution of $U(TTA)_4$ are shown in Figs 11 and 12 respectively. The spectral changes are identical to those obtained earlier and the isosbestic points clearly suggest the presence of only two absorbing species in both the cases. The plots of the change in the absorbance at a given wavelength with $[TPPO] / [U(IV)]$ are shown in Fig.13 and the point of intersection was found when the ratio of $[TPPO] / [U(IV)] = 1$, thereby suggesting the adduct formed to be $U(TTA)_4 \cdot TPPO$. Similarly the adduct formed in $U(TTA)_4$ -TBPO system would be $U(TTA)_4 \cdot TBPO$. For the reasons similar to those explained earlier in the case of $U(TTA)_4$ -TOPO system, it is not possible to calculate accurately the β_{AB} values from the data given in Fig.11 or 12. The absorption spectra were, therefore obtained at much lower concentrations of $U(TTA)_4$ and TPPO and these are shown in Fig.14. Similarly the absorption spectra obtained for TBPO are shown in Fig.15. The molar extinction coefficients, ϵ_2 , of $U(TTA)_4 \cdot TPPO$ and $U(TTA)_4 \cdot TBPO$, at different wavelengths, were calculated from the spectra recorded for $[TPPO] / [U(IV)] = 21.2$ and 42.4 and $[TBPO] / [U(IV)] = 1.90$ and 2.85 respectively for the reasons similar to those explained before. The values of the molar extinction coefficients and of β_{AB} calculated for the formation of $U(TTA)_4 \cdot TPPO$ are given in Table 6.

From these data an average value of $\beta_{AB} = 5.2 \times 10^4$ was obtained for the equilibrium represented by equation (11)



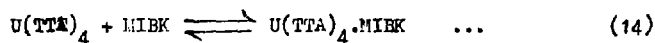
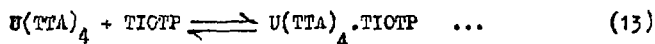
Similarly the values of the molar extinction coefficients and of β_{AB} calculated for the formation of $U(TTA)_4 \cdot TBPO$ are given in Table 7. An average value of $\beta_{AB} = 1.35 \times 10^6$ was obtained for the equilibrium shown in equation (12)



Weak Adducts

Spectral changes of the same type as discussed so far with various neutral donors are also observed when different amounts of TIOTP or MIBK are added to a benzene solution of $U(TTA)_4$ and they are shown in Figs. 16 and 17. That there are only two absorbing species in each of these solutions was clear from the observed isobestic points. As the spectral changes required the use of high ratios of $[TIOTP] / [U(IV)]$ or $[MIBK] / [U(IV)]$ it is clear that the adduct formation is much weaker compared to the earlier neutral donors. The molar extinction coefficients, E_2 , at different wavelengths, of the adducts could not be calculated as the spectrum continued to change even when the medium was completely changed to TIOTP or MIBK. Besides the large excess of TIOTP or MIBK caused partial oxidation of $U(IV)$ to $U(VI)$. It was felt that studying these systems at higher concentrations of $U(TTA)_4$ may solve the problems. But as it is difficult to realize $> 5 \times 10^{-3}$ M solutions of $U(TTA)_4$ in

benzene such studies could not be pursued. Furthermore, when higher concentrations of TIOTP or MIBK are used the medium which was essentially benzene changes partially to that of TIOTP or MIBK. In such a case the value of β_{AB} itself would change as the same is very much dependent on the medium. Hence, E_2 values were obtained by using $[TIOTP] < 0.1$ M and $[MIBK] < 0.35$ M. These data are given in Tables 8 and 9. The molar extinction coefficients E_2 for the adducts $U(TTA)_4 \cdot TIOTP$ and $U(TTA)_4 \cdot MIBK$ at various wavelengths were assumed to be same as those for $U(TTA)_4 \cdot DBBP$ or $U(TTA)_4 \cdot TBP$. Such an assumption seems to be valid as the E_2 values at a given wavelength for $U(TTA)_4 \cdot TOPO$, $U(TTA)_4 \cdot TPPO$, $U(TTA)_4 \cdot TBPO$, $U(TTA)_4 \cdot TBP$ or $U(TTA)_4 \cdot DBBP$ are same within experimental error, at most of the wavelengths studied. With these limitations the β_{AB} values of ~ 11 and ~ 0.8 were obtained as the estimates for the equilibria represented by eqs. (13) and (14) respectively



An attempt was also made to confirm the values of β_{AB} obtained for the adducts of $U(TTA)_4$ with TIOTP and MIBK by an alternate method⁽¹⁵⁾. Unlike the earlier method this does not require the knowledge of molar extinction coefficient, E_2 , to calculate the value of β_{AB} . For this $U(TTA)_4$ solution in benzene was prepared in the presence of 100-fold excess of HTTA in order to prevent the oxidation of U(IV) to

U(VI) when TIOIP or MIBK is added to it. The absorbances of the solutions containing some concentration of $U(TTA)_4$ but varying concentrations of TIOIP or MIBK were measured at different wavelengths. From these data the value of β_{AB} was calculated as described below.

When the adduct formation is weak, one can impose the condition that $[S]_{(free)} = [S]_{(total)}$ as $C_2 \ll [S]$. Under these conditions the value of β_{AB} is given by eq.(15)

$$\beta_{AB} = \frac{C_2}{C_1 \cdot [S]} \quad (15)$$

Substituting C_1 from eq.(3) into eq.(2) it follows that

$$E C = E_1 (C - C_2) + E_2 C_2 \quad (16)$$

Rearranging eq.(16)

$$\frac{E - E_1}{E_2 - E_1} = \frac{C_2}{C} \quad (17)$$

From eq.(15) it follows that

$$\frac{C_2}{C} = \frac{[S] \beta_{AB}}{1 + [S] \beta_{AB}} \quad (18)$$

From eqs. (17) and (18) eq.(19) follows:

$$\frac{[S]}{[E - E_1]} = \frac{[S]}{(E_2 - E_1)} + \frac{1}{\beta_{AB} (E_2 - E_1)} \quad (19)$$

Eq.(19) is in the form of $y = mx + c$ and a plot of $\frac{[S]}{(E - E_1)}$ versus $[S]$ would be a straight line with the slope $= 1/(E_2 - E_1)$ and intercept $= 1/\beta_{AB} (E_2 - E_1)$ from which the value of β_{AB} can be calculated. The absorbance values of U(IV), at different wavelengths,

obtained as a function of concentration of TIOTP and MIBK are given in Tables 10 and 11 respectively. Using these data the corresponding plots of $\frac{[S]}{(E - E_1)}$ versus $[S]$ for TIOTP and MIBK are shown respectively in Figures 18 and 19. An average value of $\beta_{AB} = 18.8$ was obtained for the equilibrium shown by eq. (13) and an average value of $\beta_{AB} = 0.8$ was obtained for the equilibrium shown by eq. (14). It can be seen that these values are quite close to those estimated by assuming the E_2 values.

Adduct Formation with Amines

The absorption spectrum of $U(TTA)_4$ and the changes resulting due to the addition of varying concentration of TLA, TIOA and TOA are shown respectively in Figs. 20, 21 and 22. The presence of isosbestic points, though not very well defined and the similarity of these spectra with those obtained with addition of other neutral donors suggest that in all these systems also only two absorbing species are present and 1:1 adduct between $U(TTA)_4$ and the amine is formed in all the cases. No attempt was, however, made to calculate the values of adduct formation constants as $U(IV)$ was found to oxidize slowly to $U(VI)$ in the presence of amines.

Adduct Formation with Water

In an attempt to know, at least qualitatively, whether $U(TTA)_4$ forms adduct with water, the absorption spectra of $U(TTA)_4$ dissolved in acetone were recorded by adding varying concentration of water and these are shown in Fig. 23. The changes in the spectra clearly suggest that $U(TTA)_4$ does form, presumably $U(TTA)_4 \cdot H_2O$, an adduct with water. This also clearly suggests that the adduct formation with $U(TTA)_4$ by neutral donors is by

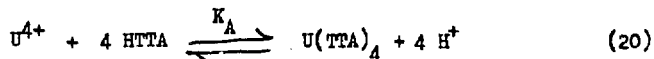
addition of the neutral donor to $U(TTA)_4$ molecule and not by substitution of water molecule.

Adduct Formation between $U(DBM)_4$ and Neutral Donors

Only qualitative studies on the adduct formation between $U(DBM)_4$ and neutral donors could be carried out as the oxidation state of U(IV) even in the presence of excess DBM, was not stable enough to permit quantitative studies. The spectra ^{of} $U(DBM)_4$ in benzene recorded in the presence of a large excess of various neutral donors are shown in Fig.24. The adduct formation is indicated only in the case of TOPO. With other neutral donors either there is no adduct formation or it is too weak to cause any spectral change. Even with TOPO the adduct formation is much weaker compared to its adduct formation with $U(TTA)_4$ as can be inferred from much higher concentration of TOPO is required to result the change in the absorption spectrum of $U(DBM)_4$. It is known that $U(DBM)_4$ chelate is stronger than $U(TTA)_4$ and also that stronger the metal chelate weaker is the adduct it forms. The present observation is in conformity with this.

Extraction of U(IV) by HTTA and HTTA + S in benzene

The extraction of U(IV) from perchloric acid into HTTA in benzene is given⁽¹³⁾ by the relation,

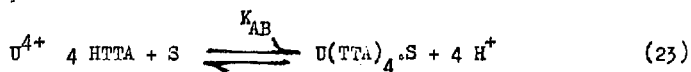


for which the equilibrium constant, K_A , is

$$K_A = \frac{[U(TTA)_4] [H^+]^4}{[U^{4+}] [HTTA]^4} \quad (21)$$

$$= K_{d(A)} \cdot [H^+]^4 [HTTA]^{-4} \quad (22)$$

where $K_{d(A)}$ is the observed distribution ratio of U(IV). Though the value of K_A was reported in the literature^(13,16), it was redetermined by assaying equilibrium U(IV) concentration in both the phases. A value of $K_A = 2.6 \times 10^5$ was obtained which is indeed close to the reported⁽¹³⁾ value (3.3×10^5). For the extraction of U(IV) from such a medium by mixtures of HTTA and a neutral donor S, the equilibrium can be represented by,



for which the equilibrium constant, K_{AB} , is given by

$$K_{AB} = \frac{[U(TTA)_4 \cdot S] [H^+]^4}{[U^{4+}] [HTTA]^4 [S]} = \beta_{AB} \cdot K_A \quad (24)$$

The absorption spectra of U(IV) extracted from perchloric acid into mixtures of HTTA and S attempted with a couple of neutral donors were found to be identical with those obtained by adding excess S to a benzene solution of $U(TTA)_4$ thus suggesting that the species extracted are 1:1 adducts between the $U(TTA)_4$ and the neutral donors. Knowing the value of K_A and using the values of β_{AB} , the values of K_{AB} for the extraction of the adducts, were calculated and are summarised in Table 12.

Destruction of Synergism

When the extraction of metal ion by HTTA is studied in the presence of increasing concentrations of S, it was reported that the extraction is enhanced initially followed by a steep decrease at higher concentration of S. This decrease in extraction is known as 'antagonism' or better as 'destruction of synergism'. This was attributed to breaking up of the adduct resulting in the formation of metal chelate, probably hydrated, due to the extraction of excess water. Spectrophotometric evidence for such break up of the adducts was reported⁽¹⁷⁾ in the case of U(VI) and Th(IV). In the present case, when excess of neutral donors, whether dry or water-equilibrated, were added to the benzene solution of $U(HTTA)_4$ they produced identical spectra and no destruction of the adducts was noticed. This observation is similar to that made earlier⁽⁶⁾ on Pu(IV). The destruction of synergism thus appears to be due to change of medium which changes from that of the diluent to that of a neutral donor rather than the destruction of the adducts. The effect of medium can be clearly seen from widely different β_{AB} values obtained for the formation of $U(HTTA)_4 \cdot TOPO$ in benzene and chloroform. In general, more polar the diluent less stable is the adduct formed between metal chelate and a neutral donor.

DISCUSSION

The absorption spectra of several 8-coordinated U(IV) compounds, both in solid state as well as in several organic solvents, were reported⁽¹⁸⁾ to be identical to each other and differ much from the

6-coordinated U(IV) spectra. In the present study, it was found that the absorption spectra of all the adducts, $U(TTA)_4 \cdot S$, studied were identical to each other whereas they differed much from that of the 8-coordinated $U(TTA)_4$. This is evident from the spectra shown in Fig.25.

Thus, the spectral changes in the present case can be attributed to an increase in coordination number from 8 to 9, suggesting that the neutral donor is directly attached to the metal. Ferraro and Healy⁽¹⁹⁾ proposed opening of the chelate ring, in the case of Th(IV), to preserve the 8-coordinate structure in the case of the adduct. The compound $Th(TTA)_4 \cdot TOPO$ was subsequently thoroughly investigated⁽²⁰⁾ and found to be 9-coordinated.

The data presented in Table 12 are in agreement with the general observation that the strength of the adduct increases with the basicity of the neutral donor attached to the same. Also $U(TTA)_4 \cdot TOPO$ was found to be weaker as compared to $Th(TTA)_4 \cdot TOPO$ ($\beta_{AB} = 5 \times 10^6$)⁽⁷⁾ and stronger as compared to $Np(TTA)_4 \cdot TOPO$ ($\beta_{AB} = 5 \times 10^5$)⁽²¹⁾. This is in agreement with the observation⁽⁸⁾ that the stronger the metal chelate, the weaker the stability of the adduct formed with it.

ACKNOWLEDGEMENTS

We sincerely thank Dr. M.V. Ramaniah, Head, Radiochemistry Division for his keen interest in this work. Thanks are also due to Shri M.N. Nadkarni for his constant encouragement during the course of this work. We thank Dr. N.V. Thakur for his help in the preparation of $U(TTA)_4$.

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Table 1 - Spectrophotometric data on the adduct
formation between $U(TTA)_4$ and DBBP

$$[U(IV)] = 1.45 \times 10^{-3} M$$

| Wavelength, nm | 570 | 580 | 590 | 600 | 610 | 620 | 630 | 640 | 650 |
|-------------------------------------|------|------|------|------|------|------|------|------|------|
| $E_1, M^{-1} \text{ cm}^{-1}$ | 168 | 120 | 82.5 | 63.9 | 63.2 | 80.7 | 98.2 | 105 | 110 |
| $E_2, M^{-1} \text{ cm}^{-1}$ | 82.5 | 38.6 | 18.8 | 17.8 | 18.9 | 20.7 | 27.4 | 38.1 | 69.0 |
| $E, M^{-1} \text{ cm}^{-1}(a)$ | 89.7 | 45.5 | 23.9 | 21.4 | 22.6 | 25.1 | 33.2 | 43.4 | 72.3 |
| $\beta_{AB}, M^{-1} \times 10^{-4}$ | 1.06 | 1.05 | 1.12 | 1.16 | 1.07 | 1.24 | 1.09 | 1.14 | 1.11 |

Table 2. Spectrophotometric data on the adduct formation between $U(TTA)_4$ and TBP

$$[U(IV)] = 1.56 \times 10^{-5} M$$

| $[TBP] / [U(IV)]$ | Wavelength, nm | 580 | 590 | 600 | 620 | 630 | 640 |
|-------------------|-----------------------------|------|------|------|------|-------|------|
| 0 | E_1 | 122 | 81.5 | 65.3 | 81.3 | 98.6 | 105 |
| 0.0 | E_2 | 40.3 | 19.2 | 17.9 | 20.5 | 20.5 | 38.5 |
| 0.4 | " | 103 | 69.8 | 54.4 | 67.8 | 83.2 | 90.2 |
| 1.0 | " | 83.8 | 54.0 | 43.3 | 52.7 | 65.3 | 73.6 |
| 1.7 | " | 69.6 | 43.2 | 34.8 | 42.0 | 52.2 | 62.4 |
| 2.0 | " | 66.6 | 40.3 | 33.3 | 39.7 | 49.3 | 58.9 |
| 0.4 | $\beta_{AB} \times 10^{-3}$ | 1.11 | 1.07 | 1.12 | 1.02 | 0.961 | 1.02 |
| 1.0 | " | 1.04 | 1.05 | 1.04 | 1.07 | 1.06 | 1.08 |
| 1.7 | " | 1.11 | 1.07 | 1.13 | 1.15 | 1.19 | 1.11 |
| 2.0 | " | 1.02 | 1.01 | 1.01 | 1.05 | 1.11 | 1.10 |

Table 3. Spectrophotometric data on the adduct formation between $(\text{TTA})_4$ and TOPO in Chloroform

$$[\text{U(IV)}] = 7.24 \times 10^{-4} \text{ M.}$$

| | | | | | | | | | |
|--|-------|------|------|------|------|------|------|------|------|
| Wavelength, nm | 570 | 580 | 590 | 600 | 610 | 620 | 630 | 640 | 650 |
| $\epsilon_1, \text{M}^{-1} \text{cm}^{-1}$ | 158 | 113 | 78.7 | 60.8 | 60.1 | 78.3 | 95.0 | 102 | 107 |
| $\epsilon_2, \text{M}^{-1} \text{cm}^{-1}$ | 84.9 | 38.3 | 18.5 | 17. | 18.0 | 18.9 | 25.1 | 34.8 | 62.2 |
| $\epsilon, \text{M}^{-1} \text{cm}^{-1}(\text{a})$ | 111 | 63.6 | 39.0 | 31.9 | 31.9 | 38.7 | 48.6 | 57.7 | 77.3 |
| $\epsilon, \text{M}^{-1} \text{cm}^{-1}(\text{b})$ | 101 | 53.0 | 31.1 | 26.4 | 26.7 | 31.1 | 39.5 | 48.8 | 71.8 |
| $\beta_{23} \times 10^{-4} (\text{a})$ | 0.891 | 1.02 | 1.02 | 1.06 | 1.11 | 1.09 | 1.06 | 1.02 | 1.05 |
| $\beta_{23} \times 10^{-3} (\text{b})$ | 8.14 | 9.76 | 8.83 | 8.85 | 9.01 | 9.10 | 9.07 | 8.90 | 8.51 |

$$(\text{a}) - \frac{[\text{TOPO}]}{[\text{U(IV)}]} = 0.921; (\text{b}) \frac{[\text{TOPO}]}{[\text{U(IV)}]} = 1.38$$

Table 4 - Spectrophotometric data on the adduct
formation between $U(TTA)_4$ and TOPO

$$[U(IV)] = 9.83 \times 10^{-5} M$$

| | | | | | | | | | | | |
|-----------------------------|------|------|------|------|------|------|------|------|------|------|------|
| Wavelength, nm | 450 | 460 | 470 | 480 | 490 | 500 | 510 | 520 | 530 | 540 | 550 |
| $E_1, M^{-1} cm^{-1}$ | 1460 | 1270 | 1090 | 931 | 814 | 705 | 593 | 498 | 425 | 359 | 308 |
| $E_2, M^{-1} cm^{-1}$ | 671 | 549 | 448 | 366 | 300 | 239 | 186 | 173 | 137 | 69.2 | 50.9 |
| $E, M^{-1} cm^{-1}(a)$ | 722 | 590 | 468 | 407 | 331 | 270 | 214 | 198 | 158 | 91.6 | 66.1 |
| $AB, M^{-1} \times 10^{-6}$ | 1.80 | 2.28 | 1.92 | 1.45 | 2.04 | 1.70 | 1.60 | 1.30 | 1.43 | 1.28 | 2.12 |

(a) $[TOPO] / [U(IV)] = 1.02$

Table 5 - Spectrophotometric data on the adduct
formation between $U(TTA)_4$ and TOPO

$$[U(IV)] = 4.92 \times 10^{-5} M$$

| | | | | | | | | | | | | | |
|-------------------------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Wavelength, nm | 410 | 420 | 430 | 440 | 450 | 460 | 470 | 480 | 490 | 500 | 510 | 520 | 530 |
| $E_1, M^{-1}cm^{-1}$ | 3500 | 2540 | 2100 | 1480 | 1480 | 1260 | 1090 | 925 | 803 | 691 | 589 | 488 | 417 |
| $E_2, M^{-1}cm^{-1}$ | 2270 | 1510 | 1110 | 854 | 681 | 549 | 447 | 366 | 301 | 234 | 183 | 173 | 132 |
| $E, M^{-1}cm^{-1}(a)$ | 2380 | 1610 | 1200 | 945 | 752 | 610 | 508 | 427 | 346 | 285 | 224 | 203 | 163 |
| $\beta_{AB}, M^{-1} \times 10^{-6}$ | 2.21 | 1.67 | 1.90 | 1.59 | 1.98 | 2.12 | 1.74 | 1.32 | 1.95 | 1.27 | 1.54 | 1.73 | 1.33 |

(a) - $[TOPO] / [U(IV)] = 1.02$.

Table 6 - Spectrophotometric data on the adduct formation between $\text{U}(\text{THA})_4$ and TPPO

$$\int \text{U}(\text{IV}) J = 9.83 \times 10^{-5} \text{ M}$$

| | | | | | | | | | | | | |
|--|------|------|------|------|------|------|------|------|------|------|------|------|
| Wavelength, nm | 440 | 450 | 460 | 470 | 480 | 490 | 500 | 510 | 520 | 530 | 540 | 550 |
| $E_1, \text{M}^{-1} \text{cm}^{-1}$ | 1730 | 1460 | 1260 | 1080 | 924 | 804 | 692 | 580 | 488 | 417 | 351 | 300 |
| $E_2, \text{M}^{-1} \text{cm}^{-1}$ | 909 | 707 | 570 | 458 | 372 | 301 | 234 | 185 | 177 | 142 | 71.2 | 47.8 |
| $E, \text{M}^{-1} \text{cm}^{-1}(\text{a})$ | 1120 | 909 | 733 | 623 | 524 | 429 | 356 | 295 | 264 | 218 | 150 | 116 |
| $E, \text{M}^{-1} \text{cm}^{-1}(\text{b})$ | 1080 | 865 | 706 | 587 | 486 | 400 | 330 | 267 | 244 | 201 | 130 | 99.7 |
| $\beta_{\text{AB}} \times 10^{-4}(\text{a})$ | 5.56 | 5.14 | 5.25 | 5.25 | 4.89 | 5.67 | 5.21 | 4.79 | 4.75 | 4.86 | 4.69 | 5.06 |
| $\beta_{\text{AB}} \times 10^{-4}(\text{b})$ | 5.26 | 5.21 | 5.73 | 5.30 | 5.34 | 5.75 | 5.22 | 5.29 | 5.00 | 5.03 | 5.19 | 5.37 |

Notes: (a) $\int \text{TPPO} J / \int \text{U}(\text{IV}) J = 1.27$, (b) $\int \text{TPPO} J / \int \text{U}(\text{IV}) J = 1.53$.

Table 7 - Spectrophotometric data on the adduct formation
between $U(TTA)_4$ and TBPO

$$[U(IV)] = 2.46 \times 10^{-5} M$$

| Wavelength, nm | 420 | 430 | 440 | 450 | 460 | 470 | 480 | 490 |
|---------------------------------|------|------|------|------|------|------|------|------|
| $E_1, M^{-1} cm^{-1}$ | 2480 | 2000 | 1660 | 1370 | 1150 | 967 | 813 | 699 |
| $E_2, M^{-1} cm^{-1}$ | 1480 | 1120 | 858 | 659 | 528 | 419 | 337 | 276 |
| $E, M^{-1} cm^{-1} (a)$ | 1630 | 1240 | 967 | 748 | 610 | 496 | 411 | 341 |
| $\beta_{AB} \times 10^{-6} (a)$ | 1.18 | 1.42 | 1.43 | 1.67 | 1.52 | 1.34 | 1.10 | 1.13 |

(a) $[TBPO] / [U(IV)] = 1.04.$

Table 8 - Spectrophotometric data on the adduction formation between $U(TTA)_4$ and TIOTP

$$[U(IV)] = 4.79 \times 10^{-3} M$$

| Wavelength, nm | 560 | 570 | 580 | 590 | 600 | 610 | 620 | 630 | 640 | 650 |
|-------------------------|------|------|------|------|------|------|------|------|------|------|
| $E_1, M^{-1} cm^{-1}$ | 246 | 171 | 121 | 83.5 | 64.9 | 64.5 | 81.2 | 98.1 | 104 | 110 |
| $E_2^*, M^{-1} cm^{-1}$ | 85.9 | 82.5 | 38.6 | 18.8 | 17.8 | 18.9 | 20.7 | 27.4 | 38.1 | 69.0 |
| $E, M^{-1} cm^{-1} (a)$ | 197 | 143 | 94.6 | 64.3 | 51.6 | 50.7 | 63.0 | 75.6 | 83.9 | 97.7 |
| β_{AB}, M^{-1} | 11.2 | 11.7 | 11.9 | 10.7 | 9.94 | 11.0 | 10.9 | 11.8 | 11.1 | 10.8 |

* Values used from NMRP data.

$$(a) - [TIOTP] / [U(IV)] = 8.56$$

Table 9. Spectrophotometric data on the adduct formation
between $U(TTA)_4$ and MIBK

$$[U(IV)] = 4.79 \times 10^{-3} M$$

| wavelength, nm | 540 | 550 | 560 | 570 | 580 | 590 | 600 | 610 | 620 | 630 | 640 | 650 |
|-------------------------|------|------|------|------|------|------|------|------|------|------|------|------|
| $E_1, M^{-1} cm^{-1}$ | 364 | 305 | 246 | 171 | 121 | 83.5 | 64.9 | 64.5 | 81.2 | 89.1 | 104 | 110 |
| $E_2, M^{-1} cm^{-1}$ | 84.7 | 63.7 | 83.9 | 82.2 | 38.9 | 18.2 | 17.1 | 18.6 | 20.7 | 27.4 | 38.6 | 71.3 |
| $E, M^{-1} cm^{-1} (a)$ | 393 | 267 | 218 | 149 | 104 | 69.7 | 54.3 | 53.4 | 68.5 | 82.9 | 90.6 | 102 |
| $\beta_{AB} \times 10$ | 8.42 | 5.63 | 5.29 | 9.92 | 7.87 | 8.07 | 8.58 | 8.58 | 8.00 | 8.25 | 7.76 | 7.85 |

Notes: (a) = $[MIBK] / [U(IV)] = 69.6$

Table 10. Variation in the absorbance of U(IV), in presence of excess HTTA, with concentration of TIOTP.

$$[U(IV)] = 1.26 \times 10^{-3} \text{ M}; \text{ path length} = 5.0 \text{ cm}$$

| [TIOTP] M | Absorbance at nm | | |
|--------------|------------------|-------|-------|
| | 570 | 580 | 590 |
| 0 | 0.980 | 0.695 | 0.482 |
| 0.0205 | 0.800 | 0.530 | 0.353 |
| 0.410 | 0.670 | 0.410 | 0.260 |
| 0.615 | 0.598 | 0.349 | 0.215 |
| 0.0820 | 0.570 | 0.330 | 0.205 |
| 0.1025 | 0.525 | 0.285 | 0.165 |

Table 11. Variation in the absorbance of U(IV), in presence of excess HTTA, with concentration of MIBK

$$[U(IV)] = 1.36 \times 10^{-3} M; \text{ path length} = 5.0 \text{ cm}$$

| [MIBK] M | Absorbance at, nm | | |
|-------------|-------------------|-------|-------|
| | 580 | 590 | 600 |
| 0 | 0.800 | 0.552 | 0.423 |
| 0.2 | 0.735 | 0.505 | 0.388 |
| 0.4 | 0.692 | 0.472 | 0.365 |
| 0.6 | 0.662 | 0.445 | 0.341 |
| 0.8 | 0.620 | 0.411 | 0.318 |
| 1.0 | 0.596 | 0.393 | 0.307 |

Table 12. Summary of equilibrium constants for the adducts between $U(TTA)_4$ and some neutral donors.

(Adduct - $U(TTA)_4 \cdot S$)

| Neutral donor (S) | Diluent | $\log K_A$ | $\log K_{AB}$ | $\log \beta_{AB}$ |
|-------------------|------------|------------|---------------|-------------------|
| TOPO | Benzene | 5.42 | 11.65 | 6.23 |
| TBPO | Benzene | 5.42 | 11.55 | 6.13 |
| TPPO | Benzene | 5.42 | 10.14 | 4.72 |
| DBBP | Benzene | 5.42 | 9.46 | 4.04 |
| TBP | Benzene | 5.42 | 8.46 | 3.04 |
| T10TP | Benzene | 5.42 | 6.69 | 1.27 |
| MIBK | Benzene | 5.42 | 5.32 | - 0.10 |
| TOPO | Chloroform | - | - | 3.98 |

CAPTIONS TO FIGURES

Fig.1. Absorption spectra of $U(TTA)_4$ in benzene

Fig.2. Absorption spectra of $U(TTA)_4$ in "inert" solvents

Fig.3. Absorption spectra of $U(TTA)_4$ in coordinating solvents

Fig.4. Absorption spectra of $U(TTA)_4$ with varying concentration of DBBP

Note : $[U(IV)] = 1.45 \times 10^{-3}$ M. For the curves numbered on lower wavelength region add 128 to the given value of λ .

Fig.5. Variation of absorbance of $U(IV)$ with $[DBBP] / [U(IV)]$

Fig.6. Absorption spectra of $U(TTA)_4$ with varying concentration of TEP.

Note : Same as given for Fig.4.

Fig.7. Absorption spectra of $U(TTA)_4$ with varying concentration of AOU in chloroform.

Note : For the curves numbered on lower wavelength region add 138 to the given λ values

Fig.8. Absorption spectra of $U(TTA)_4$ with varying concentration of TOPO.

Note : Same as given for Fig.4

Fig.9. Variation of absorbance of $U(IV)$ with $[TOPO] / [U(IV)]$

Fig.10. Absorption spectra of $U(TTA)_4$ with varying concentration of PCPO

Note : $[U(IV)] = 9.83 \times 10^{-5}$ M. For the curve No.(1)

lower wavelength region, add 1020 to the given λ values

Fig.11. Absorption spectra of $U(TTA)_4$ with varying concentration of DPE

Note : Same as that given for Fig.4

Fig.12. Absorption spectra of $U(TTA)_4$ with varying concentration of DAF

Note : For the curves numbered on lower wavelength region add 127 to the given λ values.

Fig.13. Variation of absorbance of $U(IV)$ with $[DAF] / [U(IV)]$

Fig.14. Absorption spectra of $U(TTA)_4$ with varying concentration of TPIO

Note : For curve No.1 on lower wavelength region add 1017 to the given E values

Fig.15. Absorption spectra of $U(TTA)_4$ with varying concentration of TPEO

Fig.16. Absorption spectra of $U(TTA)_4$ with varying concentration of TIOTP

Note : Same as given for Fig.4.

Fig.17. Absorption spectra of $U(TTA)_4$ with varying concentration of MIBK

Note : Same as given for Fig.4.

Fig.18. Variation of $\frac{[TIOTP]}{(E_1 - E)}$ with $[TIOTP]$

Fig.19. Variation of $\frac{[MIBK]}{(E_1 - E)}$ with $[MIBK]$

Fig.20. Absorption spectra of $U(TTA)_4$ with varying concentration of TLA

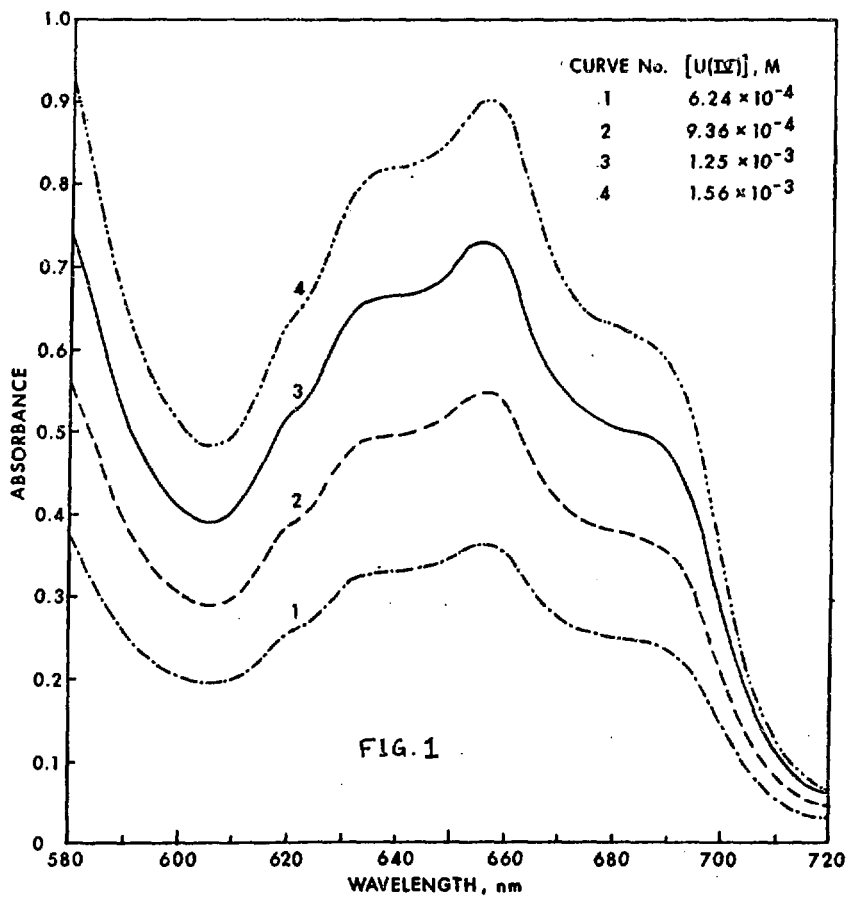
Fig.21. Absorption spectra of $U(TTA)_4$ with varying concentration of TIOA

Fig.22. Absorption spectra of $U(TTA)_4$ with varying concentration of T-n-OA

Fig.23. Absorption spectra of $U(TTA)_4$ (in acetone) with varying concentration of water

Fig.24. Absorption spectra of $U(DBM)_4$ in different media

Fig.25. Absorption spectra of the adducts of $U(TTA)_4$ with different neutral donors



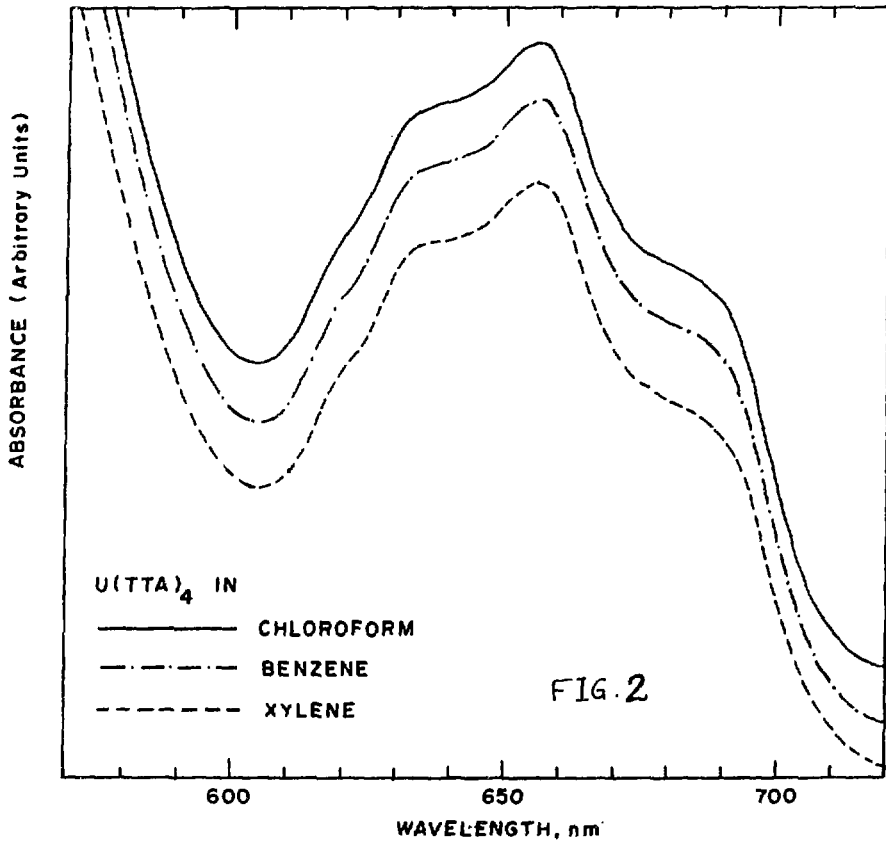


FIG. 2

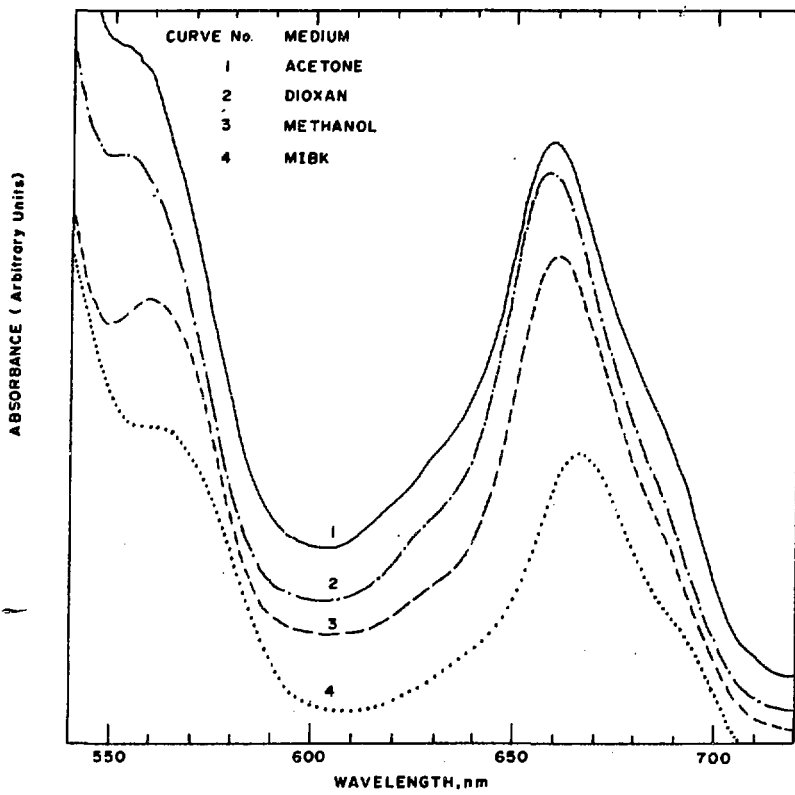


FIG. 3

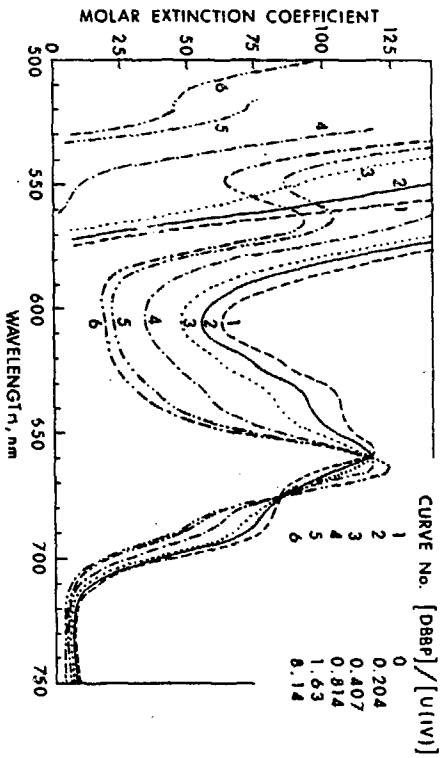


FIG. 4

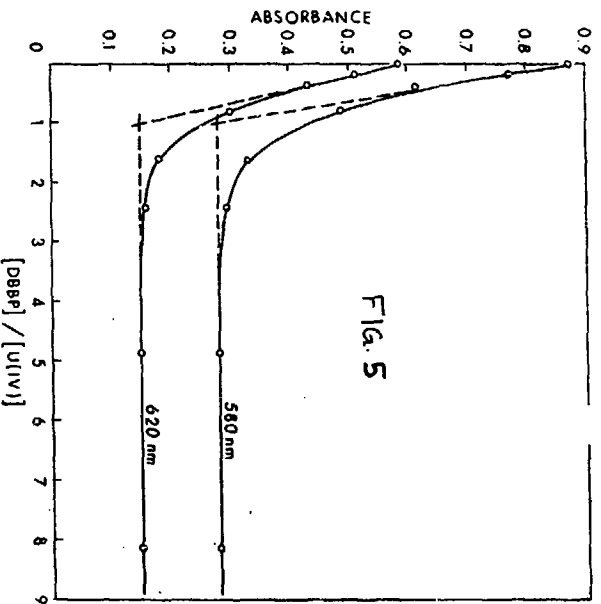


FIG. 5

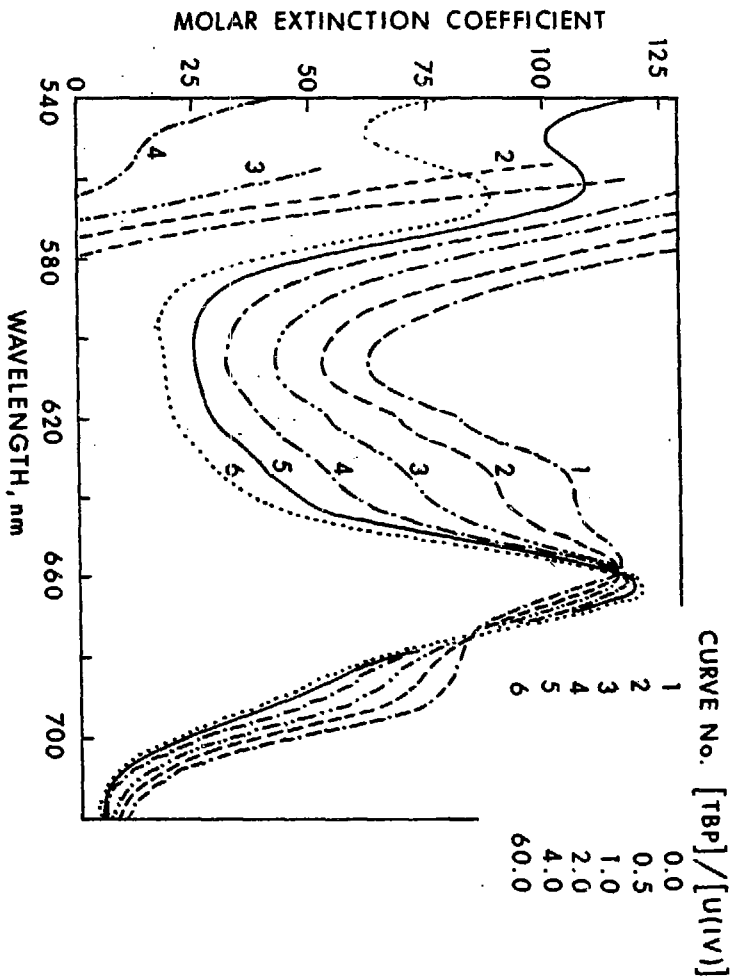
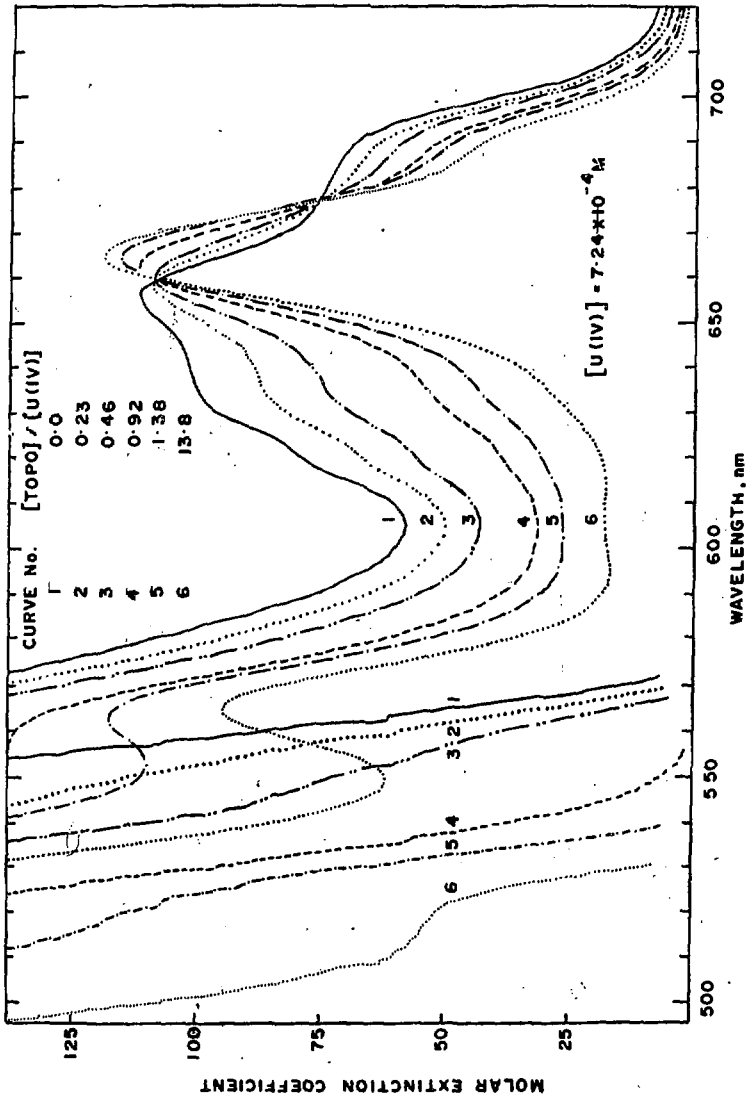


FIG. 6



WAVELENGTH, nm
 FIG. 7

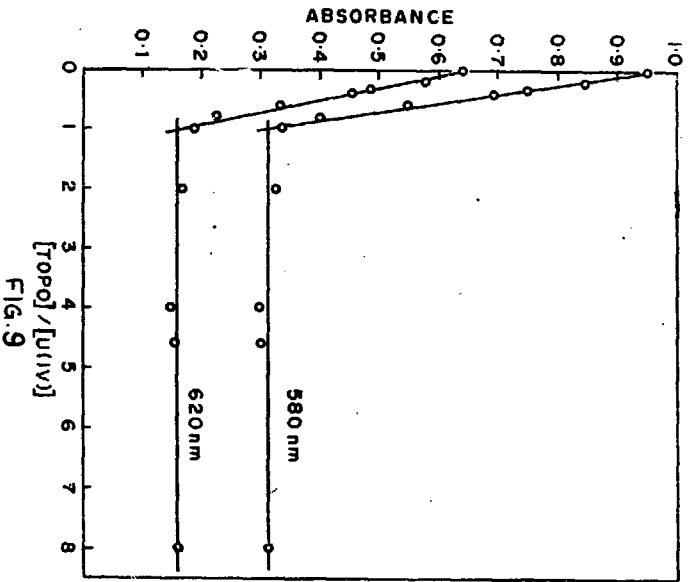
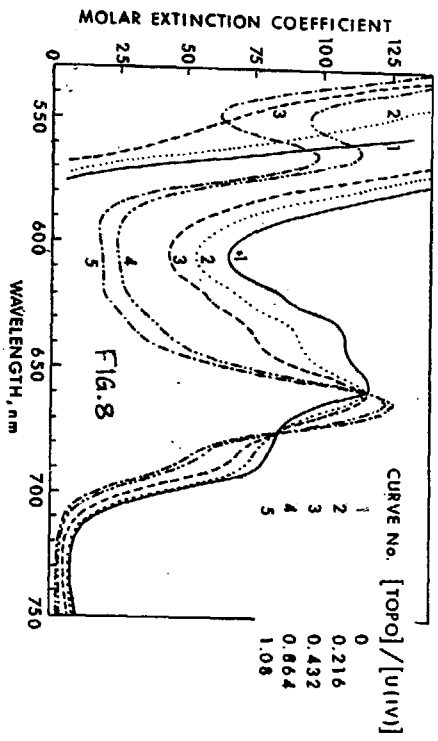
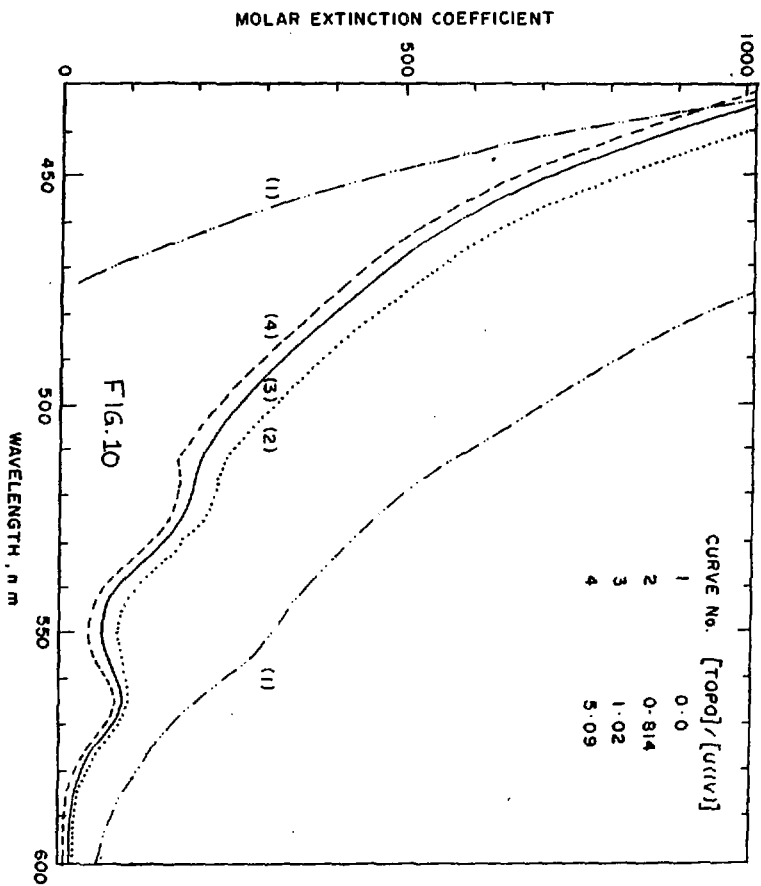


FIG. 9

FIG. 8



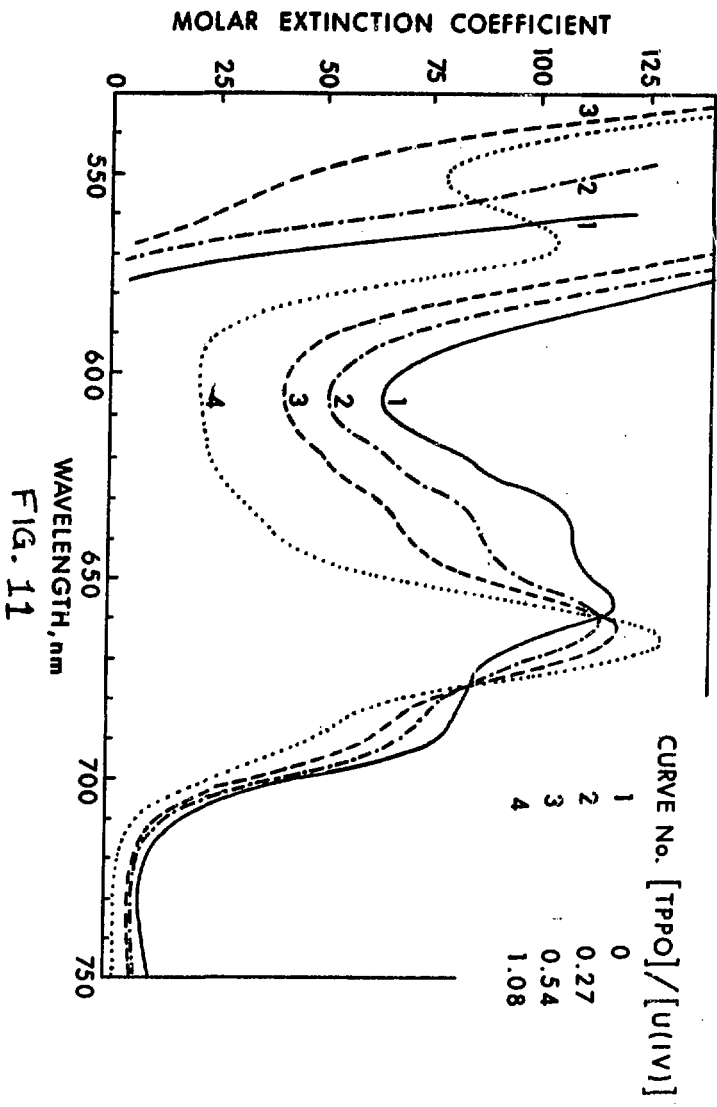


FIG. 11

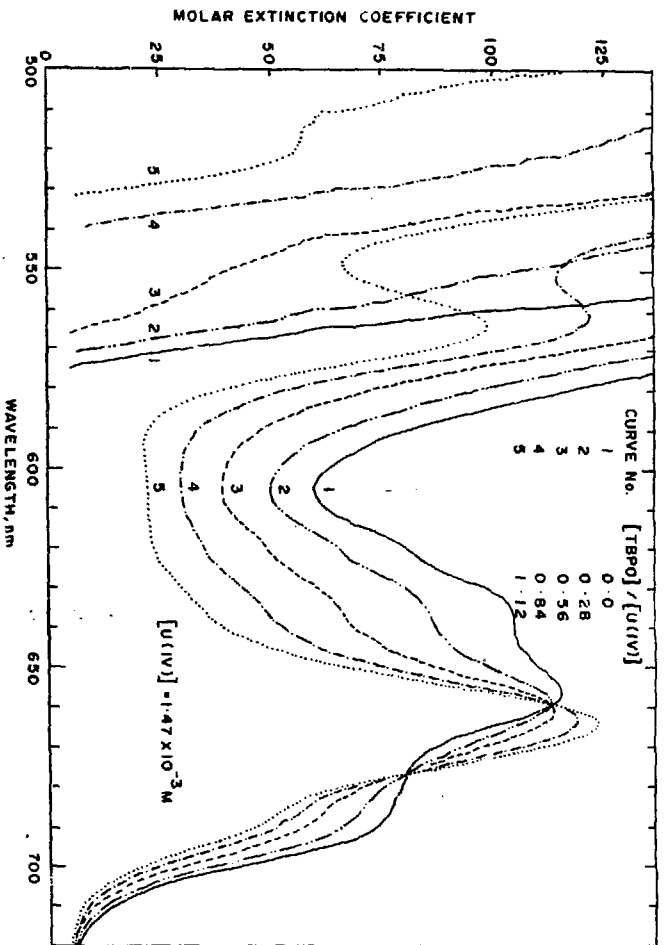


FIG. 12

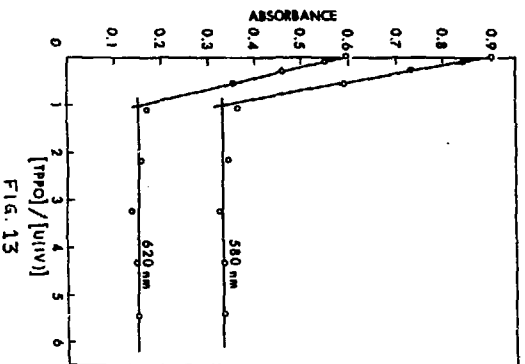
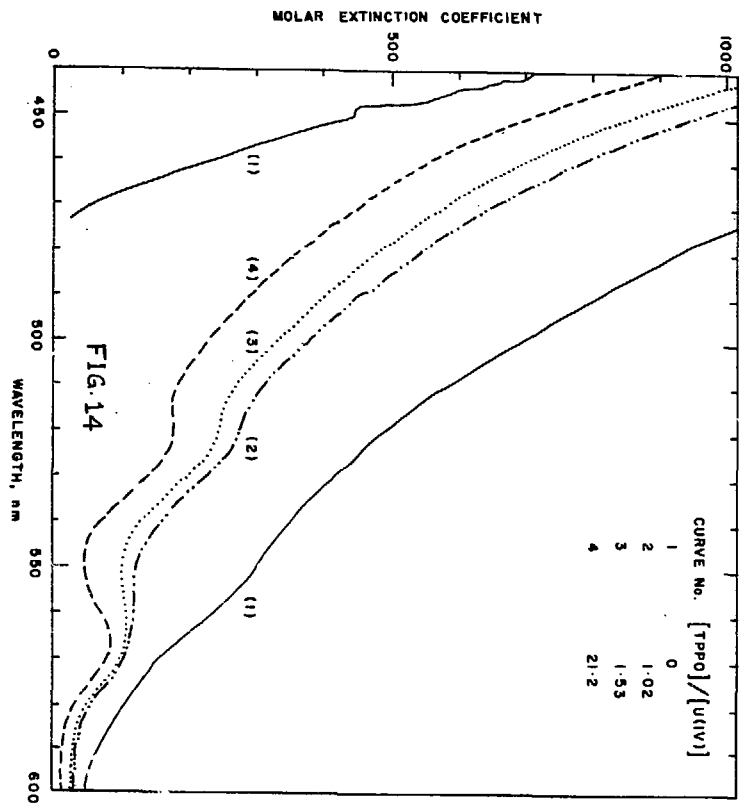
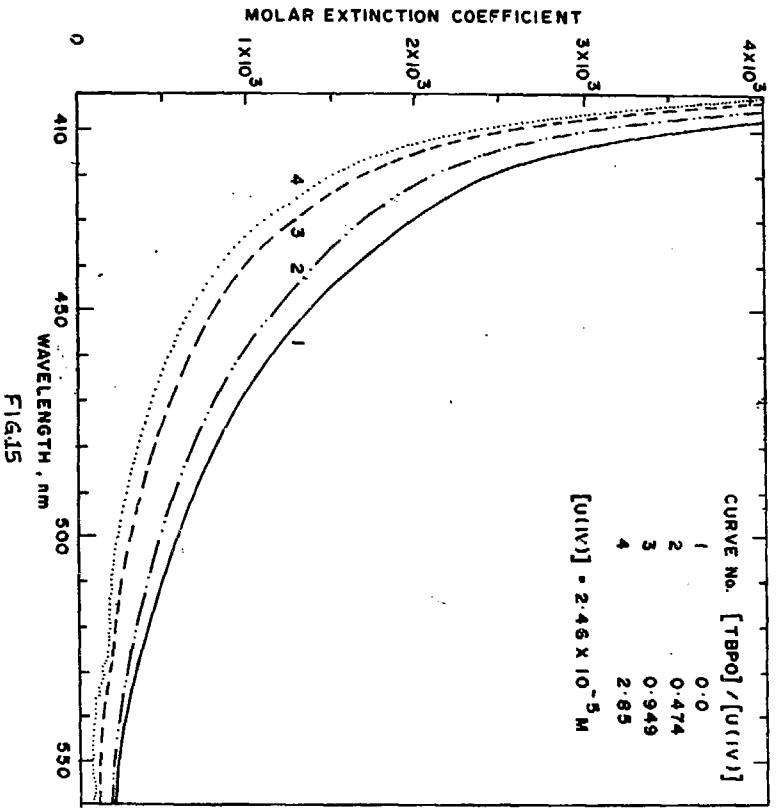
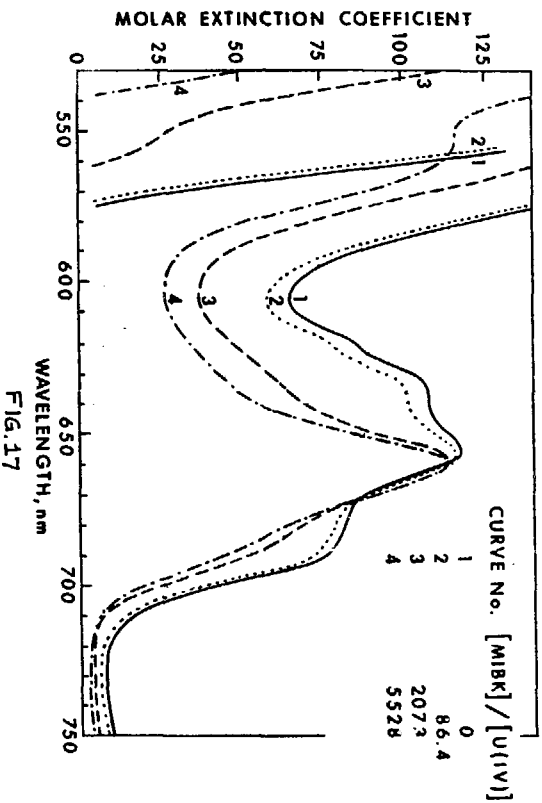
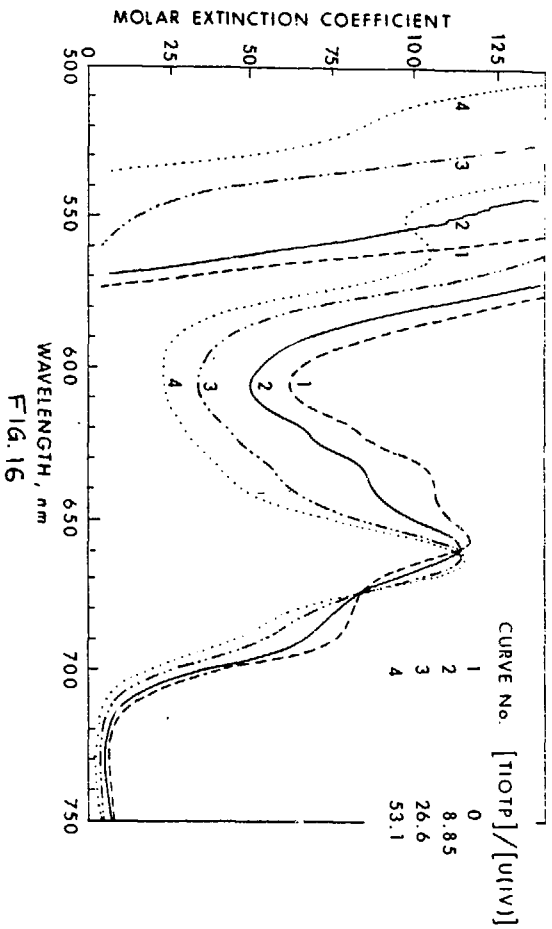


FIG. 13







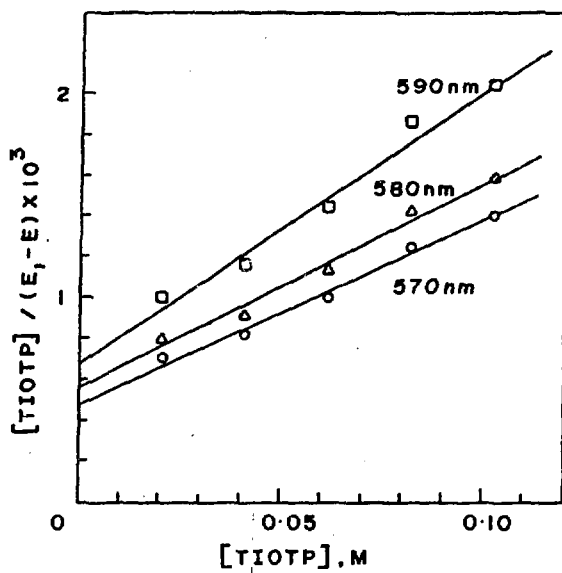


FIG. 18

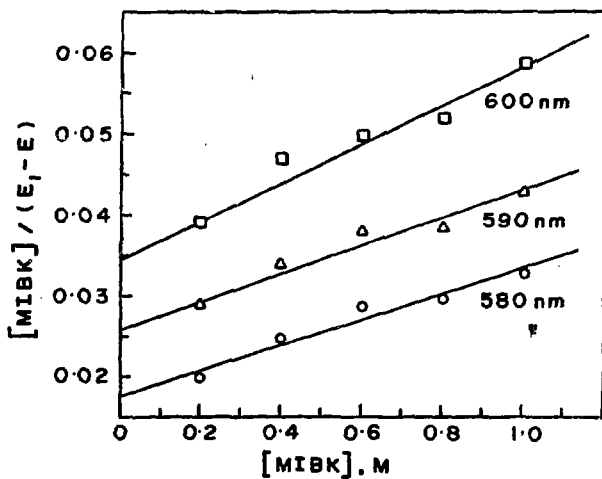
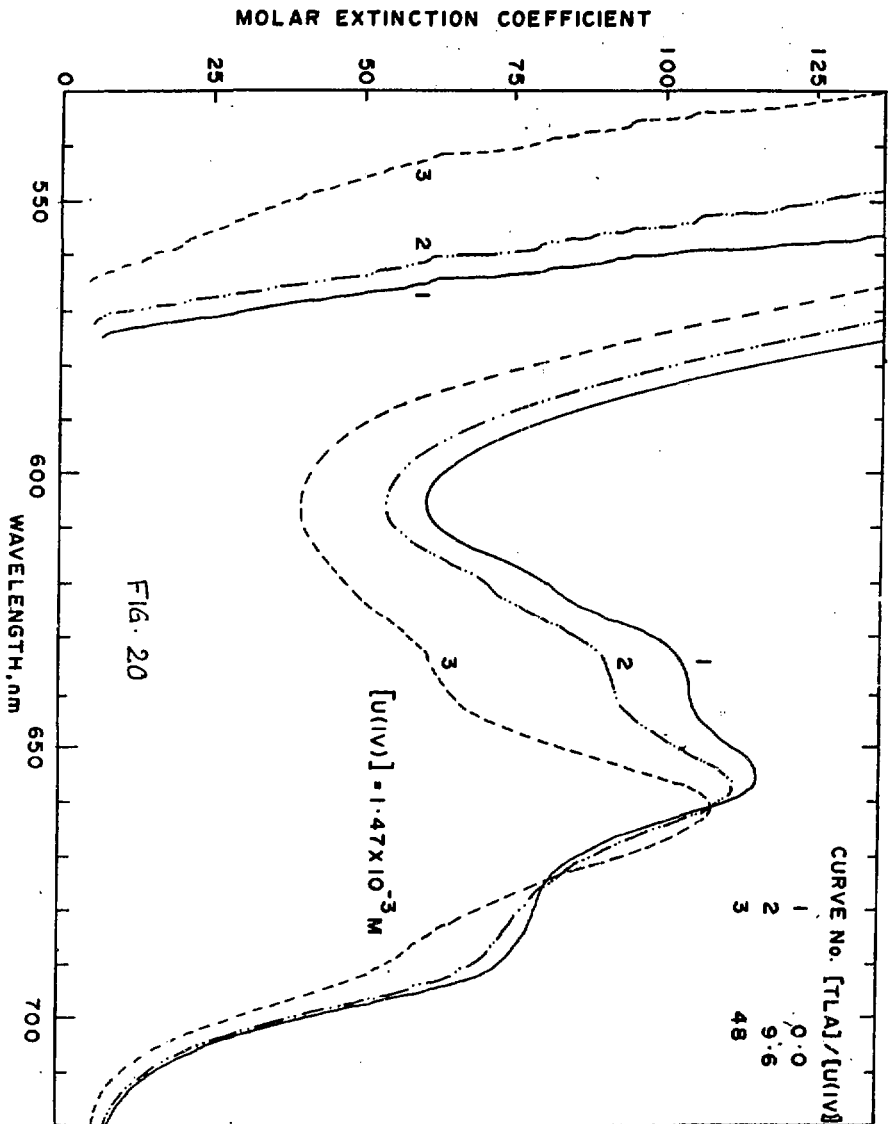
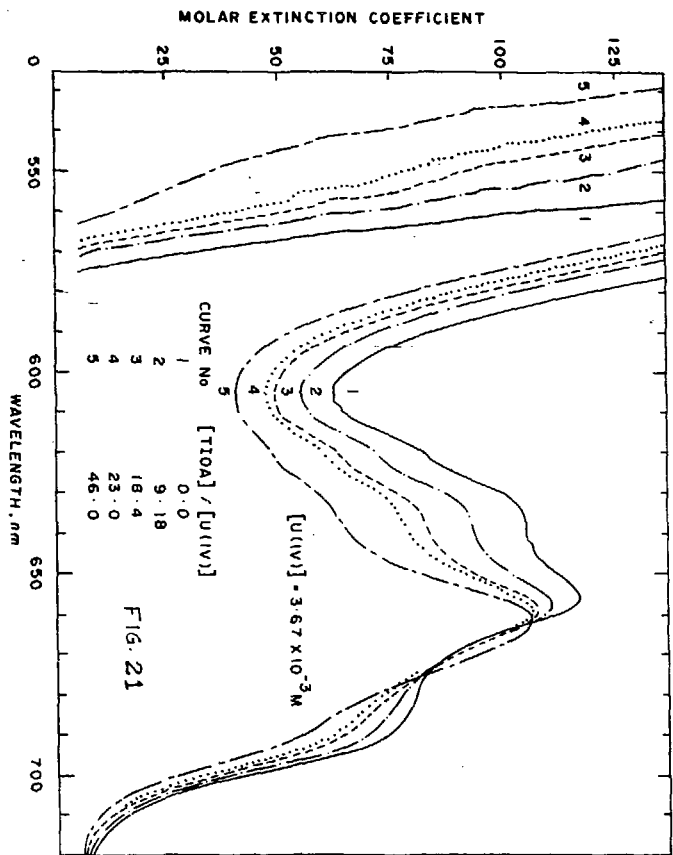
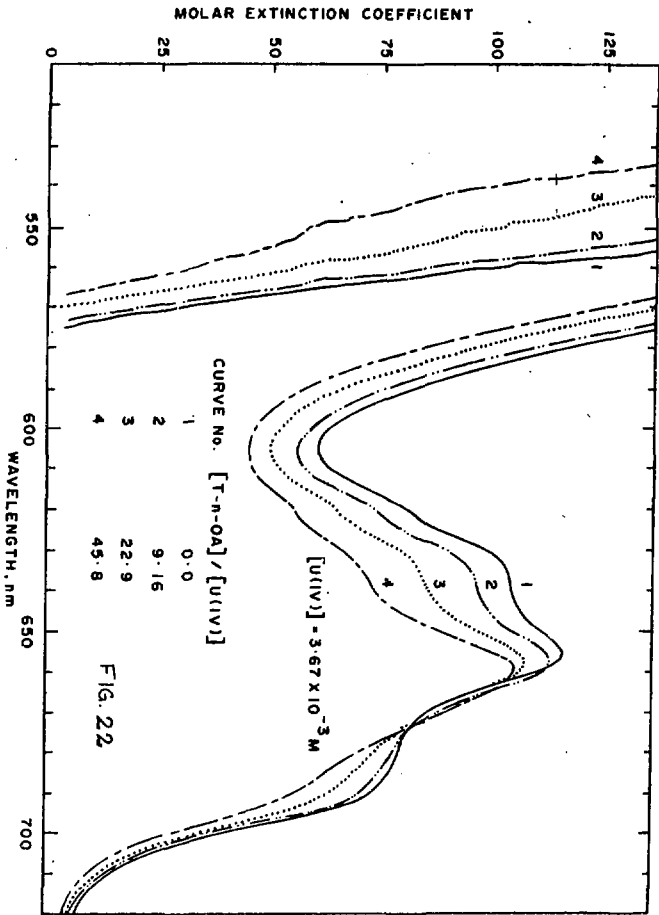
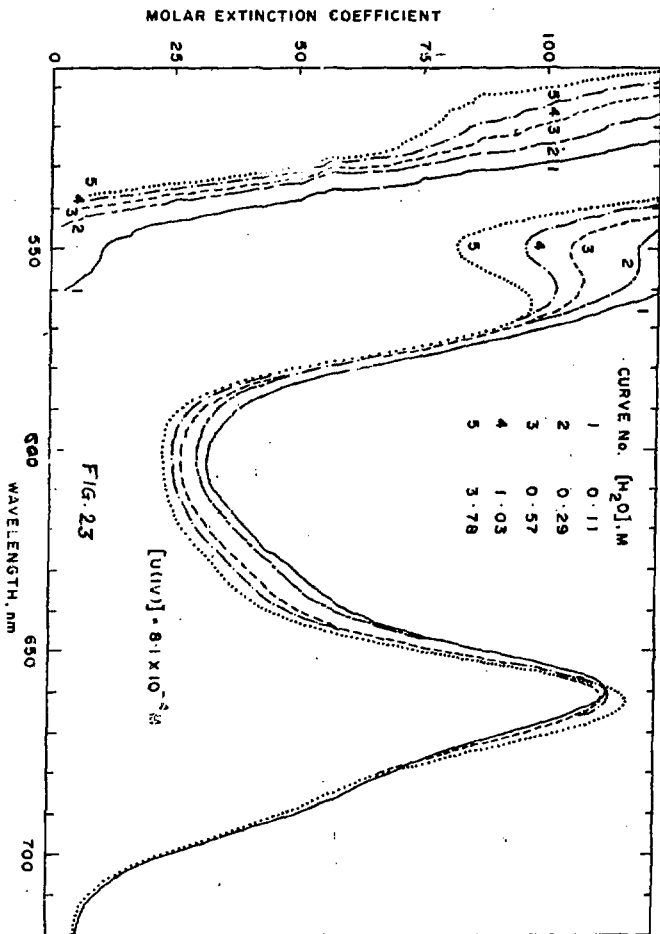


FIG. 19









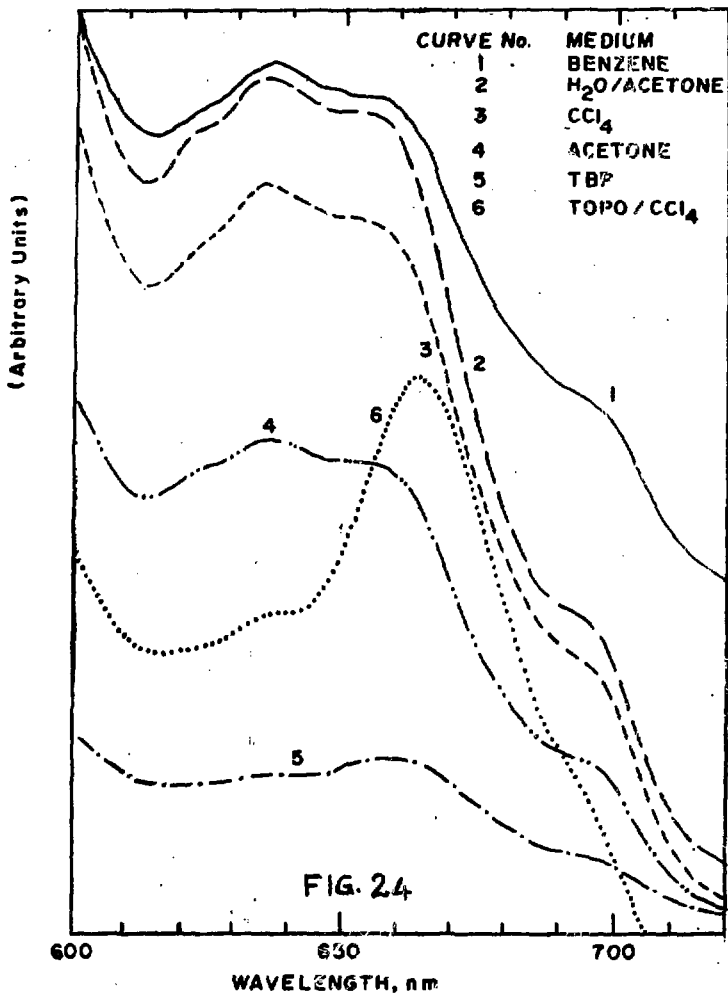


FIG. 24

