

## **Spectrophotometric Studies on the Chelate Formation between Uranium (VI) and 1 (o-Arsonophenylazo) 2 Naphthol 3:6 Disulphonate (Thoron) in Aqueous Solution**

By SATENDRA P. SANGAL and ARUN K. DEY

With 4 Figures

### **Abstract**

The composition and stability of the chelate formed between uranyl ion (II) and 1 (o-aronophenylazo) 2 naphthol 3:6 disulphonate (Thoron) have been investigated using spectrophotometric method. The chelate is red in colour and has  $\lambda_{\max}$  at 510 m $\mu$ . The composition as determined by different methods is 1:1. The chelate is stable between pH 2.5 and 5.0. The values of log K as determined by two different methods are  $4.2 \pm 0.25$  and  $4.54 \pm 0.15$  respectively at pH 3.0 and at 25°.

1 (o-aronophenylazo) 2 naphthol 3:6 disulphonate (Thoron) has extensively been used as a chelating agent in the determination of thorium<sup>1)</sup> and of many other metals<sup>2)</sup>. In spite of the large amount of work done on the chromogenic properties of this reagent, the composition and stability of metall chelates involving Thoron, have not received sufficient attention and no work appears to have been done on the uranium (VI) chelate.

### **Experimental**

#### **Materials**

A weighed amount of uranyl sulphate (B. D. H. ANALAR) was dissolved in doubly distilled carbondioxide free water to obtain a standard solution of uranium. A stock solution of Thoron was obtained by dissolving a known amount of reagent (B. D. H. ANALAR) in doubly distilled carbondioxide free water.

<sup>1)</sup> V. I. KUZNETSOV, Doklady Akad. Nauk S. S. R., **50**, 233 (1945).

<sup>2)</sup> L. P. ADOMOVICH and A. P. MIRNAYA, Sovremen Methody Analiza v Met Sbornik, 1955, 172-175; J. K. FOREMAN, C. J. RILEY and T. D. SMITH, Analyst, **82**, 89 (1957); G. W. C. MILNER, J. W. EDWARDS and A. PADDON, Atomic Energy Estab. (Gt. Brit.) AERE C/R **2612**, 6 pp. (1958); P. F. THOMASON, Anal. Chem., **28**, 1527 (1956).

### Instruments

Measurements of absorbance were carried out with a Unicam SP 500 Spectrophotometer, using matched glass cells (1 cm) supplied with the instrument. At wavelengths 625  $m\mu$  or below, the ultrasensitive phototube was used and above 625  $m\mu$ , the red sensitive phototube. The phototube circuit was kept at maximum sensitivity. All absorbance measurements were noted against distilled water blanks.

For measuring the hydrogen ion concentration a Leeds and Northrup direct reading pH indicator was used, which was standardized by buffer solution.

### Procedure

Three different methods viz. (i) method of continuous variations<sup>3)</sup> (ii) the mole ratio method<sup>4)</sup> (iii) and the slope ratio method<sup>5)</sup> were employed for establishing the composition of the chelate.

### Calculation of the stability constant

The stability constant was determined by the method of DEY and coworkers<sup>6)</sup> and further corroborated by the mole ratio method<sup>4)</sup>.

### Results and Discussions

#### Behaviour of the reagent as a colloidal electrolyte

As reported earlier<sup>7)</sup>, it was found that the reagent behaves as a colloidal electrolyte and therefore very dilute solutions of the order  $10^{-4}$  M were employed in these investigations, so that solutions may behave as true solutions.

#### Effect of time on the colour of the chelate

Colour formation was observed to be immediate and the absorbance values remained constant at least upto 75 hours. However, all mixtures were kept for two hours to obtain equilibrium.

#### Order of addition of reagent

No significant change was observed to occur when the order of the addition of reagent was altered. However, the reagent was added to the

<sup>3)</sup> P. JOB, *Compt. rend.*, **180**, 928 (1925); *Ann. Chim.*, (10) **9**, 113 (1928).

<sup>4)</sup> J. H. YOE, and A. L. JONES, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

<sup>5)</sup> A. E. HARVEY and D. L. MANNING, *J. Amer. Chem. Soc.*, **72**, 4488 (1950); **74**, 4744 (1952).

<sup>6)</sup> S. K. BANERJI and A. K. DEY, *Z. anorg. Chem.*, **309**, 226 (1961).

<sup>7)</sup> S. P. SANGAL and A. K. DEY, *J. Sci. Industr. Res.* **21B**, 600 (1962).

metallic solution, after the pH of the latter was adjusted to the proper value, in which case slightly better sensitivity was obtained.

### Nature of complexes formed

The method of VOSBURGH and COOPER<sup>8)</sup> was followed. Mixtures containing uranyl sulphate and Thoron in different stoichiometric ratios (0:1, 1:0.5, 1:1, 1:2, 1:3) were prepared and the absorbances measured. The observations show that the wavelength of maximum absorbance of Thoron lies at 485 m $\mu$ , whereas in the case of mixtures the  $\lambda_{\max}$  shifts to 510 m $\mu$ . Thus it is clear that only one chelate having  $\lambda_{\max}$  at 510 m $\mu$  is formed under the conditions of study.

### Stoichiometry of the components

The composition was established by the aforementioned methods at pH 3.0.  $c$  represents the concentration of uranyl sulphate and  $p$  the ratio  $c'/c$ ,  $c'$  being the concentration of Thoron.

A few observations are represented graphically in fig. 1.

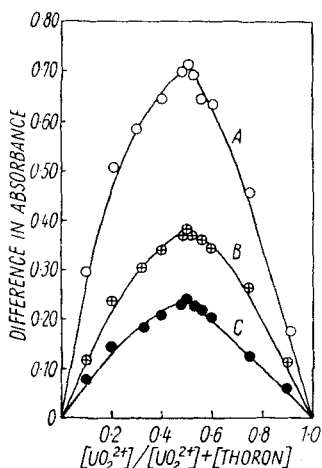


Fig. 1. Determination of the composition from the absorption spectra studies of equimolecular solutions, at pH 3.0 at 540 m $\mu$ , p 1.  
Curve A  $c$   $4.00 \cdot 10^{-4}$  M  
Curve B  $c$   $2.00 \cdot 10^{-4}$  M  
Curve C  $c$   $1.33 \cdot 10^{-4}$  M

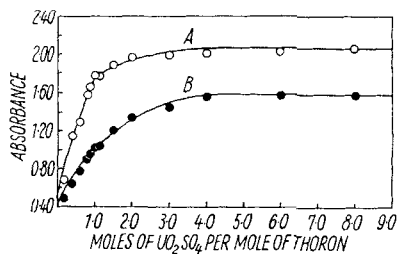


Fig. 2. Determination of the composition from the absorption spectra studies using mole ratio method at 540 m $\mu$  pH  $3.0 \pm 0.2$ , Concentration of Thoron  
A  $2.50 \cdot 10^{-4}$  M B  $1.67 \cdot 10^{-4}$  M

<sup>8)</sup> W. C. VOSBURGH, and G. R. COOPER, J. Amer. Chem. Soc., **63**, 437 (1941); **64**, 1630 (1942).

Table 1  
Composition of the chelate from the continuous variations method  
Total volume 50 ml

Experiment	Curve	$c \cdot 10^{-4}$ (M)	p	$\lambda$ ( $m\mu$ )	Peak occurs at volume of $UO_2SO_4$ ml.	Composition of the chelate $UO_2SO_4$ : Thoron
I	A	4.00	1.00	540	25.00	1:1
	B	2.00	1.00	540	25.00	1:1
	C	1.34	1.00	540	25.00	1:1
Ia*	A	4.00	1.00	550	25.00	1:1
	B	2.00	1.00	550	25.00	1:1
	C	1.34	1.00	550	25.00	1:1
Ib*	A	1.00	2.00	540	33.33	1:1
	B	2.00	0.50	540	16.67	1:1
Ic*	A	1.00	2.00	550	33.33	1:1
	B	2.00	0.50	550	16.67	1:1

\* Figures omitted to economise space.

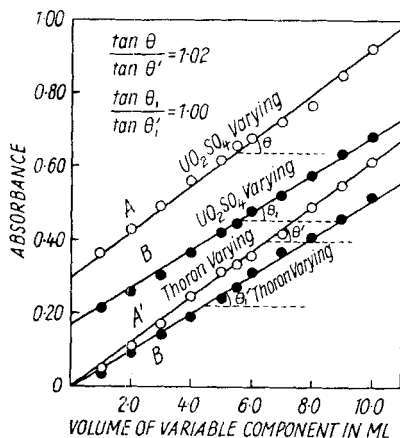


Fig. 3. Determination of the composition from absorption spectra studies using slope ratio method. pH  $3.0 \pm 0.2$ . Concentration of excess component  $5.0 \cdot 10^{-4}$  M  
A 540  $m\mu$ . B 550  $m\mu$ .

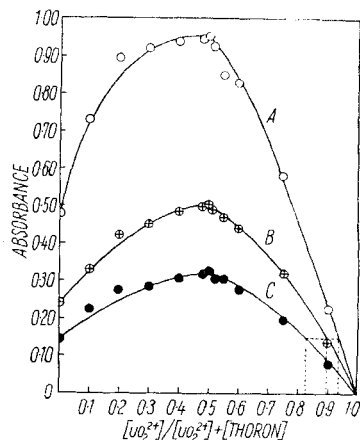


Fig. 4. Determination of stability constant from absorption data at 540  $m\mu$ . Concentrations and pH as in fig. 1

The results of the continuous variations method show that the composition of the chelate is  $UO_2$  (Thoron). This composition is further confirmed by the mole ratio method (fig. 2) and slope ratio method (fig. 3).

### Effect of hydrogen ion concentration on the stability of the chelate

The absorbance of various mixtures containing uranyl sulphate and Thoron in the ratio 1:1 at different pH were measured at various wavelengths and it was found that the  $\lambda_{\max}$  of the chelate which is  $510 \text{ m}\mu$  holds good from pH 2.5 to 5.0, indicating that the chelate is stable within this pH range. The maximum colour intensity of the chelate at its  $\lambda_{\max}$  remains constant between pH 2.5 and 4.0.

### Calculation of stability constant

The table below summarises the values of log K at pH  $3.0 \pm 0.2$  as determined by two different methods (fig. 2 and 4).

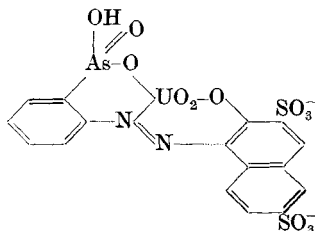
Table II  
Stability constant of the chelate

Method employed	pH	log K	$\Delta G$ at 25° (K. CALS)
Method of DEY et al	3.0	$4.25 \pm 0.2$	$-5.9 \pm 0.3$
Mole ratio method	3.0	$4.54 \pm 0.15$	$-6.3 \pm 0.2$

It may be seen that the results obtained by both the methods are in close conformity with each other.

### Suggestions on the structure of the chelate

It is well known<sup>9)</sup> that the donor properties of the azo group are weak, but azo compounds which contain a strong donor group in a position ortho to the azo group form very stable chelate rings. In Thoron there are the hydroxy group and an arsonic group in ortho position to the azo group, which makes it suited as a chelating agent. Both these groups are capable of linking the metal ion by the removal of a proton. Thus the following structure is suggested for the metal chelates of Thoron:



<sup>9)</sup> J. C. BAILAR, Jr., Chemistry of Coordination Compounds, Reinhold, New York (1956), pp. 74; 754-760.

As the chelate has been studied at pH 3.0 the sulphonic acid groups are not ionised. Thus the chelate would be neutral. This is confirmed by passing the chelate through columns of ion exchange resins; neither H (IR 45) nor OH (IR 120) varieties of Amberlite adsorbed the chelate.

The authors are thankful to the Council of Scientific and Industrial Research, India for supporting the work and for awarding a Fellowship to one of them (S. P. S.)

Allahabad (India), Chemical Laboratories, University of Allahabad.

Bei der Redaktion eingegangen am 6. September 1962.

---

Verantwortlich

für die Schriftleitung: Prof. Dr.-Ing. Dr. h. c. E. Leibnitz, Leipzig O 5, Permoserstraße 15; für den Anzeigenteil: DEWAG-Werbung Leipzig, Leipzig C 1, Friedrich-Ebert-Str. 110, Ruf 7851. Z. Z. gilt Anzeigenpreisliste 4; Verlag Johann Ambrosius Barth, Leipzig C 1, Salomonstraße 18 B; Fernruf 27681 und 27682. Veröffentlicht unter der Lizenz-Nr. 1395 des Presseamtes beim Vorsitzenden des Ministerrates der DDR

Printed in Germany



Druck: Paul Dünnhaupt, Köthen (IV/5/1) L 95/63