The 1:1 Thorium—Nitroso R Salt Chelate

By Satendra P. Sangal

With 5 Figures

Abstract

The composition and stability of the chelate formed between thorium (IV) and Nitroso R Salt has been investigated in detail using three different methods. Nitroso R Salt forms a 1:1 yellow coloured chelate with thorium having λ_{max} at 380 mμ at pH 3.5. The chelate is stable between pH 3.0 and 6.0. The values of stability constant (log K) as determined by two methods are 4.45 and 4.51 at 25°.

1-nitroso 2-naphthol 3,6-disulphonic acid has extensively been used as a colorimetric reagent for the determination of cobalt, but the work on other metal chelates of this reagent seems to have not obtained much attention. Seth and Dey[1]) studied the composition of Cu-NRS chelate and found the ratio of copper to Nitroso R Salt to be 1 : 1. Sangal and Dey[2]) observed that a 2 : 3 chelate is formed between palladium(II) and Nitroso R Salt. During our studies on the metal chelates of this reagent Thorium (IV) was observed to give a yellow colour chelate. This paper records our observations on the composition and stability of the Th-NRS chelate.

Experimental

1. Instruments

Absorbance measurements. For measuring the absorbance of the solutions a Unicam SP 500 spectrophotometer was employed using 1 cm. thick matched glass cell supplied along the instrument.

pH measurements. For measuring the pH of the solutions a Leeds and Northrup direct reading pH indicator operated on 220 V/50 cycles a. c. mains was used. Glass calomel electrodes system used was supplied by the same manufacturer.

[1]) R. L. Seth, Doctoral thesis, University of Allahabad 1962.

[2]) S. P. Sangal and A. K. Dey, J. Ind. Chem. Soc., Communicated.

2. Materials

Solution of thorium chloride. Thorium chloride (BDH Anal R) was dissolved in double distilled carbondioxide free water and standardized gravimetrically as oxide. Solutions of different concentration were obtained by suitable dilution.

Solution of Nitroso R Salt. A stock solution of standard Nitroso R salt was prepared by dissolving a BDH sample in double distilled carbon-dioxide free water.

Procedure. Three different methods viz. (i) the method of continuous variations[3]) (ii) the mole ratio method[4]) and the (iii) slope ratio method[5]) were used for determining the composition of the chelate.

For the calculations of stability constants the method of DEY and coworkers[6]) and the mole ratio method[4]) was employed.

Results and Discussion

1. Behaviour of the reagent as a colloidal electrolyte

The reagent has been observed to behave as a colloidal electrolyte[7]) and, therefore, very dilute solutions were employed in these investigations, as it has been emphasised by DEY[8]) that in case of colloidal solutions the characteristics of a true solution are often displayed when extremely dilute solutions are used.

2. Effect of time on the colour of the chelate

The colour formation was observed to be instantaneous and the absorbance values remains constant at least upto 72 hours. However, all the mixtures were kept for an hour to attain equilibrium.

3. Nature of complexes formed

Mixtures containing thorium chloride and Nitroso R Salt were prepared in the ratios 0 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 3 and 1 : 4 and their absorbances measured. The results show that the λ_{max} of the reagent lies at 365 mμ and that of the mixtures at 385 mμ. This shows that only one complex is formed having λ_{max} at 385 mμ under the condition of study (VOSBURGH and COOPERS[9]).

[3]) P. JOB, Compt. rend. **180**, 928 (1925); Ann. Chim. **9**, 113 (1928).

[4]) J. H. YOE and A. L. JONES, Ind. Eng. Chem., Anal. Ed. **16**, 111 (1944).

[5]) A. E. HARVEY and D. L. MANNING, J. Amer. chem. Soc. **72**, 4488 (1950); **74**, 4744 (1952).

[6]) A. K. MUKHERJI and A. K. DEY, J. Inorg. Nucl. Chem. **6**, 314 (1958); Anal. Chim. Acta, **18**, 324 (1958).

[7]) R. L. SETH, Doctoral thesis University of Allahabad 1962.

[8]) A. K. DEY, J. Colloid Sci. **3**, 473 (1948).

[9]) W. C. VOSBURGH and G. R. COOPER, J. Amer. chem. Soc. **63**, 437 (1941); **64**, 1030 (1942).

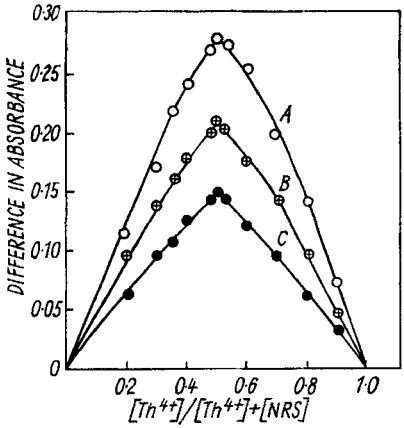

Fig. 1. Composition of the chelate using absorbance measurements by the method of continuous variations at 400 mμ and pH 3.5, p = 1.
Curve A Concn. of $ThCl_4$ $5.0 \cdot 10^{-4}$ M
Curve B Concn. of $ThCl_4$ $3.3 \cdot 10^{-4}$ M
Curve C Concn. of $ThCl_4$ $2.5 \cdot 10^{-4}$ M

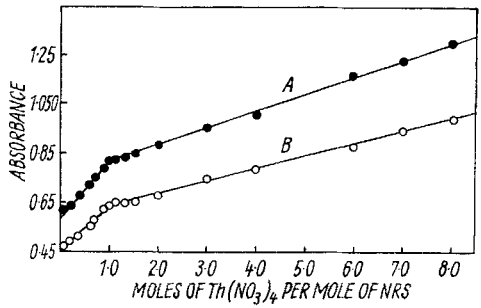

Fig. 2. Composition of the chelate using absorbance measurements by the mole ratio method at 400 mμ, pH 3.5 ± 0.2.
Curve A Concn. of NRS $1.33 \cdot 10^{-4}$ M
Curve B Concn. of NRS $1.00 \cdot 10^{-4}$ M

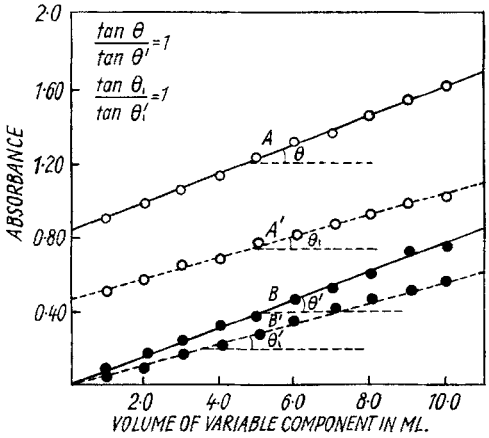

Fig. 3. Composition of the chelate using absorbance measurements by the slope ratio method at pH 3.5 ± 0.2.
AA' $ThCl_4$ varying, BB' NRS varying, solid line 400 mμ, Broken line 420 mμ.
(10 ml. $(1.00 \cdot 10^{-3}$ M) of excess component + x ml. $(3.33 \cdot 10^{-4}$ M) variable component + (15-x) ml. water

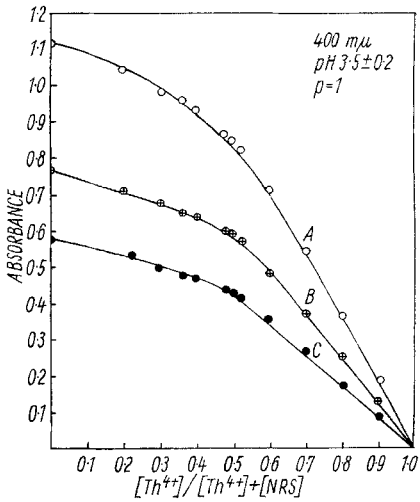

Fig. 4. Calculation of stability constant by from the absorption data, Concn. acid. pH as in fig. 1

4. Stoichiometry of components

The composition of the chelate was studied at pH 3.5 using aforementioned methods. The summary of the results obtained by the the method of continuous variations is recorded in Table 1 (c represents the concentration of thorium chloride, p the ratio c′/c, c′ being the concentration of the Nitroso R Salt). Few of the observations are graphically plotted in Fig. 1.

The results of the continuous variations method indicates that the composition of the chelate is Th(NRS). This is further corroborated by the mole ratio method (Fig. 2) and the slope ratio method (Fig. 3).

Table 1
Composition of the Th-NRS chelate from the method of continuous variations (Total volume 25 ml)

Experiment	Curve	$c \cdot 10^{-4}$ (M)	p	λ (mμ)	Vol. of $ThCl_4$ at peak (ml)	Composition of the chelate Th : NRS
I	A	5.00	1.00	400	12.50	1 : 1
	B	3.33	1.00	400	12.50	1 : 1
	C	2.50	1.00	400	12.50	1 : 1
Ia*)	A	5.00	1.00	420	12.50	1 : 1
	B	3.33	1.00	420	12.50	1 : 1
	C	2.50	1.00	420	12.50	1 : 1
Ib*)	A	3.33	1.50	400	15.00	1 : 1
	B	5.00	0.67	400	10.00	1 : 1
Ic*)	A	3.33	1.50	420	15.00	1 : 1
	B	5.00	0.67	420	10.00	1 : 1

*) Figures omitted to economise space. NRS Nitroso R Salt.

5. Effect of pH on the stability of the chelate

The absorbances of various solutions of thorium chloride and Nitroso R Salt in the ratio of 1 : 1 were measured at different pH. The results show that

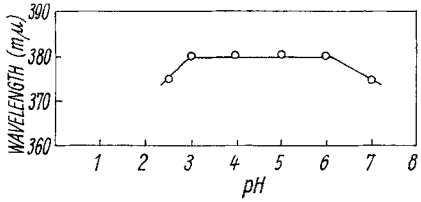

Fig. 5. Variation of λ_{max} with pH,
c $2.5 \cdot 10^{-4}$M, p = 1

the region of maximum absorbance of the chelate which is 380 mμ holds between pH range 3.0 and 6.0 showing that the chelate is stable within this range of pH (Fig. 5).

6. Calculation of stability constant (log K)

Stability constants have been determined using the method of DEY et al. (Fig. 4). and the mole ratio method (Fig. 2). The results are recorded in Table 2.

Table 2
Stability constants of Thorium—Nitroso R Salt chelate

Method used	pH	log K at 25°	ΔG in (K. Cals) at 25°
Method of DEY et al.	3.5	4.45 ± 0.1	-6.2 ± 0.2
Mole ratio method	3.5	4.51 ± 0.2	-6.3 ± 0.2

The author is thankful to the Council of Scientific and Industrial Research for an award of a fellowship. The author is further grateful to Dr. A. K. DEY for his valuable suggestions.

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

Bei der Redaktion eingegangen am 11. Juni 1963.

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 18B; 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 25/64