

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Spectrophotometric Investigations on Uranium(VI) N-(Thiobenzoyl)-N-phenylhydroxylamine Complexes

Bharat Kumar Sharma<sup>a</sup>; S. P. Mathur<sup>a</sup>; S. P. Dubey<sup>b</sup>

<sup>a</sup> Research Laboratories, Government College, Beawar, India <sup>b</sup> Department of Chemistry, Delhi College of Engineering, Delhi, India

**To cite this Article** Sharma, Bharat Kumar , Mathur, S. P. and Dubey, S. P.(1984) 'Spectrophotometric Investigations on Uranium(VI) N-(Thiobenzoyl)-N-phenylhydroxylamine Complexes', Journal of Macromolecular Science, Part A, 21: 4, 427 – 430

**To link to this Article:** DOI: 10.1080/00222338408056558

**URL:** <http://dx.doi.org/10.1080/00222338408056558>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **Spectrophotometric Investigations on Uranium(VI) N-(Thiobenzoyl)-N-phenylhydroxylamine Complexes**

BHARAT KUMAR SHARMA and S. P. MATHUR

Research Laboratories  
Government College  
Beawar 305901, India

S. P. DUBEY

Department of Chemistry  
Delhi College of Engineering,  
Delhi 110007, India

### ABSTRACT

Uranium(VI) forms an intense yellow-colored complex with N-(thiobenzoyl)-N-phenylhydroxylamine. The complex has maximum absorbance at 410 nm at pH 5.1-5.7. Beer's law is valid up to 29.4 ppm of uranium(VI). The molar absorptivity is  $1.87 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ . The effects of diverse ions, stability constants, and the structure of the complex are discussed.

### INTRODUCTION

Complexation reactions of thiols and other sulfur-containing ligands have recently been investigated because of their biological applications [1-5]. A study of the literature reveals that very little work has been carried out on the chelating behavior of thiohydroxamic acids in solution [6-8]. The present investigations are aimed at determining the

composition and stability of uranium(VI) complexes with N-(thio-benzoyl)-N-phenylhydroxylamine (TBPHA). TBPHA reacts with uranyl ion to give an intense yellow color.

## EXPERIMENTAL

TBPHA was prepared by the thionation of N-benzoyl-N-phenylhydroxylamine with phosphorous pentasulfide [9]. The purity of the compound was checked by elemental analysis, TLC, and IR spectroscopy.

The solution of uranium(VI) was prepared by dissolving uranyl nitrate (AR) in ethanol. The metal content was determined by the gravimetric method [10].

All chemicals used were of Analar grade.

Instruments. A Beckmann model DU spectrophotometer was used for all spectrophotometric measurements. All pH measurements were made with a Cambridge bench-type pH meter.

## RESULTS AND DISCUSSION

Spectral Characteristics of Complex. Absorption spectra were recorded by mixing the reagent with the solution of reagent in the ratios 1:1, 1:2, and 1:3 against the reagent blank prepared under identical conditions. The maximum absorbance was found at around 395-410 nm. All absorption measurements were taken against a reagent blank at 410 nm.

The pH of the system was maintained in the limit 5.1-5.7 because there was no change in the absorbance in this range. It was observed that there was no change in absorbance at room temperature (30°C). The color so formed remained stable up to 70°C. After 70°C the color faded slowly. The color intensity was not affected by 20 h at room temperature.

Beer's law is valid up to 29.4 ppm of uranium(VI), and Ringbom's method [11] was employed for evaluating the optimum concentration range for the effective photometric determination of uranium. The optimum range is 13.4-22.8 ppm. The molar absorptivity of the complex as calculated from Beer's law is  $1.87 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ .

Effect of Diverse Ions. The tolerance to diverse ions was studied for the uranium(VI)-TBPHA system.  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{Mg}(\text{II})$ ,  $\text{Ni}(\text{II})$ ,  $\text{Cu}(\text{II})$ , and  $\text{Co}(\text{II})$  do not interfere with the estimation, while  $\text{F}^-$ , citrate, tartrate, and titanium ions interfere seriously.

Composition of Complex. Stability constants and the stepwise formation constants  $\log K_1$  and  $\log K_2$  of uranium(VI) complexes  $\text{ML}_1$  and  $\text{ML}_2$ , respectively were calculated from graphical extrapolation methods of Leden [12] and Yatsimirskii [13]. The values of  $\log K_1$ .

TABLE 1. Stepwise Stability Constants of Uranium Complexes at  $30 \pm 0.5^\circ\text{C}$ 

Method	For 1:2 (metal:ligand) complex		
	log $K_1$	log $K_2$	log $\beta$
Leden [12]	6.29	5.16	11.45
Yatsimirskii-Fedorova [13]	6.38	5.24	11.62
Harvey-Manning [14]	-	-	11.53

and log  $K_2$  obtained by the above two methods are in agreement with the values obtained by the Harvey-Manning method [14]. The results are given in Table 1.

The composition of the complex was established by the continuous method of Job [15], the slope ratio method, and the mole ratio method [16].

The complexation between this reagent (TBPHA) and uranium(VI) is attributed to the presence of the thioketo and oxime groups. Assuming that the oxime hydrogen is replaced by the uranyl ion which coordinates through the thioketo sulfur with the fact that the mole ratio between uranium(VI) and ligand is 1:2, it has been assumed that absorbance corresponds mainly to a mononuclear colored complex species of uranium(VI). However, the stability data alone cannot definitely decide the nature of the bonding and the structure of the complex.

#### ACKNOWLEDGMENTS

The authors are grateful to the University Grants Commission of India for financial assistance. Thanks are also due to the Head of the Department of Chemistry, University of Rajasthan, Jaipur, and the Principal, Government College, Beawar.

#### REFERENCES

- [1] S. P. Mathur, R. S. Thakur, C. S. Bhandari, and N. C. Sogani, *Talanta*, **25**, 592 (1978).
- [2] S. P. Mathur, R. S. Thakur, C. S. Bhandari, and N. C. Sogani, *An. Quim.*, **74**, 673 (1978).
- [3] S. P. Mathur and M. R. Bhandari, *Chem. Ind. (Britain)*, **17**, 745 (1975).
- [4] S. P. Mathur, *Rev. Latinoam Quim.*, **7**, 141 (1976).

- [5] G. R. Clark, J. Inorg. Nucl. Chem., **25**, 353 (1963).
- [6] S. P. Mathur and C. S. Bhandari, Rec. Trav. Chim. Pays-Bas, **100**, 49 (1981).
- [7] S. P. Mathur and C. S. Bhandari, J. Macromol. Sci.-Chem., **A15**(4), 609 (1981).
- [8] R. S. Thakur, S. P. Mathur, and B. K. Sharma, Rec. Trav. Chim. Pays-Bas, **101**, 359 (1982).
- [9] Y. K. Egwa, Y. Ito Umino, and T. Okuda, J. Antibiot., **24**, 124 (1971).
- [10] A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd ed., Longmans, p. 540.
- [11] A. Ringbom, Z. Anal. Chem., **115**, 332 (1938).
- [12] L. Leden, Phys. Chem., **188**, 160 (1941).
- [13] K. B. Yatsimirskii and T. L. Fedorova, Zh. Neorg. Khim., **1**, 2310 (1956).
- [14] A. E. Harvey and D. L. Manning, J. Am. Chem. Soc., **74**, 4744 (1952).
- [15] P. Job, Ann. Chem., **9**, 113 (1928).
- [16] J. H. Yoe and A. L. Jones, Ind. Eng. Chem., Anal. Ed., **16**, 111 (1944).

Accepted by editor June 30, 1983

Received for publication July 30, 1983