

This article was downloaded by:

On: 25 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 Investigation of Vanadium (V)-N-Pyridylaminothioformyl-N'-phenylhydroxylamine

S. P. Mathur^a; R. S. Thakur^a; C. S. Bhandari^a; N. C. Sogani^a

^a Department of Chemistry, University of Rajasthan, Jaipur, India

To cite this Article Mathur, S. P. , Thakur, R. S. , Bhandari, C. S. and Sogani, N. C.(1979) 'Spectrophotometric Investigation of Vanadium (V)-N-Pyridylaminothioformyl-N'-phenylhydroxylamine', Journal of Macromolecular Science, Part A, 13: 8, 1171 – 1173

To link to this Article: DOI: 10.1080/00222337908056708

URL: <http://dx.doi.org/10.1080/00222337908056708>

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 Investigation of Vanadium (V)-N-Pyridylaminothioformyl-N'-phenylhydroxylamine

S. P. MATHUR, R. S. THAKUR, C. S. BHANDARI, and N. C. SOGANI*

Department of Chemistry
University of Rajasthan
Jaipur, India

ABSTRACT

The pink complexes of vanadium (V) and N-pyridylaminothioformyl-N'-phenylhydroxylamine are extractable into chloroform. Spectrophotometric studies show that the 1:2 complex predominates in the acidity range of 2.5-6 N HCl. The values of the stability constants, stepwise and overall, have been calculated following extended Yatsimirskii, Leden and Harvey-Manning methods.

INTRODUCTION

The analytical applications of N-substituted amino thioformyl-N'-phenylhydroxylamines are well documented [1-4]. The present communication deals with the spectrophotometric investigation of vanadium (V) complexes of N-pyridylaminothioformyl-N'-phenylhydroxylamine (PAFPH). The study has established the existence of a 1:2 (metal:ligand) complex depending on the pH.

*Deceased.

EXPERIMENTAL

Materials

The reagent was prepared following the method of Bhandari [5]. A standard vanadium solution was prepared by dissolving ammonium vanadate in warm ammonia and then diluting to known volume with distilled water. The vanadium content of the solution was determined by complexometric titration with ethylenediaminetetraacetic acid, **Erichrome Black T** being used as indicator. A standard solution of strength $(0.60 \times 10^{-3}$ mole/liter) was prepared by appropriate dilution of the stock solution containing 1.0 mg/ml vanadium.

Standard reagent solutions of desired strength in alcohol-free spectral grade chloroform were used and stored in an amber bottle.

Other chemicals and solvents used in all spectrophotometric measurements were of spectrograde quality.

A Beckman Model DU quartz spectrophotometer was used for the measurements of absorbance, and a Cambridge bench type pH meter for pH measurements.

Procedure

An aliquot of vanadium (V) solution (0.60×10^{-3} mole/liter) was taken in a 100 ml separatory funnel and the acid concentration in aqueous phase adjusted to 5 N HCl. Different amounts of equimolar reagent solution in chloroform were added in such a way that total volume of nonaqueous phase was 1:1 and mixture was then shaken for 10 min to reach equilibrium. The pink colored chloroform layer was allowed to settle, separated, and dried over anhydrous sodium sulfate. The combined extract after drying over sodium sulfate was diluted to 25 ml with chloroform. The complex shows an absorption maximum at 480 nm when measured against a solvent blank.

The vanadium complex is extractable into chloroform from 2.5 to 6 N HCl- with no appreciable change in sensitivity value. The molar absorptivity is $(2.6 \pm 0.02) \times 10^3$ /mole-cm as calculated from Beer's law.

RESULTS AND DISCUSSION

The stepwise formation constants K_1 and K_2 of vanadium complexes ML_1 and ML_2 , respectively, were calculated from graphical extrapolation method of Leden's [6] and Yatsmirskii's [7] methods. Several suitable subsidiary functions were constructed and the appropriate

TABLE 1. Stepwise Formation Constants for the Vanadium (V)-N-Pyridylaminothioformyl-N'-phenylhydroxylamine (1:2 composition) Complex at $30 \pm 1^\circ\text{C}$

Method	$\log K_1$	$\log K_2$	$\log K_1K_2$
Leden [6]	5.32	5.24	10.56
Yatsmirskii [7]	5.16	5.83	10.99
Harvey and Manning [8]	—	—	10.18

limiting values at zero ligand concentrations were utilized to arrive at the result. It is assumed that the absorbance corresponds mainly to a mononuclear colored complex species of vanadium. From the established composition 1:2 (metal:ligand), the free ligand concentration for each solution was calculated from Beer's law data. The values of $\log K_1K_2$ obtained by the above two methods are in agreement to the values obtained by Harvey-Manning's [8] method. The values are given in Table 1.

ACKNOWLEDGMENT

Thanks are due to Prof. J. N. Gaur, Head of Department of Chemistry, University of Rajasthan, Jaipur, India for providing the facilities, and to University Grants Commission of India for the award of teachers fellowship to two of us (S. P. M. and R. S. T.).

REFERENCES

- [1] S. P. Mathur and M. R. Bhandari, *Chem. Ind.* 1975, No. 13, 572
- [2] S. P. Mathur and M. R. Bhandari, *Indian J. Tech.*, **14**, 359 (1976).
- [3] S. P. Mathur and M. R. Bhandari, *Chem. Ind.* 1975, No. 17, 745.
- [4] S. P. Mathur and M. R. Bhandari, *J. Inst. Chemists*, **47**, 227 (1975).
- [5] M. R. Bhandari, Ph. D. Thesis, Rajasthan University, India, 1965.
- [6] I. Leden, *Z. Physik. Chem.*, **188**, 160 (1941).
- [7] K. B. Yatsmirskii and T. I. Fedorova, *Zh. Neorg. Khim.*, **1**, 2310 (1956).
- [8] A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, **74**, 4744 (1952).

Accepted by editor January 30, 1979

Received for publication February 20, 1979