Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Spectrophotometric Studies of V(V) Complexes of N-Methylaminothioformyl-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.(1978) 'Spectrophotometric Studies of V(V) Complexes of N-Methylaminothioformyl-N'-phenylhydroxylamine', Journal of Macromolecular Science, Part A, 12: 7, 1065 — 1068

To link to this Article: DOI: 10.1080/00222337808069404

URL: http://dx.doi.org/10.1080/00222337808069404

J. MACROMOL. SCI.–CHEM., A12(7), pp. 1065-1068 (1978)

Spectrophotometric Studies of V(V) Complexes of N-Methylaminothioformyl-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 violet-colored complexes of V(V) and N-methylaminothioformyl-N'-phenylhydroxylamine are extractable into chloroform. The spectrophotometric studies have shown that 1:3 and 1:4 (metal:ligand) complexes predominate in the acidity range 6.5-9 N and 9.5-10.5 N HCl, respectively. The values of stability constants, stepwise and overall, have been calculated by following extended Leden and Yatsimirskii methods. The analytical suitability of the reagent for the microdetermination of vanadium has also been investigated.

INTRODUCTION

The analytical usefulness of N-methylaminothioformyl-N'-phenylhydroxylamine has been studied extensively [1-4]. The present communication deals with the spectrophotometric investigation of V(V) complexes of N-methylaminothioformyl-N'-phenylhydroxylamine (MTFPH) at different acidities. The study has established the existence of 1:3 and 1:4 (metal:ligand) complexes, depending on the pH.

The analytical suitability of the reagent for microdetermination of vanadium has also been investigated.

EXPERIMENTAL

Materials

The reagent MTFPH was prepared by the method of Mathur [5]. A standard solution of vanadium (V) was prepared by dissolving the requisite amount of ammonium metavanadate in distilled water and standardizing. All chemicals used were of reagent grade. A Beckman Model DU quartz spectrophotometer was used for the measurement of absorbance and a Cambridge bench type pH meter of pH measurements.

Procedure

An aliquot of vanadium solution (6.328×10^{-5} M) was taken in a 100-ml separatory funnel and its pH adjusted to the desired value. The reagent solution (0.060 $\underline{M}$) in chloroform was then added, and the mixture shaken thoroughly for 20 min. The violet-colored nonaqueous layer was collected in a small beaker. The extraction was repeated with 6-ml portions of chloroform. The combined extract was diluted to 25 ml with chloroform and its absorption was measured at 365 and 380 nm.

RESULTS AND DISCUSSION

Due to the low reagent absorption around 365-380 nm, all the absorption measurements were taken against the reagent blank at 380 nm with 9.5 $\underline{N}$ HCl. Extraction with 8 ml of reagent was adequate for quantitative extraction with 9.5 $\underline{N}$ HCl. Measurements of absorbance of different sets of complementary solutions at 365 and 380 nm show that 1:3 and 1:4 (metal:ligand) complexes predominate in the acidity ranges of 6.5-9 $\underline{N}$ and 9.5-10.5 $\underline{N}$ HCl, respectively. The system obeys Beer's law over the concentration range 1-15 ppm with 9.5 $\underline{N}$ HCl. The optimum concentration ranges, evaluated from Ringbom's curves, were found to be 3-12 ppm at 9.5 $\underline{N}$ HCl. The molar absorptivity of the complexes, calculated from Beer's law at 9.5 $\underline{N}$ HCl (380 nm) is ($1.8 \pm 0.03 \times 10^3$/mole-cm). The sensitivity according the Sandell is 0.028 μg with 9.5 $\underline{N}$ HCl.

TABLE 1. Stepwise Stability Constants of Vanadium Complexes at 25 ± 1°C

Complex type	Stepwise stability constant	Method	
		Leden	Yatsimirskii
1:3 metal:ligand	log K_1	2.62	2.52
	log K_2	2.21	2.36
	log K_3	2.74	2.98
	log β_3	7.57	7.86
1:4 metal:ligand	log K_1	3.15	3.54
	log K_2	2.76	2.82
	log K_3	2.43	2.34
	log K_4	2.12	2.11
	log β_4	10.46	10.81

Moderate amounts of ions commonly associated with vanadium did not interfere with the estimation. Hg(II), Cu(II), Ni(II), and U(VI), however interfere in the estimation. The reagent can therefore be used for micro determination of vanadium. Following Yatsimirskii's method, stepwise formation constants (K_1, K_2, K_3, and K_4) of 1:4 system were evaluated with the help of computer. The four formation constant values obtained by the methods of Leden [6] and Yatsimirskii [7] are in very good agreement. The stepwise stability values as given in Table 1 shows the order $K_1 > K_2 > K_3 > K_4$. The overall stability constant is very low, indicating the possibility for the ligand to act as a unidentate one. However, the stability data alone cannot definitely decide the nature of bonding and structure of the complex.

ACKNOWLEDGMENT

Thanks are due to Prof. J. N. Gaur, Head of Chemistry Department, University of Rajasthan, Jaipur, India for the facilities provided and the University Grants Commission of India for the award of financial assistance.

REFERENCES

[1] S. P. Mathur and M. R. Bhandari, Chem. Ind. 1975, No. 13, 572.

[2] S. P. Mathur and M. R. Bhandari, Chem. Ind. 1975, No. 17, 745.
[3] S. P. Mathur and M. R. Bhandari, Indian J. Technol., 14, 359 (1976).
[4] S. P. Mathur and M. R. Bhandari, J. Inst. Chemists, 47, 227 (1975).
[5] S. P. Mathur, Bangladesh J. Sci. Ind. Res., 11, 144 (1976).
[6] I. Leden, Z. Physik. Chem., 188, 160 (1941).
[7] K. B. Yatsimirskii and T. I. Fedorova, Zhur. Neorg. Khim., 1, 2310 (1956).

Accepted by editor January 15, 1978
Received for publication April 14, 1978