Spectrophotometric Investigation of Ti(IV) Complex of N-Pyridyl-N' β-naphthylthiourea

V. P. Mehta[a]; C. S. Bhandari[b]; S. P. Mathur[b]

[a] Research Laboratories, Government College, Beawar, India [b] Department of Chemistry, University of Rajasthan, Jaipur, India

PLEASE SCROLL DOWN FOR ARTICLE

Spectrophotometric Investigation of Ti(IV) Complex of N-Pyridyl-N '-β-naphthylthiourea

S. P. MATHUR and V. P. MEHTA

Research Laboratories
Government College
Beawar, India

C. S. BHANDARI

Department of Chemistry
University of Rajasthan
Jaipur, India

ABSTRACT

The intense yellow colored complexes of Ti(IV) and N-pyridyl-N'-β-naphthylthiourea are extractable into isoamyl alcohol. The spectrophotometric studies following Job's and molar ratio methods have shown that 1:2 and 1:3 (metal:ligand) complexes predominate in the acidity ranges of 2.5-6 and 7-9.5 $\underline{N}$ HCl, respectively. The values of the stability constants, stepwise and overall, have been calculated following extended Leden's, Yatsimirskii's, and Harvey-Manning's methods. The analytical suitability of the reagent for microdetermination of titanium has also been investigated.

INTRODUCTION

The applications of pyridyl-substituted thioureas are well documented [1-4]. The present paper deals with the spectrophotometric

377

investigation of Ti(IV) complexes of N-pyridyl-N'-β-naphthylthiourea (PNT) at different acidities. The study has established the existence of 1:2 and 1:3 (metal:ligand) complexes depending on the pH. The analytical suitability of the reagent for the microdetermination of titanium is explored in the light of the above observations.

EXPERIMENTAL

The reagent PNT was prepared following the method of Mathur [2]. A stock solution of titanium (1.96 mg/mL) was prepared from potassium titanyl oxalate (A.R.) and was standardized [5]. All chemicals used were of reagent grade. A Beckmann 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 titanium solution (7.634×10^{-5} M) was taken in a 100 mL separatory funnel having its pH adjusted to the desired value. The reagent solution (0.074 M) in isoamyl alcohol was then added and the mixture shaken thoroughly for 15 min. The intense yellow colored nonaqueous layer was collected in a small beaker. The extraction was repeated with 5 mL portions of isoamyl alcohol. The combined extract was diluted to 25 mL with isoamyl alcohol and its absorption was measured at 375 and 390 nm.

RESULTS AND DISCUSSION

Due to the low reagent absorption around 375-390 nm, all the absorption measurements were taken against the reagent blank at 390 nm with 7 N HCl. Extraction with 7 mL of reagent was adequate for quantitative extraction with 7 N HCl. Measurements of absorbance of different sets of complementary solutions (both Job's and molar ratio methods) at 375 and 390 nm show that 1:2 and 1:3 (metal: ligand) complexes predominate in the acidity ranges of 2.5-6 and 7-9.5 N HCl, respectively. The systems obey Beer's law over the concentration range 1-12 ppm with 7 N HCl. The optimum concentration ranges, evaluated from Ringbom's curves, were found to be 4-10 ppm at 7 N HCl. The molar absorptivity of the complexes, calculated from Beer's law at 7 N (390 nm) is $(2.3 \bullet 0.04) \times 10^3/\text{mol}^{-1} \text{ cm}^{-1}$. The sensitivity according to Sandell is 0.034 μg with 7 N HCl.

Moderate amounts of ions commonly associated with titanium did *not interfere* with the estimation. Ni(II), Cu(II), Fe(III), and U(VI), however, interfere in the estimation. The reagent can therefore be used for the microdetermination of titanium following Yatsimirskii's

TABLE 1. Stepwise Stability Constants of Titanium Complexes at 30 ± 1°C

| Method | For 1:2 (metal:ligand) | | | For 1:3 | | | |
	$Log K_1$	$Log K_2$	$Log \beta_2$	$Log K_1$	$Log K_2$	$Log K_3$	$Log \beta_3$
Leden's [6]	2.13	3.47	6.60	2.56	2.21	2.89	7.66
Yatsimirskii's [7]	3.04	3.93	6.97	2.66	2.11	3.43	8.20
Harvey-Manning's [8]	-	-	6.74	-	-	-	7.96

method. Stepwise formation constants K_1, K_2, and K_3) of 1:3 system were evaluated after solving a fourth degree polynomial equation in K_2, and the results are given in Table 1.

ACKNOWLEDGMENTS

REFERENCES

[1] S. P. Mathur and M. R. Bhandari, Rev. Latinoam. Quim., 6, 160 (1975).
[2] S. P. Mathur, J. Inst. Chem., In Press.
[3] S. P. Mathur, Ibid., 47, 173 (1975).
[4] S. P. Mathur, Ibid., 47, 60 (1975).
[5] A. I. Vogel, Quantitative Inorganic Analysis, 3rd ed., Longmans, Green, London, 1960, p. 790.
[6] I. Leden, Z. Phys. Chem., 188, 160 (1941).
[7] K. B. Yatsimirskii 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).