The ratio of log K_1/log K_2 is positive and that the separation factor between the first and the second formation constant is well within the range. A bigger difference between log K_1 and log K_2 is due to the possible steric hindrance on the linking of the second ligand molecule expected for Tl(I) ion.

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SPECTROPHOTOMETRIC INVESTIGATION OF Ti(IV) COMPLEXES OF N-SALICYL PHENYL HYDROXYLAMINE

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ABSTRACT

Yellow coloured complexes of Ti(IV) and N-salicyl phenyl hydroxylamine 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 N and 7·5–9 N HCl respectively. The values of the stability constants, stepwise and overall, have been calculated following extended Yatsimirskii's, Leden's and Harvey-Manning's methods. An electronic computer, IBM 1130, using FORTRAN Programming was utilized for evaluating stability constants of 1 : 3 system. The analytical suitability of the reagent for microdetermination of titanium has also been investigated.

INTRODUCTION

THE application of the aryl hydroxamic acids and their N-phenyl analogues are well documented[1-5]. But in many cases[6,7], investigations were carried out to study the complexes with the variation of acidity. The present paper deals with the spectrophotometric investigation of Ti(IV) complexes of N-salicyl phenyl hydroxylamine (NSPHA) at varied acidities. The study has established the existence of 1 : 2 and 1 : 3 (metal : ligand) complexes depending on the pH. The stepwise and overall formation constants are evaluated by extended Yatsimirskii's[8], Leden's[9] and Harvey-Manning's[10] method. The analytical suitability of the reagent for microdetermination of titanium is explored in the light of above observations.

MATERIALS

A stock solution of titanium (2·18 mg/ml) was prepared from potassium titanyl oxalate (A.R.) and was standardised[11]. The reagent, NSPHA (m.p. 106–107° C), was prepared following the method of Shome[12]. Chemicals used in all spectrophotometric measurements were of A.R. or spectrograde quality. A Hilger Uvispek spectrophotometer was used for spectrophotometric measurements. For evaluation of the formation constants, a IBM 1130 scientific and electronic computer based on FORTRAN Programming was employed.

EXPERIMENTAL

An aliquot of titanium solution ($8·352 \times 10^{-5}$ M) was taken in a 100 ml separatory funnel and its pH adjusted to the desired value. The reagent solution (0·087 M) in isoamyl alcohol was then added and the mixture shaken thoroughly for 10 minutes. The yellow coloured nonaqueous layer was collected in a small beaker. The extraction was repeated with a 5 ml portions of isoamyl alcohol. The combined extract, after drying over sodium sulphate, was diluted to 25 ml with isoamyl alcohol and its absorption was measured at 390 and 400 nm.

RESULTS AND DISCUSSION

The absorbance measurements of the complex solution at 8 N HCl show maximum absorbance at 370 nm. Due to low reagent absorption around 390–400 nm, all the absorption measurements were taken against the reagent blank at

TABLE I

Stepwise stability constants of titanium complexes at 27 $\pm$ 2° C

Method	For 1 : 2 (Metal : Ligand)			For 1 : 3			
	log K_1	log K_2	log β_2	log K_1	log K_2	log K_3	log β_3
Yatsimirskii's	2·29	2·43	4·72	2·15	1·49	3·05	6·69
Leden's	1·28	2·89	4·17	2·13	2·04	3·17	7·34
Harvey-Manning's	..	..	4·34	..	..	..	7·57

400 nm with 8 N HCl. Extraction with 6 ml of reagent was adequate for quantitative extraction with 8 N HCl. Measurements of absorbance of different sets of complementary solutions (both Job's and molar ratio methods) at 390 and 400 nm show that 1 : 2 and 1 : 3 (metal : ligand) complexes predominate in the acidity ranges of 2–5 N and 7·5–9 N HCl respectively. The systems obeyed Beer's law over the concentration ranges 1–15 ppm with 8 N HCl. The optimum concentration ranges, evaluated from Ringbom's curves, were found to be 5–14 ppm at 8 N HCl. The relative analysis error per one per cent absolute photometric error, following Ayre's equation, was found to be of the order of 2·72. The molar absorptivity of the complexes, calculated from Beer's law data at 8 N (400 nm), is (1·9 $\pm$ 0·02) $\times$ 10^3 l.mole^{-1} cm^{-1}. The sensitivity, according to Sandell, is 0·021 μg with 8 N HCl.

Moderate amounts of ions, commonly associated with titanium, did not interfere with the estimation. Fe(III), V(V), Cr(VI), Mo(VI) and U(VI) however interfere in the estimation. The reagent can therefore be used for microdetermination 'of titanium.

The stepwise formation constants of 1 : 2 and 1 : 3 systems were determined in the manner stated earlier[1,3]. Following Yatsimirskii's 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 by a scientific and electronic computer (IBM 1130) using FORTRAN Programming and the results are given in Table I.

In the light of the data given in Table I, the formula of 1 : 2 complex may be represented as [TiOR$_2$] where HR stands for NSPHA.

The higher value of K_3 for the 1 : 3 complex may be due to the formation of internally hydrogen bonded 1 : 3 chelate system.

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