

Complex Formation between Cobalt and Thiosalicylic Acid

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With 5 Figures

Abstract

Cobalt (II) forms a deep-brown colour with thiosalicylic acid (hereafter abbreviated as TSA). Spectrophotometric studies show that cobalt and TSA are present in the ratio of 1:3 at a pH range, 3–11.5. The value of stability constant (log K) of the complex ion, as calculated spectrophotometrically, comes out to be 11.76 at pH 5.5 and 30°C. Potentiometric studies reveal the formation of two complex species, where cobalt and TSA are present in the ratio of 1:1 and 1:3 respectively. Magnetic susceptibility measurements on the complex ion (in solution) mixing cobalt and TSA in the ratio of 1:3 at pH 6.5, gave a value of 2.3 B.M., indicating the presence of one unpaired electron. From the above data, a tentative structure of the complex ion has been proposed.

There is little quantitative information on complex formation between thiosalicylic acid and transition metals, although a number of workers have used it as a ligand for complexation with Hg²⁺)³⁾ (II), Pb⁴⁺)⁵⁾ ⁶⁾ (II) and Ni⁷⁾)⁸⁾ (II). Its antimony⁹⁾)¹⁰⁾ ¹²⁾ and arsenic¹²⁾)¹³⁾ compounds have found use in medicine. This has also been used for the quantitative estimation of zirco-

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mium¹⁴) and thorium¹⁵). TANAKA and YOKOYAMA¹⁶)¹⁷) used various derivatives of thiosalicylic acid to study their complex formation with cobalt and other transition metals.

The present communication deals with the detailed studies of cobalt-thiosalicylic acid complexes by spectrophotometric, potentiometric and magnetic susceptibility measurements. It is found that the acid and the metal are present in the ratio of 1:1 and 1:3, the brown deep coloured complex ions are soluble in 40% alcoholic medium and are not extractable in any common solvent.

Reagents and Apparatus

Stock solution of cobalt (II) was prepared from $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, an AnalaR grade reagent in double distilled water and was standardised by using 8-hydroxyquinoline¹⁸). Thiosalicylic acid used was an EVAN'S Chemetics product of 99.7% purity. Fresh solution of thiosalicylic acid was prepared in alcohol whenever needed by direct weighing. Sodium hydroxide, hydrochloric acid and sodium acetate, used for adjusting pH values, were also of AnalaR grade. Absorbance measurements were made on a Unicam S.P. 600 spectrophotometer, using quartz cells of 1 cm. The pH measurements were made with the help of BECKMAN'S pH meter, model 112, fitted with an all purpose glass electrode.

Experimental

Absorption spectra of cobalt-TSA complex in 40% alcoholic medium (by mixing cobalt and TSA in different ratios) at different wave-lengths shows that there is only one absorption maxima at 440 m μ . The absorbance due to cobalt sulphate is negligibly small at this wave-length and also the absorbance due to ligand is negligible at wave-length higher than 410 m μ . Therefore the readings were taken against water-alcohol (40% Alcohol) as a blank, and the necessary corrections were made in absorbance plots due to the absorbance of ligand (if any) by measuring its absorbance against water-alcohol as a blank.

Effect of pH

When solutions having cobalt (having final conc. M/1250) and ligand in the ratio of 1:10 were prepared at different pH values, no appreciable coloration was observed below pH 6, but on increasing the pH of the solution, a deep-brown coloured complex was formed which was stabilized within two minutes and the absorbance of the complex ion was almost same from pH, 6.2–7.0, and above pH 7, the absorbance decreases slightly but remains appreciable even at pH values more than 11.5. But once the colour is developed at pH 6.0, it remains stable even upto 2.5, pH and below this pH value the complex starts precipitating.

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Stoichiometry of the complex

JOB's method of continuous variation¹⁹⁾ was used for a number of sets, having pH range, 3–7.5 and at a wide range of wave-length 380–700 m μ . The pH of all the sets of solution was brought up to about 6.0 by adding sodium acetate and when the colour was

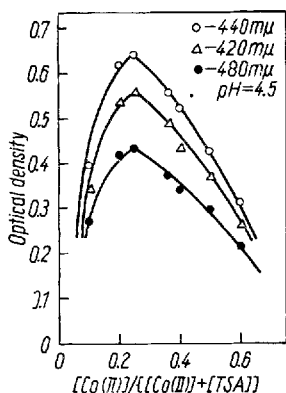


Fig. 1. Composition by JOB's method. Initial concentration of the reactants = M/500. Total volume = 12.5 ml.

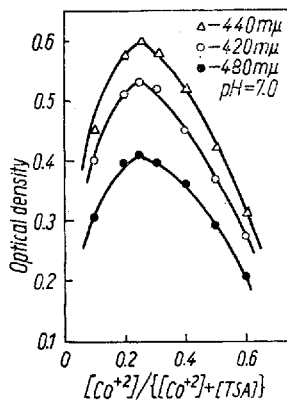


Fig. 2. Same as in Fig. 1

fully developed, it was brought down by adding dilute hydrochloric acid to the required value (sodium acetate was used in order to avoid any chance of cobalt hydroxide formation at high pH values, in those solutions where metal was in excess than the ligand, though

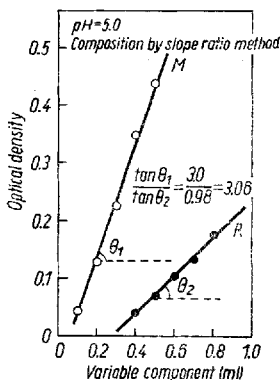


Fig. 3. Initial concentration of the reactants = M/500. Volume of the fixed component = 5.0 ml. Total volume = 12.5 ml. Wave length = 440 m μ .

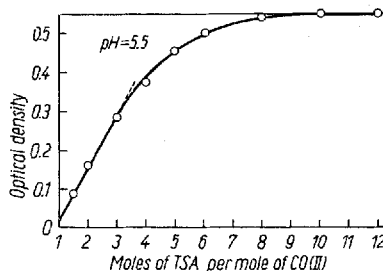


Fig. 4. Initial concentration of the reactants = M/500. Volume of Co²⁺ in each solution = 1.0 ml. Total volume = 25 ml, wavelength = 440 m μ .

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the results were essentially the same by using sodium hydroxide as well). Some of the typical observations are plotted in Fig. 1 and 2, clearly indicating that cobalt and the ligand are in the ratio of 1:3. This has also been confirmed by using slope ratio method²⁰) (Fig. 3) and mole-ratio method (Fig. 4). The stability²¹) constant ($\log K$), calculated by using mole-ratio²²) method (Fig. 4) comes out to be 11.76 at pH 5.5 and at 30°C. The corresponding free energy of formation $\Delta F^\circ = 13.35$ Kcals. at 30°C. A 40% alcoholic medium was maintained throughout the observations.

Potentiometric Studies

The plots between pH values and the volume of sodium hydroxide on the titrations of medium (50% alcoholic), ligand, and a mixture of ligand and metal against sodium hydroxide (50% alcoholic) are shown in Fig. 5. The first inflexion (C) occurs where metal and the ligand are in the ratio of 1:1, while the inflexion (C') corresponds where cobalt and TSA are in the ratio of 1:3. The method could not be used for calculating stability constant as the curve shows two inflexions corresponding to two different complex species.

Magnetic susceptibility of the complex was measured in solution, by mixing cobalt and TSA in the ratio of 1:3 at pH 6.5 and 29.5°C in 40% alcoholic medium by Gouy's method. The complex ion was found to be paramagnetic giving a spin-only value of 2.3 B.M. at 29.5°C.

Discussions

The spectrophotometric measurements reveal that a cobalt and TSA are present in the ratio of 1:3, but potentiometric studies show the existence of another complex (1:1) as well. The efforts to detect the lower complex, spectrophotometry did not bear fruit. The magnetic susceptibility measurements gave a value of 2.3 B. M which shows that the complex is paramagnetic and spin-paired with one unpaired electron. Spin-paired complexes²³) of cobalt are either tetra co-ordinated square-planar ($3d4S4p^2$) having a relatively large orbital contribution ($\mu_{\text{eff}} = 2.2-2.9$ B. M) or are

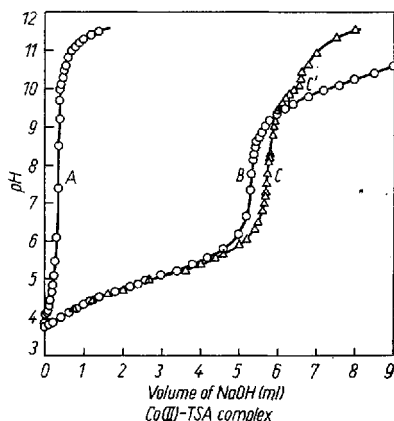


Fig. 5. Potentiometric titrations against M/10 sodium hydroxide.

- A = contains 2 ml. (M/25)
 NaClO_4 + 5 ml. (M/100) HClO_4
 B = contains 2 ml. (M/25)
 NaClO_4 + 5 ml. (M/100) HClO_4
 + 5 ml. (M/10) TSA
 C = contains 2 ml. (M/25)
 NaClO_4 + 5 ml. (M/100) HClO_4
 + 5 ml. (M/10) TSA
 + 5 ml. (M/100) Co^{2+}

Total volume in each case = 110 ml.,
 medium is 50% alcoholic

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hexacoordinated ($3d^24S4p^3$) having the magnetic moment of the order of 1.7–1.9 B. M. In the present case TSA appears to act as a bidentate ligand and hence 1:3; Co:TSA-complex is expected to be a hexacoordinated that should give the magnetic moment of 1.7 to 1.9 B. M, but potentiometric titrations reveal another complex of the stoichiometry 1:1, which should evidently be a square-planar ($\mu_{\text{eff}} = 2.2-2.9$ B. M). Perhaps the admixture of (1:1) square-planar complex with (1:3) octahedral complex might be responsible for the observed ($\mu_{\text{eff}} = 2.3$ B. M) value of the magnetic moment. Alternatively, reference to Fig. 5, would show that in the curve C, there are two inflexions one at C (corresponding to 1:1) and the other at C' (corresponding to 1:3). Crossing of the curves show that from some source electrons (OH^- ions) are being released which are consuming the protons (H^+ ions). This release of electrons can only be explained if we assume that at higher pH values (> 9.0), Co(II) is being at least partially oxidised to Co(III).

Electrolysis of 50% alcoholic solution of the higher complex (1:3) shows the migration of the brown coloured complex ion towards the positive electrode, showing an anionic character of the complex ion.

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