

Analytical Application of 2-Hydroxy-4-Isobutoxy Acetophenone Oxime for the Determination of Cobalt

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ABSTRACT

2-Hydroxy-4-isobutoxy acetophenone oxime(HIBAO) has been used for the spectrophotometric determination for Co(II) at pH range 6 to 10 in chloroform medium. Job's method for continuous variation, Yoe and Jones' mole ratio method, the slope ratio method show metal ligand ratio in complex to be 1:2. The stability constant of the complex is found to be 5.73×10^9 . The brown coloured complex obeys Beer's law in the concentration range 5.89 $\mu\text{g/ml}$ to 47.14 $\mu\text{g/ml}$ for Co(II) ion, while the optimum concentration range from Ringbom plot is found to be 11.79 to 41.25 ppm. The photometric sensitivity and molar absorptivity at the 600nm are found to be 0.055 $\mu\text{g/cm}^2$ and 1074 $\text{mol}^{-1}\text{cm}^{-1}$ respectively. The standard free energy of formation of complex is -13.52 kcal/mole at 30°C. The complex is stable for 48 hrs. The reagent has also been found to give quite satisfactory results for Co(II) present in alloy like brass, bronze and synthetic mixtures. The antimicrobial Activity of HIBAO and Co-HIBAO complex have also been checked.

Keywords : HIBAO, pH, Cobalt, Acetophenone Oxime, 2-Hydroxy-4-Isobutoxy

I. INTRODUCTION

Various o-hydroxy phenones, phenone oximes, phenyl hydrozones, chalknoneoximes, etc, have been used as an analytical reagent for the spectrophotometric and gravimetric determination of Cobalt and other transition metal ions 1-5. In the present work the use of 2-hydroxy-4-isobutoxy acetophenone oxime (HIBAO) as photometric reagent for Co(II) has been described.

II. METHODS AND MATERIAL

A 0.1M stock solution of Co(II) has been prepared by dissolving Cobalt chloride (A.R) in distilled water containing few drops of hydrochloric acid. The amount of Co(II) in this solution was determined following standard procedures⁶.

Preparation of 2-hydroxy-4-isobutoxy acetophenone oxime (HIBAO):

Resacetophenone was prepared from resorcinol by standard methods⁷. 2-hydroxy-4-isobutoxyacetophenone(HIBA) has been prepared by refluxing resacetophenone and isobutyl bromide in

suitable solvent for 4 hrs. 2-hydroxy-4-isobutoxyacetophenoneoxime(HIBAO)⁸ has been prepared by refluxing HIBA with hydroxyl amine hydrochloride in the presence of sodium acetate in ethanol medium for 4 hrs. The reagent when recrystallized from ethanol was obtained in the colourless, needle like crystals (m.p. $102^\circ\text{C} \pm 1^\circ\text{C}$), with M.W 223.40 (calcd. for $\text{C}_{12}\text{H}_{17}\text{NO}_3 = 223.27$). The reagent is insoluble in water but soluble in alcohol, acetone benzene chloroform, carbon tetrachloride, etc. The elemental analysis and spectral analysis of the compound confirm its structure.

Preparation of Co(II)-HIBAO complex and selection of solvent

When an alcoholic solution of HIBAO was added to 0.01 M aqueous metal ion solution, Brown precipitates of complex were obtained in the pH range 6.0 - 10.0. The complex was found to be insoluble in polar solvents like water, methanol or ethanol but soluble in non-polar solvents like chloroform, benzene, CCl_4 etc. As Co-HIBAO complex was more soluble in chloroform, it was selected as a solvent for extractive spectrophotometric determination of Co(II).

Apparatus : Spectrophotometric measurements were made with a Systronics UV/VIS spectrophotometer (model-118) using 10mm glass cells. All pH measurements were made with Systronic pH meter (model-324).

III. RESULTS AND DISCUSSION

Results are given in Fig. I-IV and Table I-II.

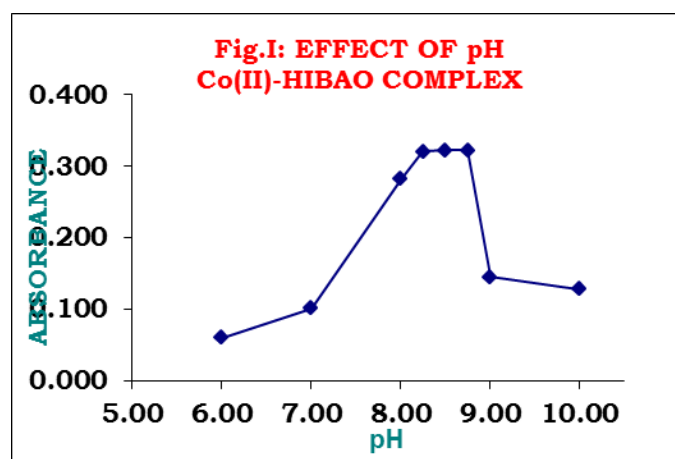


Figure I : Effect of pH

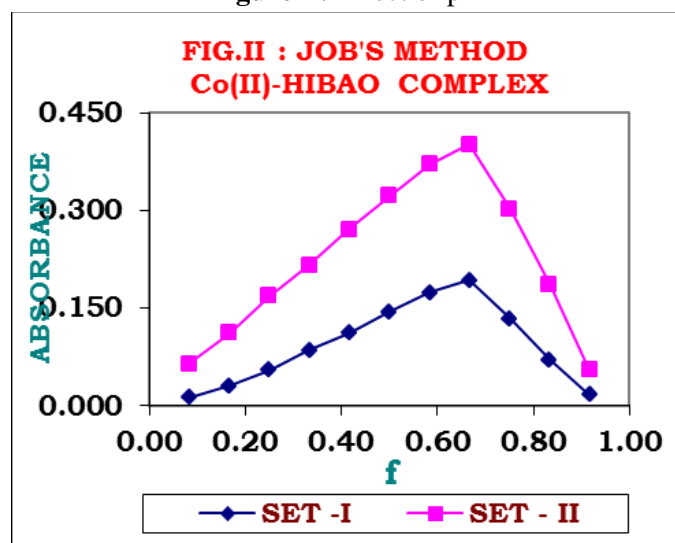


Figure II : Job's method of continuous variation

Set-I : 0.01 M Co(II) and 0.01 M HIBAO

Set-II : 0.02 M Co(II) and 0.02 M HIBAO

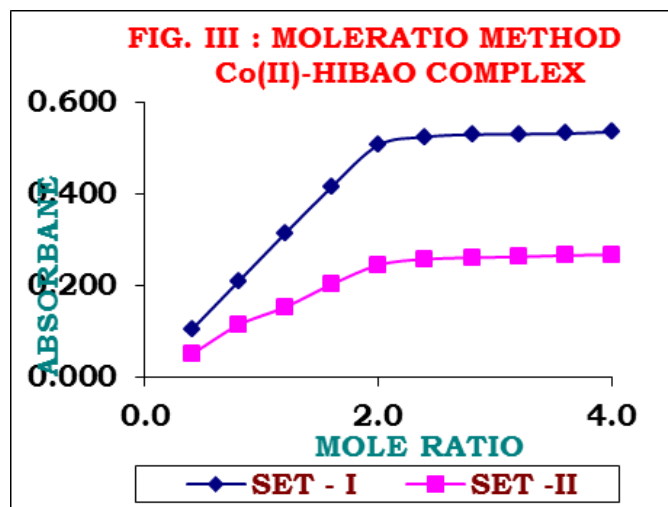


Figure III : Yoe and Jones mole ratio method

Set-I : 0.005M Co(II) and 0.010M HIBAO,

Set-II : 0.0025M Co(II) and 0.005M HIBAO

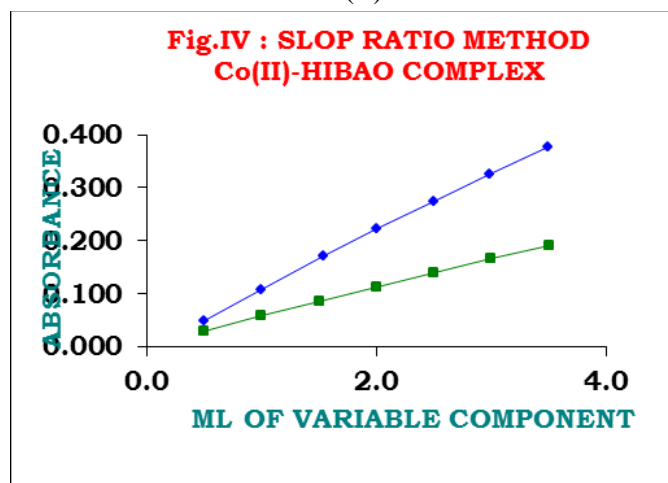


Figure IV : Slope ratio method.

10 ml 0.01 M HIBAO ; 0.01M Co(II) (variable)
10 ml 0.01 M Co(II) ; 0.01 M HIBAO (variable)

Table I: Stability Constant of Co(II) –HIBAO Complex at 30°C

Method employed	Em	Es	α	K (n=1)
Mole ratio method				
Set-I	0.535	0.507	0.05234	6.61×10^9
Set-II	0.268	0.245	0.08582	5.79×10^9
Job's Method				

Set-I	0.215	0.193	0.10233	5.24×10^9
Set-II	0.430	0.402	0.06512	5.29×10^9
Mean K Stab				5.73×10^9

Table II: Analysis of Cobalt in various samples

Sample	"Co" taken		Absorbance	"Co" found		Relative error(%)
	µg	%		µg	%	
Vitallium	345.0	63.89	0.632	346.5	64.50	0.96
			0.635	348.1		
			0.639	350.3		
			Avg.	348.3		
Synthetic mixture No. 1	117.9	-	0.193	105.8	-	1.07
			0.210	115.1		
			0.235	128.8		
			Avg.	116.6		
Synthetic mixture No. 2	235.7	-	0.415	227.5	-	0.77
			0.425	233.0		
			0.440	241.2		
			Avg.	233.9		
Synthetic mixture No. 3	176.8	-	0.328	179.0	-	0.74
			0.317	173.0		
			0.334	182.3		
			Avg.	178.1		

Optimum pH and Selection of Wavelength : The pH of the solution has pronounced effect on the reaction between Co(II) and HIBAO and the stability of the complex. On the other hand the absorbance is dependant upon the wavelength used. Both the parameters were therefore controlled to give maximum absorbance. Absorbance measurements of the reagent in chloroform show maxima at 282nm, 321nm and 322nm with negligible absorbance beyond 400nm. The absorbance measurements of Co(II)-HIBAO complex show a maxima at 400nm and 600nm. As the interference due to the reagent appeared to be negligible a wavelength of 600 nm was selected for the present work.

To determine the optimum pH for complex formation series of buffer solutions with pH values ranging from 3.0 to 10.0 were prepared. To above buffer solutions, 2.0 ml of 0.01 M Co(II) solution and 10 ml 0.01 HIBAO solution in chloroform were added. After shaking the mixture for two minutes, the brown coloured complex was extracted. The absorbance of organic layer containing complex was measured at 600nm against a

blank. From the results given in Fig. I, it may be generalized that maximum absorbance takes place at pH range 8.25 to 8.75. Hence a pH of 8.5 and wavelength of 600nm have been selected for the present work.

Reproducibility : Absorbance measurements of a set of ten solution prepared in a similar way and containing the same concentrations of all the reagents show that the reproducibility of measurements are quite good with a standard deviation of ± 0.452 Units, i.e., 0.19%.

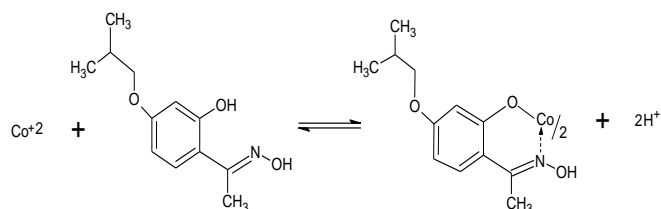
Effect of time and temperature : To determine the effect of time and temperature on the intensity of colour and the stability of the Co(II)- HIBAO complex, absorbance was measured at room temperature (30°C) at regular intervals of time up to 48 hrs and also at temperatures of 30°C to 55°C. The results show that complex is stable ($\pm 2\%$ deviation) for two weeks and up to 45°C.

Stoichiometry and Stability Constant of the Complex : The method of Vosbough and Cooper⁹ showed that one complex is formed. To determine the stoichiometry of complex, Yoe and Jones mole ratio method¹⁰ the slope ratio method¹¹ and Job's method of

continuous variation¹² were employed (Fig. II-IV). All the three methods show a 1:2 metal:ligand ratio in the complex.

The value of the stability constants calculated from the job's method as well as from the mole ratio method are given in Table-I. From the table the average value of stability constant may be taken as 5.73×10^9 . The standard free energy of formation of the complex, ΔG° , is -13.52 kcal/mole at 30°C.

The IR spectras of reagent and complex revealed that the -OH (stretch) band of 3393cm^{-1} for the reagent disappears when the complex is formed i.e., the complex formation takes place through the N of oximino group and O- of the 2-hydroxy group. Based on above data the Co(II)-HIBAO complex can be assigned the following structure.



Conformity to Beer's law and the optimum concentration range : Beer's law is obeyed between the range 5.89 to 47.14 ppm of Co(II). At higher concentrations negative deviations occur. The optimum concentration range for determination of Co(II) in solution, as deduced from the Ringbom plot¹³, is found to be 11.79.08 to 41.25 ppm. The molar absorptivity (ϵ) of the complex is $1074 \text{ mol}^{-1}\text{cm}^{-1}$ and the photometric sensitivity as per Sendell's definition¹⁴ is found to be $0.055\mu\text{g}/\text{cm}^2$ at 600nm.

Effect of diverse ions : The interference due to the presence of other ions on the determination Cobalt ions as Co(II)-HIBAO complex has also been studied. A difference of more than $\pm 2 \%$ in the absorbance value has been considered as interference. According to this criterion, the tolerance limits of various ions, expressed in μg , for a solution containing 117.86 μg (Co(II)) are as follows.

up to 100000 μg : Na+, K+, NH4+
 up to 10000 μg : Ca+2, Ba+2, Sr+2, Mg+2, Al+3,
 Zn+2, Cd+2, Citrate,
 tartrate, oxalate

up to 1000 μg : Ag+,Cr+3, UO2+2, Pd+2
 up to 100 μg : Vanadium, Cu+2, Mn+2, Fe+3
 up to 10 μg : EDTA

Determination of Cobalt from various samples : To determine the usefulness of the reagent in estimation of Cobalt from various samples containing Cobalt were taken and estimated by HIBAO. For this purpose, the alloy samples containing Cobalt metal were dissolved in 1:1 nitric acid by heating on a sand bath. The resulting solution was made up to 250 ml with distilled water in a volumetric flask. The synthetic mixtures containing Cobalt metal were also taken for analysis. Aliquot of this sample solution was pipeted out and its spectrophotometric determination was carried out by the proposed method. The result are given in Table-II.

Antimicrobial Activity :

HIBAO and Co-HIBAO were screened for their antibacterial activity against Gram positive bacteria i.e. *Bacillus subtilis* and Gram negative bacteria i.e. *Pseudomonas aeruginosa* using Cup-plate agar diffusion method. The Fungi *Aspergillus niger* was used for antifungal activity of above compound using Cup-plate agar diffusion method. HIBAO exhibit good antibacterial activity and excellent antifungal activity with respect to standard drugs while the Co-HIBAO complex found quit good antibacterial and Excellent antifungal activity.

IV. ACKNOWLEDGEMENTS

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V. REFERENCES

- [1]. T Talati, J.D and K.S.Parikh, "Anarta", J. North Gujarat Uni., 3, 93, (1992).
- [2]. Talati, J.D and K.S.Parikh, J. Inst. Chemists (INDIA), 65, 84, (1993).
- [3]. Talati, J.D and K.S.Parikh, Asin J. Chem., 6, (1994).
- [4]. J.A.dave and S.S.Shah,Asian J. Chem., 20, 4141,(2008).

- [5]. Suketu I. Desai, Vikas A. Desai and H.B.Niak, Asian J. Chem.,20,4919,(2008).
- [6]. A.I.Vogel, "A Text Book of Quantitative Inorganic Analysis", 4th Ed., (Longaman, London), 1978, p.379.
- [7]. Brewster, C.M. and J.C.Harris, J.Amer Chem Soc., 52, 4866 (1930).
- [8]. A.I.Vogel, "A Text Book of Practical Organic Chemistry, 3rd Ed., (Longaman, London), p. 341 (1966).
- [9]. W.C.Vosburgh and G.R.Cooper, J.Amer.Chem.Soc., 63, 473 (1941).
- [10]. J.H.Yoe and A.L.Jones, Ind.Eng.Chem., Anal. Ed., 16, 111 (1944).
- [11]. Harvey, A.E. and D.L.Manning, J.Amer.Chem.Soc., 72, 4488 (1950).
- [12]. P.Job, Ann. Chem., 9, 113 (1928).
- [13]. Ringbom, Anal. Chem., 115, 332 (1938).
- [14]. E.B.Sandell, "Colorimetric determination of traces of metals", 3rd Ed., (inderscience, New York), pp.83, (1959).