

SPECTROPHOTOMETRIC STUDY OF THE COMPLEXATION REACTION BETWEEN COBALT (II) AND 2-HYDROXY-4N-BUTOXY-5-BROMO ACETOPHENONE OXIME

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ABSTRACT

2-Hydroxy-4n-butoxy acetophenone (HBA) was earlier employed as an analytical reagent for the gravimetric, amperometric and spectrophotometric determination of various metal ions. Further study on its bromo substituted oxime shows that it forms a stable to give yellowish brown complex with Cobalt(II) and a detailed spectrophotometric study is carried out. This complex obeys Beer's law 14.73 $\mu\text{g/ml}$ to 117.86 $\mu\text{g/ml}$ of Co(II) in chloroform at 640 nm. The stability constant of the chelate is 4.45×10^8 . The molar absorptivity and Sendell's sensitivity are found to be $312 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.19 \mu\text{g cm}^{-2}$, respectively at 640 nm. The solid complex is isolated and its UV and IR spectra are studied.

Keywords: spectrophotometric, oxime, cobalt(II), stability constant, complex.

INTRODUCTION

A number of reagents¹⁻⁵ have been used for the spectrophotometric determination of cobalt. In the present work, we report the applicability of 2-Hydroxy-4n-butoxy-5-bromo acetophenone oxime (HBBAO) for spectrophotometric determination of Co(II). In slightly basic medium cobalt forms a yellowish brown complex, extractable into chloroform layer. Effect of pH, reagent concentration, diverse ions effect etc. on the extraction behaviour have been studied. The nature of the extracted species has also been studied.

EXPERIMENTAL

All reagents and chemicals of A.R. grade were used. 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).

Resacetophenone⁶ was prepared from resorcinol, gla. acetic acid and anhydrous zinc chloride. 2-hydroxy-4n-butoxy acetophenone (HBA) was prepared by reported method⁷. 2-hydroxy-4n-butoxy-5-bromo acetophenone (HBBA) was prepared by Bromination⁸ of HBA. The oxime of HBBA was prepared by sodium acetate method⁹⁻¹⁰. It was crystallised from ethanol, colourless needle like crystals were obtained, with m.p. of $68 \pm 1^\circ\text{C}$.

The standard solution of cobalt chloride was prepared in distilled water and standardised by known method¹¹. Standard solution of diverse ions were prepared from their chloride or sulphate or from alkali salts. Dilute HCl and/or NaOH were used to maintain different pH.

RESULTS AND DISCUSSION

Spectrophotometric Studies

It has been found that cobalt complex can be extracted into non-polar solvents like chloroform, benzene, carbon tetrachloride and toluene etc. The complex was better

extracted in chloroform and therefore, the subsequent studies may have been carried out in this medium.

Effect of pH

It has been found that the extraction Co(II) complex starts at pH 5.0 and the absorbance

was maximum and constant between pH 7.0-9.0. Hence, all the measurements were done at pH 8.0. The percentage extraction and Distribution Ratio (D) at various pH and at 640 nm are given in table-1.

Table 1: Percentage Extraction and Distribution Ratio at Various pH for Co(II)-HBBAO Complex

pH	A At 640 nm	% E	D
5.0	0.135	57.69	1.36
6.0	0.175	74.79	2.97
7.0	0.231	98.72	77.00
8.0	0.232	99.15	116.00
9.0	0.229	97.86	45.80
10.0	0.152	64.96	1.85
11.0	0.091	38.89	0.64

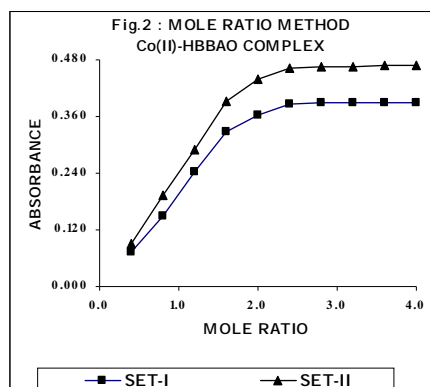
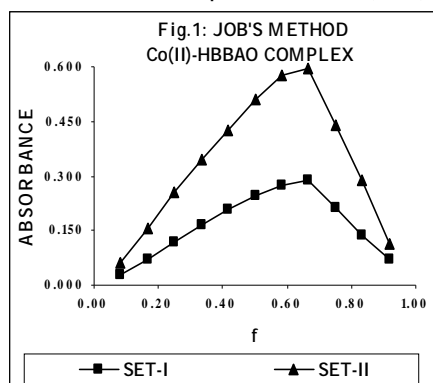
Table 2: Physico-chemical data of Co(II)-HB BAO

Characteristics	Results
Beer's law Limit (ppm)	14.73-117.86
Opt. Conc. Range (ppm)	44.20-117.86
Molar absorptivity, ϵ ($L \text{ mole}^{-1} \text{ cm}^{-1}$)	312
Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$)	0.190
Stability constant (K)	4.45×10^8
ΔG° (k.cal)	-12.00
M:L	1:2

Nature and Composition of the complex

The method of Vosburgh and Cooper's¹² shows that only one complex is formed. The composition of the complex as 1:2 (M:L)

was determined by Job's method of continuous variation¹³ (Fig.1), Yoe and Jones mole ratio method¹⁴ (Fig.2) and slope ratio method¹⁵.



Stability Constant of the Complex

The stability constant of the complex was calculated using the following conventional relationships:

$$\alpha = (E_m - E_s) / E_m \text{ and } K = (1 - \alpha) / 4C^2\alpha^3$$

The average stability constant was found to be 4.45×10^8 and free energy of formation ($\Delta F = -RT \ln K$) was -10.73 kcal/mole at 30°C are given in Table-3.

Table 3: Stability constant of Co(II)-HBBAO complex at 30°C

Method Employed	Em	Es	$\alpha = (E_m - E_s) / E_m$	K (n=1)
Job's	0.312	0.287	0.08013	4.47×10^8
	0.627	0.595	0.05104	4.46×10^8
Mole ratio	0.390	0.363	0.06923	4.49×10^8
	0.468	0.439	0.06197	4.38×10^8
Average K				4.45×10^8

Spectral Studies

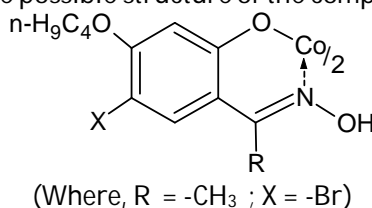
The IR spectra of ligand and complex were recorded on model No. 8400 FTIR, Shimadzu-Japan using Nujol as a solvent. The ligand shows the strong absorption bands of phenolic groups but no such bands are obtained in complex. The disappearance of this band clearly points out to the

replacement of phenolic hydrogen by the metal. The C=N frequency is also lowered in the complex. The lowering in C=N frequency and replacement of phenolic hydrogen atom indicates that chelation takes place through the oxygen of -OH group and nitrogen of =N-OH group. Some main frequencies are given in table-4.

Table 4: IR frequency data of the ligand and complex

Compound	Ligand (C ₁₂ H ₁₆ O ₃ NBr)	Complex Co(C ₁₂ H ₁₅ O ₃ NBr) ₂
OH (phenolic) cm ⁻¹	3404	-
OH (oximino) cm ⁻¹	2962	2954
-C=N cm ⁻¹	1635	1602

On the basis of above results, the possible structure of the complex was found to be

**Effect of Diverse ions**

The effect diverse ions on the estimation of 30 µg of Co(II) with the reagent was studied by extracting the complex in presence of

cobalt was studied by adding varying amounts of foreign ions at pH 8.0. Tolerance for the variation is fixed to cause $\pm 2\%$ error in the recovery of cobalt (Table-5). However, Cu(II), Ni(II), Mn(II), Pd(II), Fe(III), UO₂(II), interfere seriously.

Table 5: Interference of diverse ions

S. No.	Ions added	Tolerated (mg)
1.	Cl ⁻ , Br ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , CH ₃ COO ⁻ and S ₂ O ₃ ²⁻	30
2.	perchlorate iodate, phosphate and thiocyanate	15
3.	pyrosulphate, permanganate, thiourea, oxalate, tartrate, oxalate, Ca ²⁺ , Tl ³⁺ , Zn ²⁺ and Cd ²⁺	7.0
4.	Pb ²⁺ , As ³⁺ , Mo ⁶⁺ , Mn ²⁺ , Mg ²⁺ and Cr ³⁺	3.5
5.	Be ²⁺ , Li ⁺ , V ⁵⁺ and Sr ²⁺	1.5

Determination of cobalt in alloy and synthetic mixtures

The complex formed between Co(II) and HBBAO is stable and can be used for

analysis. The method has been applied for the analysis microgram quantities of cobalt in alloy and some synthetic mixtures. The result are shown in Table-6.

Table 6: Analysis of cobalt in various sample

S.No.	Sample	Cobalt taken (μg)	Cobalt found* (μg)
1	Vitallium	1022.4	1017.4
2	Synthetic Mixture-1	294.6	292.1
3	Synthetic Mixture-2	442.0	436.9
4	Synthetic Mixture-3	589.3	588.0

(* indicate average value of three result)

CONCLUSIONS

The reagent (HBBAO) is used for the determination of cobalt in microgram quantities. The Molar absorptivity and Sandell's sensitivity are $312 \text{ l mole}^{-1} \text{ cm}^{-1}$ and $0.19 \mu\text{g/cm}^2$, respectively. The method has been applied for the analysis cobalt in synthesized mixtures and also in alloys.

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