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Spectrophotometric Determination of Cu(II) using 2-Hydroxy-4N-butoxy-5-bromo Acetophenone Oxime

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2-Hydroxy-4N-butoxy-5-bromo acetophenone oxime (HBBAO) has been used for the spectrophotometric determination for Cu(II) at pH 4-6 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 6.63×10^8. The standard free energy change for the complex formation reaction is found to be -12.24 kcal/mol at room temperature. The Beer's law obeyed in the concentration range 31.77 to 254.16 ppm for Cu(II) ion, while the optimum concentration range from Ringbom plot is found to be 95.31 to 254.16 ppm. The sandell's sensitivity and molar absorptivity at the 650 nm are found to be 0.47 μg/cm^2 and 134 L mol^{-1} cm^{-1}, respectively. The complex is stable for 48 h. The reagent has also been found to give quite satisfactory results for Cu(II) present in alloy like brass, bronze and synthetic mixtures.

Key Words: Copper(II), Complex, 2-Hydroxy-4N-butoxy-5-bromo acetophenone oxime.

INTRODUCTION

Oximes, hydrazones, thiosemicarbazone, semicarbazone of aromatic aldehydes and ketones in which there is hydroxy group in *ortho*-position to carbonyl group are better suited as chelating agent because they form the metal chelates in which rings have least strain and chelates have more stability. Many such oximes and other reagents as above have been used as an analytical reagent for the spectrophotometric and gravimetric determination of copper and other transition metal ions[1-5]. In the present work the use of 2-hydroxy-4N-butoxy-5-bromo acetophenone oxime (HBBAO) as analytical reagent for Cu(II) has been described.

EXPERIMENTAL

A 0.1 M stock solution of Cu(II) has been prepared by dissolving copper sulphate (AR) in distilled water containing few drops of sulphuric acid. The amount of Cu(II) in this solution was determined by following standard procedures[6].

Preparation of 2-hydroxy-4N-butoxy-5-bromo acetophenone oxime (HBBAO): Resacetophenone was prepared from resorcinol by standard methods[7]. 2-hydroxy-4N-butoxy acetophenone (HBA) has been prepared by refluxing resacetophenone and *n*-butyl bromide in suitable solvent for 8 h. 2-Hydroxy-4N-butoxy-5-bromo acetophenone (HBBA) has been prepared by bromination[8] of HBA. 2-Hydroxy-4N-butoxy-5-bromo acetophenone oxime (HBBAO) has been prepared by refluxing HBBA with hydroxylamine hydrochloride in the presence of sodium acetate in ethanol medium for 4 h. The reagent when recrystallized from ethanol was obtained in the colourless, needle like crystals (m.p. 68 ± 1 ºC), with m.w. 301.9 (calcd. for $C_{12}H_{16}NO_3Br$). 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 Cu(II)-HBBAO complex and selection of solvent: When an alcoholic solution of HBBAO was added to 0.01 M aqueous metal ion solution, dark green precipitates of complex were obtained in the pH range 3-10. The complex was found to be insoluble in polar solvents like water, methanol or ethanol but soluble in non-polar solvents like chloroform, benzene, carbon tetrachloride, *etc*. As Cu(II)-HBBAO complex was more soluble in chloroform, it was selected as a solvent for extractive spectrophotometric determination of Cu(II).

Spectrophotometric measurements were made with a systronics UV/Vis spectrophotometer (model-118) using 10 mm glass cells. All pH measurements were made with systronic pH meter (model-324).

RESULTS AND DISCUSSION

Optimum pH and selection of wavelength: The pH of the solution has pronounced effect on the reaction between Cu(II) and HBBAO and the stability of the complex. On the other hand the absorbance is dependent upon the wavelength used. Both the parameters were therefore controlled to give maximum absorbance. Absorbance measurements of the reagent in chloroform show maxima at 410 and 650 nm. The absorbance measurements of Cu(II)-HBBAO complex show a maxima at 410-650 nm. As the interference due to the reagent appeared to be negligible at wavelength of 650 nm was selected for the present work.

To determine the optimum pH for complex formation series of buffer solutions with pH values ranging from 2.0 to 9.0 were prepared. To above buffer solutions, 3 mL of 0.005 M Cu(II) solution and 10 mL 0.01 M HBBAO solution in chloroform were added. After shaking the mixture for 2 min, the dark green coloured complex was extracted. The absorbance of organic layer containing complex was measured at 650 nm against a blank. From the results given in Fig. 1, it may be generalized that maximum absorbance takes place at pH 4-6. Hence a pH of 5 and wavelength of 650 nm have been selected for the present work.

Reproducibility: Absorbance measurements of a set of 10 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 ± 2.45 units, *i.e.*, 0.15 %.

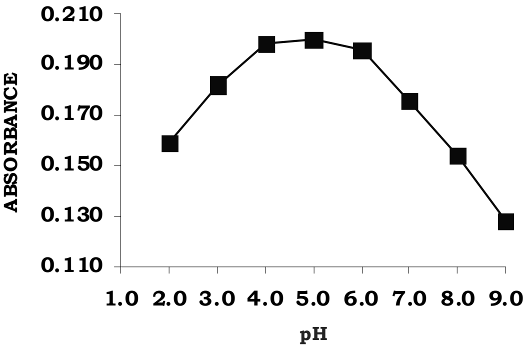

Fig. 1. Effect of pH in formation of Cu(II)-HBBAO complex

Effect of time and temperature: To determine the effect of time and temperature on the intensity of colour and the stability of the Cu(II)-HBBAO complex, absorbance was measured at room temperature (30 ºC) at regular intervals of time up to 48 h and also at temperatures of 30-55 ºC. The results show that complex is stable (± 2 % deviation) for 1 week and up to 45 ºC.

Stoichiometry and stability constant of the complex: The method of Vosbourgh and Cooper[9] showed that one complex is formed. To determine the stoichiometry of complex, Yoe and Jones mole ratio method[10], the slope ratio method[11] and Job's method of continuous variation[12] were employed (Fig. 2-4). All the three methods show a 1:2 metal:ligand ratio in the complex.

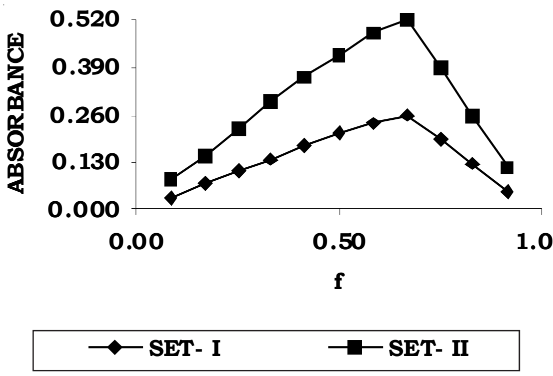

Fig. 2. Job's method of continuous variation Set-I: 0.01 M Cu(II) and 0.01 M HBBAO, Set-II: 0.02 M Cu(II) and 0.02 M HBBAO

The value of the stability constant calculated from the Job's method as well as from the mole ratio method are given in Table-1. From the table the average value of stability constant may be taken as 6.63×10^8. The standard free energy of formation of the complex, ΔGº, is -12.24 kcal/mol at 30 ºC.

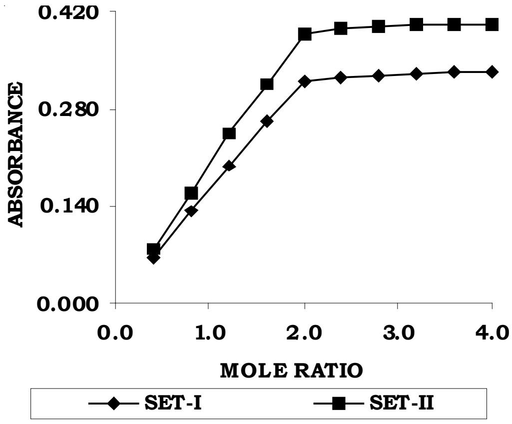

Fig. 3. Yoe and Jones mole ratio method Set-I: 0.0025 M Cu(II) and 0.01 M HBBAO, Set-II: 0.003 M Cu(II) and 0.012 M HBBAO

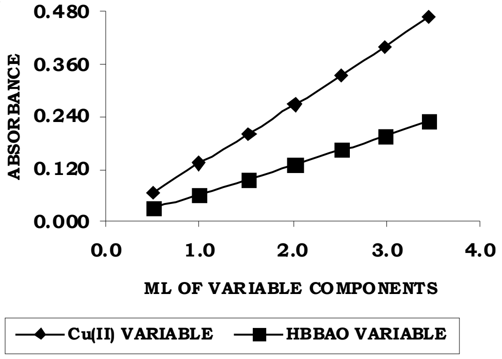

Fig. 4. Slope ratio method

TABLE-1
STABILITY CONSTANT OF Cu(II)-HBBAO COMPLEX AT 30 °C

Method employed	Em	Es	α	K (n = 2)
Mole ratio method				
Set-I	0.335	0.322	0.03881	6.58×10^8
Set-II	0.402	0.388	0.03483	6.35×10^8
Job's method				
Set-I	0.268	0.256	0.04478	6.65×10^8
Set-II	0.534	0.519	0.02809	6.85×10^8
Mean K stab	–	–	–	6.63×10^8

The IR spectra of reagent and the copper(II) complex revealed that the -OH (stretch) band of 3404 cm^{-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 Cu(II)-HBBAO complex can be assigned the following structure.

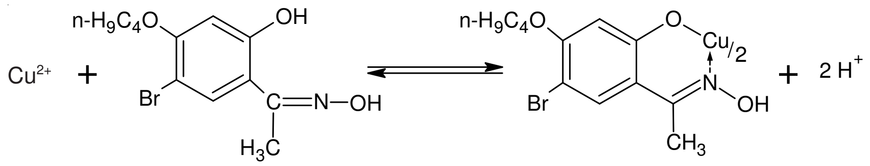

TABLE-2
ANALYSIS OF COPPER IN VARIOUS SAMPLES

Sample	Copper taken		O.D.	Copper found		Relative error (%)
	µg	%		µg	%	
Brass	1072.0	67.00	0.225	1066.9	66.48	0.77
			0.224	1062.2		
			0.224	1062.2		
			Avg.	1063.7		
Bronze	1404.8	87.80	0.296	1403.6	87.03	0.88
			0.294	1394.1		
			0.291	1379.9		
			Avg.	1392.5		
Synthetic mixture-1	953.1	–	0.201	953.1	–	1.16
			0.198	938.9		
			0.197	934.1		
			Avg.	942.0		
Synthetic mixture-2	794.3	–	0.168	796.6	–	0.71
			0.166	787.1		
			0.165	782.4		
			Avg.	788.7		
Synthetic mixture-3	635.4	–	0.136	644.9	–	0.25
			0.133	630.7		
			0.132	625.9		
			Avg.	633.8		

Conformity to Beer's law and the optimum concentration range: Beer's law is obeyed between the range 31.77 to 254.16 ppm of Cu(II). At higher concentrations negative deviations occur. The optimum concentration range for determination of Cu(II) in solution, as deduced from the Ringbom plot[13], is found to be 95.31 to 254.16 ppm. The molar absorptivity (ε) of the complex is 134 mol^{-1} cm^{-1} and the photometric sensitivity as per Sendell's definition[14] is found to be 0.47 $\mu g/cm^2$ at 650 nm.

Effect of diverse ions: The interference due to the presence of other ions on the determination copper ions as Cu(II)-HBBAO complex has also been studied. A difference of more than ± 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 1270.80 µg Cu(II) are as follows:

up to 100000 µg : Na^+, K^+, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, CH_3COO^-
up to 10000 µg : Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Cd^{2+}, MoO_4^-, citrate, tartrate, oxalate
up to 1000 µg : Cr^{3+}, UO_2^{2+}, Pd^{2+}
up to 100 µg : Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+}
up to 10 µg : EDTA

Determination of copper from various samples: To determine the applicability of the reagent in estimation of copper from various samples containing copper were taken and estimated by HBBAO. For this purpose, the alloy samples containing copper metal were dissolved in 1:1 nitric acid by heating on a sand bath. Excess nitric acid was removed by evaporation carefully. The resulting solution was made up to 250 mL with distilled water in a volumetric flask. The synthetic mixtures containing copper metal were also taken for analysis. Aliquot of this sample solution was pipetted out and its spectrophotometric determination was carried out by the proposed method. The result are given in Table-2. From results, it may be concluded that 2-hydroxy-4N-butoxy-5-bromo acetophenone oxime (HBBAO) can be used as an extractive spectrophotpmetric reagent for detection and estimation of copper as well as their various alloy with an error of measurement not exceeding ± 1.5 %.

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