

Spectrophotometric Determination of Copper(II) and Iron(III) with 2,4-Dihydroxy-5-Bromoacetophenone Thiosemicarbazone

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2,4-Dihydroxy-5-bromoacetophenone thiosemicarbazone (DHBAT) was synthesized and used as a spectrophotometric reagent for copper and iron. Cu(II) and Fe(III) form yellow coloured complex at pH 6.0 and 4.0 and show maximum absorption at 420 nm and 380 nm respectively. Molar absorptivities for Cu(II)-DHBAT and Fe(III)-DHBAT are 0.145×10^4 lit/mol cm and 0.6×10^4 lit/mol cm respectively. Cu(II)-DHBAT has 1 : 1 (M : L) stoichiometry while Fe(III)-DHBAT complex has 1 : 2 (M : L) stoichiometry. Beer's law is obeyed up to 12.7 ppm of Cu(II) ion and 9.41 ppm of Fe(III) ion. The reagent has been found to give satisfactory results for the analysis of copper in brass and iron in pharmaceutical preparation. Formation of the complex has also been supported from the IR spectral data.

INTRODUCTION

Many organic compounds like *o*-hydroxy ketoximes, phenylhydrazones¹, oximes², semicarbazones³, thiosemicarbazones^{4,5} have been used for spectrometric determination of copper and iron. Here, we report the new reagent 2,4-dihydroxy-5-bromoacetophenone thiosemicarbazone (DHBAT) for spectrophotometric determination of Cu(II) and Fe(III).

EXPERIMENTAL

Spectrophotometric measurements were made on a Shimadzu UV-16 recording spectrophotometer. All the pH measurements were done on Equip-Tronic electronic pH-meter Model Eq-614 and buffer solutions of required pH were obtained using sodium acetate-acetic acid and hydrochloric acid-sodium acetate buffers of suitable concentrations. The IR spectra were recorded on Perkin-Elmer spectrophotometer (Model-237) in KBr pellets.

Synthesis of 2,4-dihydroxy-5-bromoacetophenone thiosemicarbazone (DHBAT)

Resacetophenone was prepared according to method of Robinson and Shah⁶. 2,4-Dihydroxy-5-bromoacetophenone (DBA) was prepared by bromination of resacetophenone using bromine in glacial acetic acid at 20–25°C; the colourless compound was crystallized from ethanol (m.p. 171°C). 2,4-Dihydroxy-5-

bromoacetophenone thiosemicarbazone was prepared from DBA (0.01 mol), thiosemicarbazide (0.015 mol) taken in 50 mL of ethanol and 5 mL of acid. The mixture was refluxed on water-bath at 80–85°C for 4 h. Excess of ethanol was distilled off and yellow solid was obtained. It was crystallized from ethanol (m.p. 128°C; nitrogen: found 13.80% and calculated 13.81%; sulphur: found 10.52% and calculated 10.54%).

Preparation of solutions

All the chemicals used in the work were of analytical grade purity. Stock solution of ligand (DHBAT) (0.02 M) was prepared dissolving thiosemicarbazone in ethanol. Stock solution of Cu(II) (0.025 M) has been prepared by dissolving copper sulphate in double distilled water with the little free acid and standardised titrimetrically⁷. Fe(III) (0.025 M) was prepared by dissolving anhydrous ferric chloride in double distilled water with little free acid and solution was standardised gravimetrically⁸.

Preparation of Cu(II)-DHBAT complex

A series of buffer solutions with pH values ranging from 3.0 to 6.5 were prepared using acetic acid-sodium acetate. To 1.0 mL of 0.002 M Cu(II) solution, 5 mL buffer solution and 5.0 mL of 0.01 M ethanolic solution of DHBAT were added and the solution was diluted up to 25 mL keeping final concentration of alcohol 50%. The spectra of the above solutions were recorded from 340 nm to 800 nm.

Preparation of Fe(III)-DHBAT complex

To 2.0 mL of 0.002 M Fe(III) solution, taken in different flasks, 5 mL buffer solution (pH 2.0 to 5.0) and 4.0 mL of 0.01 M ethanolic solution of DHBAT were added and the solution was diluted up to 25 mL keeping final concentration of alcohol 50%. The spectra of the above solutions were recorded from 340 nm to 800 nm.

In case of Cu(II) maximum complex formation occurs at pH 6.0 and for Fe(III) at pH 4.0. Hence in all further studies these pH values were used. Wavelength of maximum absorption were found to be 420 nm for Cu(II) and 380 nm for Fe(III). Obeysance of Beer's law was studied for Cu(II) at 420 nm and for Fe(III) it was studied at 380 nm. Results of Job's method of continuous variation⁹ and mole ratio method indicated¹⁰ 1 : 1 (M : L) ratio for Cu(II) complex and 1 : 2 (M : L) ratio for Fe(III) complex.

Interference

While determining 12.7 ppm of Cu(II) at pH 6.0 using the reagent, many anions like F⁻, Cl⁻, Br⁻, NO₃⁻, SO₄²⁻ do not interfere, even when they are present in 50-fold excess. Thiourea (20), thiosulphate (20), oxalate (2) can be tolerated. A 30-fold excess of Zn(II), Sr(II), Ca(II), Mg(II), Cd(II), Al(III), Na(I), K(I), Ba(II) do not interfere.

While determining 9.41 ppm of Fe(III) at pH 4.0 using the reagent, Cl⁻, Br⁻, NO₃⁻, SO₄²⁻ do not interfere even when they are present in 150-fold excess. A

90-fold excess of Zn(II), Ca(II), Cd(II), Sr(II), Ba(II) and Mg(II) do not interfere. There is no interference from Ni(II), Mn(II), Co(II) at this pH when present in equal amount.

Determination of copper in brass and iron in medicinal sample

Brass sample (0.150 g) was dissolved in nitric acid (1 : 1) by gently heating on a sandbath till the sample dissolved. Excess of nitric acid was removed and the solution was diluted to 100 mL. A suitable aliquot was taken to determine Cu(II) spectrophotometrically using DHBAT at 420 nm.

Contents of "Fefol" capsule were transferred to evaporating dish. 10 mL 1 : 1 nitric acid was added and the matter was decomposed, excess of nitric acid was removed and the solution was diluted to 100 mL. Taking suitable aliquot from this solution, Fe(III) was determined spectrophotometrically at 380 nm.

RESULTS AND DISCUSSION

TABLE-1
SPECTRAL DATA FOR 2,4-DIHYDROXY-5-BROMOACETOPHENONE
THIOSEMICARBAZONE COMPLEX OF Cu(II) AND Fe(III)

Characteristic	Cu(II)-DHBAT	Fe(III)-DHBAT
δ_{\max} (nm)	420	380
Optimum (pH)	3.0-6.5	2.0-5.0
Colour	yellow	yellow
Beer's law obedience maximum concentration (ppm)	12.7	9.41
Molar absorptivity $\times 10^4$ (lit/mol cm)	0.145	0.602
Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$)	0.043	0.0092
Stability constant of complex (K_s)	3.12×10^6	4.48×10^{10}
ΔG° at 25°C (kcal/mol)	-8.882	-14.568

TABLE-2
DETERMINATION OF COPPER IN BRASS AND IRON IN MEDICINAL SAMPLE

Sample	Metal	Amount of metal in (%) or (mg)		Relative error (%)
		Expected	Found	
Brass	Copper	70.48%	68.62%	-2.71%
Fefol	Iron	55.12 mg	54.10 mg	-1.88%

IR spectra of ligand and complexes

The complexes were obtained in solid state by refluxing stoichiometric amount of ligand and metal solution for 4 h and then removing the solvent. The spectra were recorded in KBr pellets.

The infra-red spectrum of ligand (DHBAT) shows intense strong $\nu(\text{C}=\text{S})$, $\nu(\text{O}-\text{H})$ and $\nu(\text{C}=\text{N})$ bands at 1310 cm^{-1} , 3350 cm^{-1} and 1595 cm^{-1} respec-

tively. In case of Cu(II)-BHBAT complex $\nu(\text{C}=\text{N})$ band shows downward shift to 1580 cm^{-1} and $\nu(\text{C}=\text{S})$ band to 1240 cm^{-1} , while in case of Fe(III)-DHBAT, $\nu(\text{C}=\text{S})$ band is observed at 1280 cm^{-1} and $\nu(\text{C}=\text{N})$ band at 1600 cm^{-1} . This shift indicates the coordination of metal ion through azomethine nitrogen and sulphur atom. The ligand shows $\nu(\text{N}-\text{H})$ at 1140 cm^{-1} which shows downward shift to 1100 cm^{-1} in Cu(II)-DHBAT complex and upward shift to 1150 cm^{-1} in Fe(III)-DHBAT complex.

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