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5-Ethyl-2-Hydroxy Acetophenone Oxime as an Analytical Reagent—Studies on Cu(II) Chelate

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2-Hydroxy-5-ethyl acetophenone oxime was synthesized and used as an analytical regent for copper. The structure of the buff coloured Cu(II) complex has been assigned on the basis of Job's method, mole-ratio method and IR-structural data.

INTRODUCTION

Many organic reagents like oximes[1–5], hydrazones, semicarbazones, chalcones, chalcone oximes, etc. are found to interact with metal ions giving precipitation or colouration due to complex formation. These all reagents have been used for the spectrophotometric and gravimetric determination of copper and other transition metal ions. In the present work, we report the use of 2-hydroxy-5-ethyl acetophenone oxime (HEAO) as spectrophotometric and gravimetric reagent for Cu(II).

EXPERIMENTAL

The 0.05 M stock solution of Cu(II) has been prepared by dissolving copper sulphate (AR, BDH) in distilled water and little acid. The amount of Cu(II) in this solution was determined volumetrically with EDTA.[6]

Preparation of 2-hydroxy-5-ethyl acetophenone oxime (HEAO): 2-hydroxy-5-ethyl acetophenone oxime was prepared from 2-hydroxy-5-ethyl acetophenone following the method of Kuskor and Naumov.[7] In the first step, *p*-ethylphenyl acetate was prepared from *p*-ethylphenol using acetic anhydride. Then, 2-hydroxy-5-ethyl acetophenone was prepared by Frie's migration. Its oxime was prepared by sodium acetate method and crystallised from petroleum ether (100–120°C) into colourless needles, m.p. 119°C (reported[7] m.p. 119°C). The reagent is soluble in solvents like ethanol, acetone, benzene, carbon tetrachloride etc.

Preparation of Cu(II) HEAO complex: A series of buffer solutions with pH values ranging from 3.5 to 6.5 were prepared using hydrochloric acid-sodium acetate and acetic acid-sodium acetate. Then an ethanolic solution of ligand was mixed with an aqueous solution of the copper sulphate in molar ratio (1 : 2). The pH of the reaction mixture was adjusted by previously prepared buffer solution. The buff complexes precipitated were digested on water bath, filtered and washed with water followed by ethanol and dried at 110°C.

Spectrophotometric measurements were made on Bausch and Lomb spectrophotometer (Spectronic-20) and Shimadzu UV Spectronic. All the pH measurements were made with an Elico pH-meter.

Gravimetric procedure: An aliquot of 0.05 M solution of Cu(II) was diluted to 100 mL. with distilled water, warmed to about 70–80°C on a water-bath; the

pH was adjusted to 4.5–5.0 using acetic acid-sodium acetate buffer. Then 1% solution of HEAO in 90% ethanol was added till precipitation was complete. The buff precipitate obtained was digested on water bath at 60–70°C for about 30 minutes. The precipitate was filtered through a previously weighed sintered glass crucible (G–4), and washed with warm water followed by 50% ethanol dried at 110°–115°C and weighed as $Cu(C_{10}H_{12}O_2N)_2$ (gravimetric factor = 0.1514). Triplicate experiments were performed in each case and the mean values have been reported.

Spectrophotometric procedure: The precipitate of Cu(II)-HEAO complex was insoluble in absolute ethanol or methanol. However, it was soluble in nonpolar solvents like benzene, chloroform, carbon tetrachloride, etc. The complex was, therefore, extracted in chloroform layer. The absorbance of the organic layer was recorded against the reagent blank prepared under similar conditions.

RESULTS AND DISCUSSION

Spectrophotometric determination of copper optimum pH and selection of wavelength: The pH of the solution has a pronounced effect on the reaction between Cu(II) and HEAO and the stabilility 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.

The absorbance measurements of Cu(II)-HEAO complex show that the absorbance of the coloured solution of the complex increases continuously towards the shorter wavelength. The absorbance shows a shoulder at 410 nm. A wavelength of 410 nm is selected for the present work.

For the selection of pH, absorbance of the organic layer containing Cu(II)-HEAO complex extracted from the aqueous solution of different pH values was measured. From the results given in Table-1 it is evident that the maximum absorbance occurs in the pH range 4.0–6.0. A pH of 4.5–5.0 was selected for the present work.

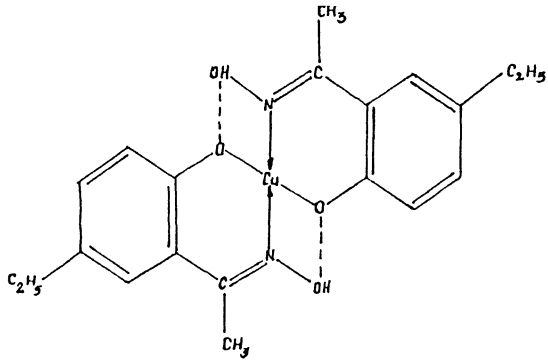
TABLE-1

pH	Absorbance	Buffer
2	0.345	dil. HCl + CH_3COONa
3	0.510	dil. HCl + CH_3COONa
4	0.636	CH_3COOH + CH_3COONa
5	0.636	CH_3COOH + CH_3COONa
6	0.636	CH_3COOH + CH_3COONa
7	0.514	CH_3COOH + NH_3
8	0.316	NH_3 + NH_4Cl
9	0.425	NH_3 + NH_4Cl
10	0.375	NH_3 + NH_4Cl

Validity of Beer's law: The buff Cu(II) HEAO complex in $CHCl_3$ obeys Beer's law up to 30.49 ppm of copper. Beyond this concentration the absorbance plot does not show linearity. The average molar absorptivity of the complex obtained from the absorbance data is found to be 7.38×10^2 lit. mol^{-1} cm^{-1} at 410 nm. The photometric sensitivity as per Sandell's definition is 0.0859 $\mu g/cm^2$ at 410 nm.

Stoichiometry and stability constant of the complex: The stoichiometry of the Cu(II)-HEAO complex was studied by (i) Job's method of continuous variation[8] and (ii) Yoe and Jone's mole ratio method.[9] All the two methods gave the metal: ligand ratio of 1 : 2. The gravimetric determination as well as elemental analysis of the complex also confirmed this ratio. In the IR spectrum of HEAO two bands are observed in the —OH stretch region, at 3370 cm^{-1} due to the 2-hydroxy group and the other at about 3000-2990 cm^{-1} due to the oximino group. In the IR spectrum of Cu(II)-HEAO complex the first band at 3370 cm^{-1} disappeared while the second band is slightly shifted. This suggests the formation of Cu(II)-HEAO chelate through O^- of the phenolic group and N of the oximino group.

Based on the above data the copper complex with HEAO can be assigned the structure:



Copper-2-hydroxy-5-ethylacetophenone oxime complex.

The stability constants for the complex for different values on "n" were calculated from the data of mole-ratio method. The stability constant is 1.7020×10^{10}, the value of ΔG being – 13.95 kcal/mole.

Effect of diverse ion: To determine the effect of foreign ions on the estimation of Cu(II), 8–10 mg of various cations were added to a known amount of Cu(II) solution of pH 6.0. It was observed that Ca(II), Sr(II), Mg(II), Mn(II), Ni(II), Zn(II) do not interfere at this pH. Many common anions like chloride, bromide, iodide, nitrate were not found to interfere.

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