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2′-Hydroxy-4′-Ethoxy-4-Methoxychalcone Oxime as an Analytical Reagent for Copper

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In the present work, the authors describe 2′-hydroxy-4′-ethoxy-4-methoxychalcone oxime (HEMCOX) as a gravimetric and spectrophotometric reagent for copper.

INTRODUCTION

Oximes are selective and sensitive reagents for the gravimetric and spectrophotometric determination of metal ions. Many such oximes have been used as analytical reagents for different metal ions. Very few workers[1–3] have used chalcone oximes as analytical reagents. Here we report the use of 2′-hydroxy-4′-ethoxy-4-methoxychalcone oxime (HEMCOX) as an analytical reagent for Cu(II).

EXPERIMENTAL

Spectrophotometric measurements were done on "Spectronic-20" and "Hitachi U-2000 spectrophotometer". All pH measurements were done on Elico pH meter.

2-Hydroxy-4-ethoxyacetophenone was prepared from resacetophenone following the method of eijkmann *et al.*[4] using ethyl iodide and anhydrous potassium carbonate in acetone.

2′-Hydroxy-4′-ethoxychalcone was prepared by adding an aqueous solution of potassium hydroxide (40%) to ethanolic solution of 2-hydroxy-4-ethoxyacetophenone and *p*-anisaldehyde keeping temperature 20–25°C. On crystallisation from benzene yellow crystals with m.p. 166 ± 2°C were obtained.

The 2′-hydroxy-4′-ethoxy-4-methoxychalcone oxime (HEMCOX) was prepared by the sodium acetate method. On crystallization from petroleum ether, pure HEMCOX in the form of colourless crystals with m.p. of 185 ± 1°C was obtained [Found: N, 4.43%; $C_{18}H_{19}O_4N$ required: N, 4.47%].

Stock solution of the reagent (0.05 M) was prepared by dissolving the oxime in 60% aqueous ethanol.

Stock solution of $CuSO_4{\cdot}5H_2O$ (0.05 M) was prepared by dissolving the pure salt in doubly distilled water and was used after standardization[5] with EDTA.

Gravimetric procedure: An aliquot of 0.05 M solution of copper(II) sulphate

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was diluted to 100 mL with distilled water, warmed and the pH of solution was adjusted in the range of 6.0–6.5 with suitable buffer. Then 0.05 M solution of HEMCOX in ethanol was added till precipitation was complete. The buff precipitate was digested on water-bath at 60–70°C for 1 h and filtered through a previously weighed sintered glass crucible (G_4). The precipitate was washed with hot water and then finally with 60% aqueous ethanol to remove any reagent which might have precipitated on dilution. The precipitate was dried and weighed as $Cu(C_{18}H_{18}O_4N)_2$. Duplicate experiment was performed in each case and the mean values have been reported. The conversion factor (metal/metal complex) is 0.0922.

Spectrophotometric procedure: The precipitates of Cu(II)-HEMCOX were insoluble in absolute ethanol or methanol. Therefore, the complex was directly extracted in chloroform layer. For this purpose, a suitable aliquot of copper(II) sulphate solution was taken and pH was adjusted to 6.0–6.5 with acetic acid-sodium acetate buffer and slight excess of HEMCOX solution was added. The complex thus precipitated was extracted with two or three portions of chloroform and the volume of chloroform extract was made to 20 mL. The absorbance of the organic layer was recorded against the reagent blank prepared under similar conditions.

RESULTS AND DISCUSSION

Gravimetric determination of copper

To determine the feasibility of the reagent for gravimetric estimation of Cu(II), the metal ion was precipitated from solution having pH values in the range 3.0 to 9.0. Complete precipitation occurred at pH 6.0–6.5. Estimations using different aliquots of Cu(II) were done at pH 6.0–6.5. In all cases, the error in Cu(II) content did not exceed ±0.3%.

Spectrophotometric determination of copper

Selection of wavelength: For recording the absorption spectra, 1.5×10^{-4} M solution of the chelate in chloroform was used and the absorbance was measured in the range of 330–1000 nm. It was observed that the absorbance of the coloured solution increases continuously towards the shorter wavelength. The absorbance spectrum shows a shoulder at 370 nm and hence all the measurements were carried out at this wavelength.

Validity of Beer's law and optimum concentration range

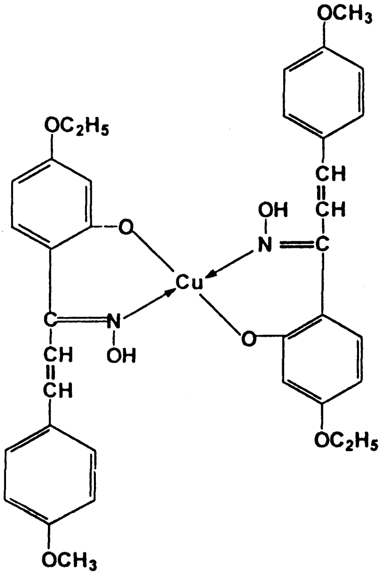
The Cu(II)-HEMCOX complex in chloroform obeys Beer's law up to 20 ppm of Cu(II) in organic layer. Beyond this concentration, the absorbance plot shows a negative deviation from linearity. The molar absorptivity (E) of the complex obtained from the absorbance data is found to be 1.3362×10^4 L mol^{-1} cm^{-1} at 370 nm.

Stoichiometry and structure of complex

The stoichiometry of the Cu(II)-HEMCOX complex was studied by (1) Yoe and Jones mole ratio melthod[6], and (2) Job's method of continuous variation[7].

Both the melthods gave the metal : ligand ratio of 1 : 2. The gravimetric determination as well as the elemental analysis of the complex (N : Found, 4.058%, required: 4.072%) also confirmed this ratio. Comparison of the IR spectra of ligand with that of chelate helped in establishing the nature of linkage of metal and the site of coordination. IR spectrum of the ligand shows two bands in O—H stretching region. One band at 3438 cm^{-1} which disappears in the spectrum of chelate is due to phenolic —OH group. Deprotonation of —OH group takes place and metal coordinates with the oxygen by covalent bond. The coordination of metal through N of oximino group may be shown by the lowering of C=N frequency from 1622 cm^{-1} in ligand to 1610 cm^{-1} in chelate. The position of oximino —OH group (2980 cm^{-1}) remains unaffected in the ligand and chelate.

Based on above data the copper chelate may be assigned the following structure:



Stability constant of the complex

For evaluating stability constant of the complex, the degree of dissociation (α) was calculated from the data of mole ratio method. The results obtained are as follows:

E_m	E_s	α	$K_s = 1 - \alpha/\alpha^2C$
0.1308	0.1192	0.0886	8.25×10^6

The standard free energy change for the complex formation reaction of room temperature was calculated using the relationship $\Delta G^\circ = -RT \ln K$ and it was found to be –9.49 kcal/mol.

The Cu(II)-HEMCOX complex exhibits effective magnetic moment[8] 2.02 B.M. corresponding to one unpaired electron indicating paramagnetic nature.

Interference from other ions

A definite quantity of interfering ion was added to the solution of copper ion and the gravimetric determination was carried out as described earlier. It was observed that anions like chloride, bromide, iodide, nitrate, sulphate and cations like Ba(II), Sr(II), Ca(II), Mg(II), Zn(II) did not interfere. The error in any case did not exceed ±0.5%.

Preanalysed sample of brass (0.7440 g) was dissolved in nitric acid (1 : 1) by heating for 30 min. The solution was evaporated to a volume of 5 mL. The resulting solution was diluted to 250 mL with doubly distilled water in volumetric flask. An aliquot of the above diluted solution (25 mL) was taken in a clean beaker and copper was determined gravimetrically using HEMCOX as per the procedure described earlier.

Results

1.	Weight of Cu(II)-HEMCOX (average of three determinations)	0.4792 g
2.	Copper found in 25 mL diluted solution	0.0442 g
3.	Copper found in brass sample	0.4426 g
4.	Copper found in brass sample	59.5%
5.	Copper reported in brass sample	60.0%
6.	Error	0.5%

The same reagent is being studied for complexation with other transition metal ions.

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