2-Hydroxy-4-*n*-Propoxy Butyrophenone Oxime as an Analytical Reagent for Copper

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In the present work, the authors describe 2-hydroxy-4-*n*-propoxy butyrophenone oxime as a gravimetric and photometric reagent for copper.

INTRODUCTION

Oximes, hydrazones, thiosemicarbazones, semicarbazones of aromatic aldehydes and ketones in which there is hydroxy group in *ortho*-position to carbonyl group are better suited as chelating agents 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 gravimetric and/or spectrophotometric reagents for different metal ions. 2-Hydroxy-4-ethoxy acetophenone oxime[1-3] and 2-hydroxy-2-ethoxy propiophenone oxime[4] have been reported earlier. Here, we report the use of 2-hydroxy-4-*n*-propoxy butyrophenone oxime [HPBO] as gravimetric and spectrophotometric reagent for Cu(II).

EXPERIMENTAL

Instruments: Spectrophotometric measurements were made with a B/L Spectronic-20 spectrophotometer. All pH measurements were made with an Elico pH meter LI–10T.

Reagent: 2-Hydroxy 4-*n*-propoxy butyrophenone (HPB) was prepared from resbutyrophenone following the method of Eijkmann *et al.*[5] using *n*-propyl bromide and anhydrous potassium carbonate in acetone. On crystallization from ethanol colourless needle-like crystals with m.p. 39 ± 2°C were obtained. The oxime of HPB was prepared by the sodium acetate method. On crystallisation from alcohol pure HPBO in the form of colourless needles with m.p. of 68 ± 1°C was obtained. The reagent is soluble in solvents like ethanol, chloroform, carbon tetrachloride and acetone etc. The molecular weight of HPBO was found to be 237.29 (calcd. 237.69). The elemental analysis of the oxime showed its composition to be C = 65.65%, H = 7.58%, N = 5.85% (calcd. C = 65.75%, H = 7.65%, N = 5.89%).

Stock solution: 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 standardisation[6] with EDTA. Stock solution of HPBO (0.05M) was prepared by dissolving the oxime in 70% aqueous ethanol.

Gravimetric procedure: An aliquot of 0.05 M solution was diluted to 100 mL with distilled water, warmed and the pH of solution was adjusted in the range of 4.0–10.0 with suitable buffer. Then 0.05 M solution of HPBO in ethanol was added till precipitation was complete. The light green precipitates were digested

on water-bath at 70–80°C for 45 min. and filtered through a previously weighed sintered glass crucible (G-4), the precipitates were washed with hot water and then finally with 70% aqueous ethanol to remove any reagent which might have precipitated on dilution. The precipitates were dried and weighed as $Cu(C_{13}H_{17}O_3N)_2$. Duplicate experiments were performed in each case and the mean values have been reported.

Spectrophotometric procedure: The precipitates of Cu(II)-HPBO complex were insoluble in absolute ethanol or methanol. They were soluble in non-polar solvents like chloroform, carbon tetrachloride, benzene and toluene etc. Therefore, the complex was directly extracted in chloroform layer. For this purpose, a suitable aliquot of Cu(II) solution was taken and pH was adjusted to 5.0 with sodium acetate buffer and ten excess of HPBO 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 25 mL. The absorbance of the organic layer was recorded against the reagent blank prepared under similar conditions.

RESULTS AND DISCUSSION

Gravimetric determination of copper: The 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 2.0 to 10.0. There was incomplete precipitation at pH 2.0–3.0, whereas between pH 4.0–10.0 complete precipitation occurred, the error being maximum ($\leq 0.1\%$) in the pH range 4.0–10.0. Estimations using different aliquots of Cu(II) were done at pH 5.0. In all cases, the error in Cu(II) content did not exceed $\pm 0.25\%$ (Table-1).

TABLE-1
EFFECT OF Cu(II) CONCENTRATION ON GRAVIMETRIC ESTIMATION OF
COPPER AS Cu(II)-HPBO COMPLEX AT pH = 5.0

Copper taken (mg)	Cu-HPBO complex obtained (mg)	Copper found (mg)	Error (mg)	Error (%)
15.89	133.60	15.85	–0.04	–0.25
31.78	267.80	31.77	–0.01	–0.03
47.67	402.30	47.71	+0.04	+0.08

To determine the selectivity of the reagent, qualitative tests were carried out for precipitation of various metal ions in the pH range 1.0–10.0 using HPBO. The results are shown in Table-2.

TABLE-2
pH-RANGE FOR PRECIPITATION OR COLOUR FORMATION WITH
VARIOUS METAL IONS USING HPBO

Metal ion	pH-range	Colour of precipitate
Ni(II)	5.0–11.0	Green
Pd(II)	1.0–6.0	Yellow
Mn(II)	6.0–11.0	Brown
Mg(II)	1.0–4.0	Yellow colouration

Spectrophotometric determination of copper

Selection of wavelength: To take the absorbance spectra, 2 mg chelate was dissolved in 10 mL chloroform and the absorbance was measured in the range of 330–600 nm using Spectronic-20 spectrophotometer. It was observed that the absorbance of the coloured solution increases continuously towards the shorter wavelength. The absorbance spectrum shows a shoulder at 400 nm and hence all the measurements were carried at this wavelength.

Validity of Beer's law and optimum concentration range: The Cu(II)-HPBO complex in chloroform obeys Beer's law upto 57.15 ppm of Ni(II) in organic layer. Beyond this concentration, the absorbance plot shows a negative deviation from linearity. The optimum concentration range for the complex inorganic layer is found to be 12.7–57.15 ppm. The molar absorptivity (ε) of the complex obtained from the absorbance data is found to be 683.33 L mol^{-1} cm^{-1} at 400 nm. The photometric sensitivity as per Sandell's definition is 0.37 µg/cm^2 at 400 nm.

Stoichiometry and stability constant of complex: The stoichiometry of the Cu(II)-HPBO complex was studied by (i) Yoe and Jones mole ratio method[7] (Fig. 1), (ii) Job's method of continuous variation[8] (Fig. 2). Both the methods gave
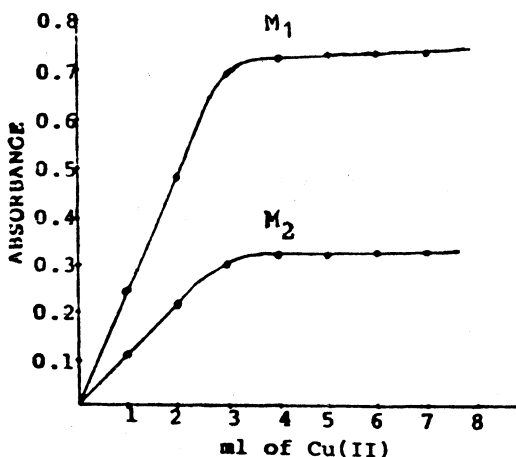

Fig. 1   Plots of the ratio method (M$_1$, M$_2$) for determination of M : L ratio:
M$_1$: 0.01 M Cu(II), 0.01 M HPBO; M$_2$: 0.005 M Cu(II); 0.005 M HPBO

the metal : ligand ratio of 1 : 2. The gravimetric determination as well as the elemental analysis of the complex (N: found 5.12%, calc. 5.22%) 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 3320 cm^{-1} which disappears in the spectrum of chelate is due to 2—OH group. The H of this —OH group is removed and metal joins with the oxygen by covalent bond. The coordination of metal through N of oximino group may be shown by the
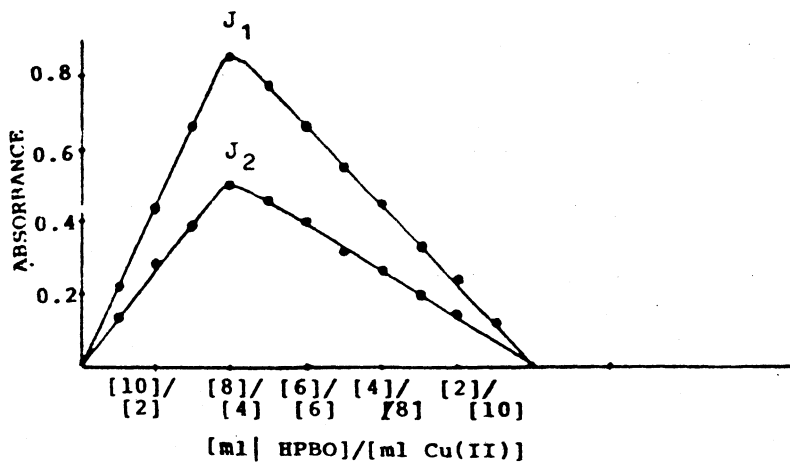
Fig. 2   Plots of Job's method of continuous variation (J_1, J_2) for determination of M : L ratio.
J_1: 0.01 M Cu(II), 0.01 M HPBO; J_2: 0.005 M Cu(II); 0.005 M HPBO

lowering of C$=$N frequency from 1620 cm^{-1} in ligand to 1600 cm^{-1} in chelate. The position of oximino —OH group changes from 2860 cm^{-1} in ligand to 2870 cm^{-1} in chelate. This also may be due to coordination metal through nitrogen.

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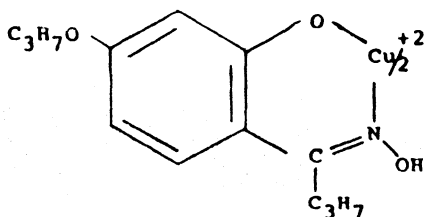

TABLE-3
STABILITY CONSTANT OF Cu(II)-HPBO AT 30°C

Method employed	E_m	E_S	α	K (n = 2) $\times 10^{+9}$
Mole ratio method	0.3200	0.3010	0.05937	3.12
	0.7150	0.6882	0.03748	3.26
Job's method	0.5200	0.4948	0.04846	3.17
	0.8800	0.8538	0.02977	3.52

Mean K_S = 3.26 $\times 10^{+9}$

The standard free energy change for the complex formation reaction is found to be −13.19 kcal/mole at room temperature.

Interference from other ions

It was observed that in the determination of Cu(II) (35 ppm) at pH 5.0, 1000 ppm of acetate, sulphate, chloride, bromide, iodide, nitrate; 1000 ppm of Na(I), K(I), Cd(II), Sr(II), Mg(II), Ca(II), Be(II); 500 ppm Zn(II), Mn(II) could be tolerated. Maximum error in any case did not exceed ± 0.85% in metal ion.

Fe(II) gives a coloured complex with HPBO at pH 6.5, while Fe(III) does so at pH 3.0, and hence both these cations interfere. However, the determinations in presence of these ions could be carried out by sequestering Fe(II) and Fe(III) with potassium tartarate. The error in any case did not exceed ± 1.0%.

Determination of copper in brass: Preanalysed sample of brass 0.6166 gm was dissolved in nitric acid (1 : 1) by heating for 30 min. The solution is evaporated to a volume of 5 mL but not to dryness and bulk of nitric acid was removed. The resulting solution was diluted to 250 mL with doubly distilled water in volumetric flask.

An aliquot of above diluted solution (25 mL) was taken in a clean beaker and copper was determined gravimetrically using HPBO as per the procedure described previously.

RESULT

1.	Weight of Cu(II)-HPBO complex (average of three determinations)	0.3650 gm
2.	Copper found in 25 mL diluted solution	0.0433 gm
3.	Copper found in brass sample taken	0.4331 gm
4.	Percentage copper found in brass sample	70.23%
5.	Percentage copper found in brass sample	70.48%
6.	Error	−0.25%

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

ACKNOWLEDGEMENT

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