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2-Hydroxy-4-Methoxybenzophenone Oxime as an Analytical Reagent for Copper(II)

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Abstract: 2-hydroxy-4-methoxybenzophenoneoxime (HMBO) was developed as a new analytical reagent for the gravimetric determination of Cu(II). In pH 2.5-9.0 the reagent gives brown coloured precipitate with Cu(II). Spectrophotometric methods revealed that the stoichiometry of the complex is 1:2 (metal : ligand). Beer's law is obeyed up to 31.75 ppm of Cu(II). Molar absorptivity and Sandell's sensitivity at 400 nm were found to be $7.0 \times 10^2 \text{ Lmol}^{-1}\text{cm}^{-1}$ and $0.090 \mu\text{g/cm}^2$ respectively. The stability constant of Cu(II)-HMBO complex is found to be 6.13×10^9 . Gibb's free energy change for complex formation reaction was found to be -13.93 Kcal/mol. The reagent can be used for the analysis of brass.

Key words: Oxime, Analytical reagent, 2-hydroxy-4-methoxybenzophenoneoxime, HMBO

Introduction

In the current scenario of analytical chemistry, many reagents are widely available for gravimetric and spectrophotometric determination of metal ions. They include o-hydroxy ketoxime¹⁻³, phenyl hydrazones, thiosemicarbozones⁴, chalcone oximes⁵ etc. In this work, we report the use of 2-hydroxy-4-methoxybenzophenoneoxime (HMBO) as a gravimetric reagent for Cu(II). Spectrophotometric methods have been used to confirm the stoichiometry of the complex and to determine the stability constant of the complex. The reagent is used to determine copper in brass.

Experimental

Spectrophotometric measurements were made on a shimadzu UV 160-A recording spectrophotometer. All the pH measurement were done on Elico pH meter (LI-10T) and buffer solution of required pH were obtained using sodium acetate-acetic acid & hydrochloric acid-sodium acetate buffers of suitable concentration.

Synthesis of 2-hydroxy-4-methoxybenzophenone oxime (HMBO)

2-hydroxy-4-methoxybenzophenone manufactured by sigma was converted to oxime by sodium acetate method. It was crystallized from ethanol. Colourless needles (m.p. $62 \pm 1^\circ\text{C}$) (N found = 5.76 %, calculated = 5.82). The oxime is soluble in solvents like ethanol, acetone, carbontetrachloride etc.

Stock solution

Stock solution of Cu(II) (0.05M) was prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water and was used after standardization with EDTA. Stock solution of HMBO (0.05 M) was prepared by dissolving oxime in 70 % aqueous ethanol.

Gravimetric procedure

A 10.0 ml aliquot of Cu(II) was diluted to 100 ml with distill water, warmed and the pH of the solution was adjusted in the range of 2.5 - 9.0 with suitable buffer. Then 0.05 M solution of HMBO in ethanol was added till precipitation was complete (about 22.0 ml added). The brown precipitate was digested on a water-bath at 60°C for 1 hr and filtered through a previously weighed sintered glass crucible G_4 . The precipitate was washed with hot water and finally with 70 % aqueous ethanol to remove any reagent which might have precipitated on dilution. The precipitates were dried on at 110°C and weighed.

Gravimetric determination of Cu

To establish the applicability of the reagent for gravimetric estimation of Cu(II), the metal ion was determinate in the pH range 2.5 - 9.0 . The maximum error being $\pm 1\%$. Estimation were done at pH 5 using different aliquots of Cu(II). In all cases the error in Cu(II) content did not exceed $\pm 0.06\%$ (Table - 1).

Table -1. Result of gravimetric estimation copper (II) at pH 5; Cu(II) HMBO

Copper taken (mg)	Complex obtained (mg)	Copper found (mg)	Error (mg)	Percentage %
15.89	0.1370	15.90	+0.01	+0.06
31.77	0.2737	31.76	-0.01	-0.03
47.66	0.4110	47.68	+0.02	+0.04
63.56	0.5480	63.57	+0.01	+0.01

Effect of diverse ions

In gravimetric determination of copper (31.77 mg) at pH 5, it was found that Ba^{+2} , Ca^{+2} , Sr^{+2} , Al^{+3} , Zn^{+2} and common anions Cl^- , Br^- , NO_2^- , SO_4^- did not interfere. At this pH Pd^{+2} , Co^{+2} & Fe^{+3} interfere seriously.

Spectrophotometric studies

For taking the absorbance spectra 5 mg chelate was dissolved in 25 ml chloroform and the absorbance was measured in the range of 350 - 800 nm. It was observed that absorbance of the solution increased continuously towards the shorter wavelength. The absorbance spectrum showed a shoulder at 400 nm and hence all measurements were carried out at 400 nm.

The Cu(II)-HMBO complex is insoluble in methanol and ethanol. It is soluble in solvents like chloroform, MIBK, 1:4 dioxane etc. Hence the complex was extracted in chloroform. For spectrophotometric studies varying amount Cu(II) solution was taken and pH was adjusted to 5 with ($\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$) buffer and HMBO solution was extracted with three 5 ml portion of CHCl_3 and the volume of CHCl_3 extract was made up to 25ml the absorbance of CHCl_3 extract was measured against solvent blank.

Validity of Beer's law

The Cu(II)-HMBO complex in chloroform obeys law up to 31.75 ppm of Cu(II). Beyond this concentration the absorbance plot showed deviation from linearity. The molar absorptivity of the complex obtained from absorbance data is found to be $7.0 \times 10^2 \text{ Lmol}^{-1} \text{ cm}^{-1}$ at 400 nm. The Sandell was found $0.090 \mu\text{g/cm}^2$ of Cu(II) at 400 nm.

Graph - 1*Stoichiometry and stability constant of complex*

The stoichiometry of Cu(II)-HMBO complex was determined by (1) Job's method⁶ of continuous variation and (2) Yoe and Jones mole-ratio method⁷. Both the methods gave the metal : ligand ratio of 1 : 2. The stability constants were calculated using the formula:

$$K_s = 1 - \alpha / 4\alpha^3 c^2$$

Where, $\alpha = E_m - E_s / E_m$, (E_m is the maximum absorbance found from graph and E_s is the absorbance at stoichiometric molar ratio of the reagent in the complex), and it was found to be 6.13×10^9 from K_s value. Gibb's free energy change for complex formation reaction was calculated and its value was found -13.43 Kcal/mol at 27 °C. The graphs were shown below:

Graph - 2. Job's method for Cu(II)-HMBO complex

Plots of Job's method of continuous variation for determination of M:L ratio
0.005 M Cu(II), 0.005 M HMBO; $pH = 5.0$; $\lambda = 400 \text{ nm}$

Graph - 3: Mole ratio method for Cu(II)-HMBO complex

Yoe and Jone's mole ratio method for determination of M:L ratio
 0.005 M Cu(II), 0.005 M HMBO;
 pH = 5.0; $\lambda = 400$ nm

Determination of copper in brass

Exactly 0.5041 gm of brass was taken dissolved in nitric acid (1 : 1). The excess nitric acid was boiled off and the solution was dilute to 100 ml with distilled water. The aliquot 10 ml was taken and Cu(II) was determined gravimetrically at pH 5.0 as described previously. Zn(II) and other trace metals did not interfere at this pH. The experiment was repeated three times. Cu (found): 69.23 %, Cu (reported): 70.69%

The same reagent has been taken for the determination of the other transition metal ions.

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