Dehydroacetic Acid Oxime as a New Ligand for Spectrophotometric Determination of Copper

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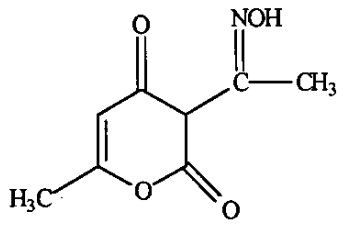
Summary: Dehydroacetic acid oxime (DAO) has been used as a ligand for spectrophotometric determination of copper. The reaction takes place in slightly acidic medium and the Cu-DAO complex absorbs radiation in the visible region at 460 nm. The absorption is free from any spectral interference as far as the reagent itself is concerned.

Introduction

Acetylacetone [1], azide ion [2], dithiocarbamates [3], dithizone [4], EDTA [5], ethylenediamine [6], nitroso-R-salt [7], xylenol orange [8], 8-hydroxyquinoline [9], thiocyanate [10], and dimethyl glyoxime are all well known ligands. Other ligand such as aliphatic hydroxyoxime [11] is well known for extraction of copper (II), nickel (II), cobalt (II) and iron (II) but are tedious and time consuming. There is some other organic simple reagent such as dehydroacetic acid oxime which has not been explored to a great extent for its metallochromic properties. The purpose of this work is to synthesize and evaluate the metal-complexation reaction of such a class of new reagent (I) which has oxygen-containing heterocyclic ring system and shows its colour reaction and stability towards Cu(II) ion. This thus seems suitable for spectrophotometric determination of metal ions.



Dehydroacetic acid oxime (DAO)

Results and Discussion

Dehydroacetic acid oxime and its infra-red spectrum

Spectrum is usually simple with few peaks.

O–H stretch occurs around 3764 cm^{-1} which is due to free oxime.

C–H stretch occurs around 3144 cm^{-1} which shows olefinic unsaturation.

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C=N stretch (or C=O stretch) around 1644 cm^{-1} may be due to oxime, ester or ketone.

O–H deformation around 1416 cm^{-1} is a characteristic absorption of the oxime.

C–O strech around 1262 cm^{-1} appears most probably from the cyclic skeleton.

H–C–H bending around 1166 cm^{-1} occurs due to methyl group.

C–C vibration appears around 1030 cm^{-1}

N–O stretch occurs around 932 cm^{-1} showing the presence of oxime.

Finally =NOH group has a characteristic absorption of approximately 682 cm^{-1}.

All these IR spectral information show that the compound is an oxime having structure 1. This, however, needs confirmation by elemental analysis (which we have not done).

Absorption spectra

The complexing reagent, dehydroacetic acid oxime (DAO), was found to give reaction with copper chloride in solution, preferably in acetonitrile solvent system. The complex formed was yellowish green and found to absorb at 460 nm Fig. 1. The absorption spectra as shown in Fig. 1 showed wavelength of maximum absorption for Cu-DAO complex. It also gave the wavelength of maximum absorption for DAO and copper chloride solutions alone at 285 nm and 325 nm respectively. This clearly shows that all these absorb at different wavelengths. The determination of copper is thus free from any spectral interference as far as the complexing reagent is concerned.

Determination of mole ratio

For this the mole concentration of the oxime was varied by taking 1 to 8 ml of 0.002M oxime solution for each 2 ml of 0.002M solution of $CuCl_2.2H_2O$ taken separately in different 10ml measuring flask. The reaction procedure was the same as described in the experimental part. The

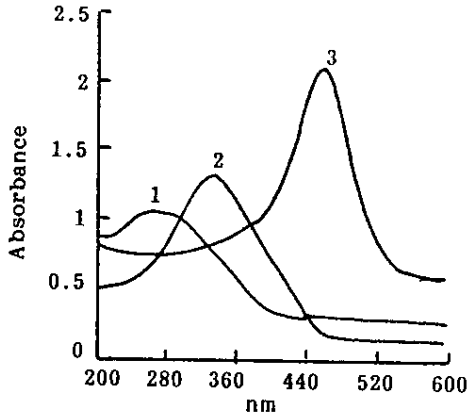

Fig. 1: Absorbance spectra.
1:DAO; 2. $CuCl_2.2H_2O$; 3. Cu-DAO complex.

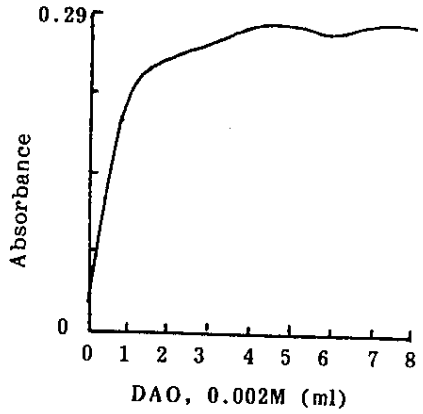

Fig. 2: Determination of mole ratio in metal-ligand complexation reaction.

absorbances were measured and plotted against the varying amounts of oxime used in the reaction. It was observed that the absorbance reached its maximum for the quantity of oxime when it was exactly double that of the metal (Cu) content, Fig. 2. This indicates that the reaction between the metal and the reagent was in the mole ratio of 1:2. This, however, needs further confirmation.

Effect of pH and the temperature

The experiment showed that the reaction in a medium at pH 5.8 was more reliable, although reaction below pH 5.8 was equally good. The reaction was also found to depend greatly upon

temperature. A temperature of 70°C (by heating in a water bath) gave maximum absorbance and this temperature was maintained during experimentations. The reaction is very fast and is complete within a minute or two to give reproducing results.

Stability of the metal-oxime complex

In order to establish that the complex formed is suitable and can safely be considered as an analytically important reaction for the estimation of copper, the absorbances of the complexes produced for varying concentrations of copper were measured at regular intervals of time. The absorbances remained unchanged even on long standing.

Fig. 3 clearly showed that complexes irrespective of copper being at high or low concentration were independent of time and had very little change in the absorbance readings. A concentration of copper varying from 0.002M to 0.004M gave complexes of copper with oxime which were stable for over a period of 2 hours with very minimal decaying of the complex.

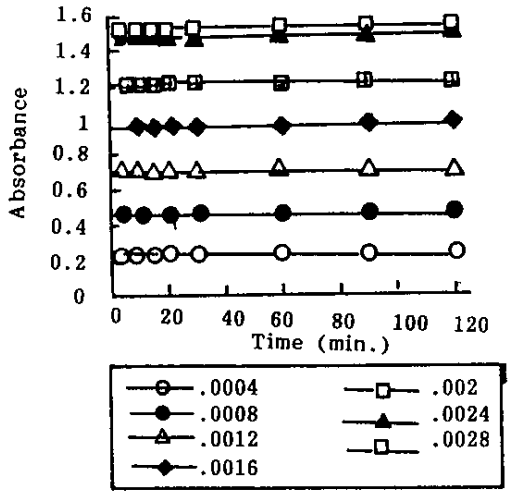

Fig. 3: Study of the stability of the metal ligand.

Absorbance versus concentration relationship

The reaction is quantitative. It was observed that the metal content in the concentration range of 2-100 ppm was suitable to give a linear relationship for complexation reaction with oxime, Fig. 4.

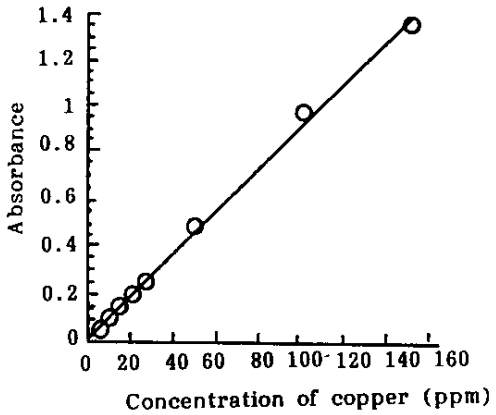

Fig. 4: Calibration curve.

Experimental

Chemicals

Dehydroacetic acid, hydroxylamine hydrochloride and sodium acetate were obtained from BDH. Acetonitrile, dimethyl sulphoxide and dimethyl formamide were from E. Merck. All other chemicals used were of analaR grade.

Reagents

1. Standard Copper (II) chloride solution (0.1M) was obtained by dissolving 1.7 g of copper chloride ($CuCl_2,2H_2O$) in acetonitrile and volume was made upto one litre. This was diluted five times to obtain its 0.002M solution.

2. Standard oxime solution (0.01M) was obtained by dissolving 1.89g of dehydroacetic acid oxime in acetonitrile and making the volume upto one litre in the same solvent.

3. Hydrochloric acid solution (-9.0, 6.0 and 4.0M) were obtained by diluting 776ml, 517ml and 666.5ml of analytical grade hydrochloric acid (11.6M) to one litre with distilled water in measuring flasks to obtained respective solutions.

4. Dehydroacetic acid oxime (DAO) was prepared according to the procedure in the literature [12].

General Experimental Procedure

5 ml of 0.01M (or any other) copper solution were pipetted out into a 25 ml beaker. 10 ml of 0.01M dehydroacetic acid oxime solution were introduced in it and pH was checked that it is between 5 and 5.8. The solution was warmed on water bath upto 70°C. Then it was cooled and transferred to a 25 ml measuring flask. The volume was made upto the mark with acetonitrile solvent. The absorbance was measured at 460 nm against a reagent blank, using a cell of 1 cm path length. The wavelength 460 nm was experimentally found to give maximum absorbance.

Conclusion

The reagent is simple, cheap and suitable for quantitative estimation of Copper in an acidic medium, preferably at pH 5.8. The other metallic ions may also be estimated by maintaining a suitable pH other than 5.8.

References

1. A.H.I. Ben-Basssat and G. Frydman-Kupler, *Chemist-Analyst*, **51**, 44 (1962); *ibid*, *52*, 8 (1963).
2. F. Maggio and F.P. Cavasino, *Ann. Chem.*, **51**, 1392 (1961).
3. J.A. Barbron, P.A. Schaeffer, A. Truchan and L. Deal, *Ind. Eng. Chem., Anal.* edn., **18**, 554 (1946).
4. H.W. Pender, *Anal. Chem.*, **30**, 1915 (1958).
5. G. Schwarzenbach and H. Flahka, Complexometric titration, trans. H.M.N.H. Irving, 2nd ed., Methuen and Co., London (1969).
6. V.A. Shormanov, A.A. Pyatachkov and G.A. Krestov, *Zh. Fiz. Khim.*, **59**, 1306 (1985) (Russ.).
7. S.P. Sangal, J. Parkt. *Chem.*, **29**, 76 (1965).
8. O. Otomo, Jap. Anal., 14, 45 (1965).
9. Kwok-Yuen Chan and Ton-Pal-Tam, *Chemistry* (Taipei) (1969).
10. R.E. Stoner and W. Daster, *Clin. Chem.*, **10**, 367 (1964).
11. F. Fiegl, *Ber. dt. Chem.Ger.*, **56**, 2083 (1923).
12. J. Iqbal, M. Aminuddin and A. Tahir, *J. Pure and Applied Sci.* **13**(2), 11 (1994).