Asian Journal of Chemistry Vol. 10, No. 4 (1998), 910–914

Use of 2-Hydroxy-4-Isopropoxypropiophenone Oxime as a Spectrophotometric Reagent for Iron

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2-Hydroxy-4-isopropoxypropiophenone oxime (HIPPO) has been developed as a new spectrophotometric reagent for iron. The reagent gives purple coloured Fe(III) complex in the pH range 2.0–3.0. The stoichiometry of the complex is found to be 1 : 1 by Job's method and mole ratio method. The molar absorptivity of complex at 490 nm is found to be 1.214×10^3 lit. mol^{-1} cm^{-1} and Sandell's sensitivity is found to be 0.046 $\mu g/cm^2$. The stability constant of the complex is found to be 1.41×10^5 and Gibb's free energy change for complex formation reaction is calculated to be –7.06 kcal/mol at 27°C. The Beer law is obeyed up to 7.84 ppm of Fe(III) ion. The reagent has been found to give quite satisfactory results for the analysis of iron in pharmaceutical preparations and dolomite ore. The reagent has been used as an indicator for the photometric titration of Fe(III) with EDTA.

INTRODUCTION

Various *o*-hydroxy ketoximes[1–3], phenyl hydrazones, chalcones, chalcone oximes etc. have been used for the spectrophotometric and gravimetric determination of iron and other transition metal ions. 2-Hydroxy-4-ethoxy acetophenone oxime[4] and 2-hydroxy-4-n-propoxyvalerophenone oxime[5] have been used to determine Fe(III). Here we report the use of 2-hydroxy-4-isopropoxypropiophenone oxime as a spectrophotometric reagent for Fe(III).

EXPERIMENTAL

Spectrophotometric measurements were mode on Bausch and Lomb spectrophotometer [Spectronic-20]. All the pH measurements were done on Elico pH-meter (LI-10 T).

Synthesis of 2-hydroxy-4-isopropoxypropiophenone oxime (HIPPO)

Respropiophenone was prepared from resorcinol, propionic acid and anhydrous zinc chloride according to the method of Brewster and Harris.[6] 2-Hydroxy-4-isopropoxypropiophenone was prepared from respropiophenone using isopropyl bromide and anhydrous potassium carbonate in acetone. 2-Hydroxy-4-isopropoxypropiophenone oxime was prepared by sodium acetate method. It was crystallized from ethanol. Colourless needles (m.p. 93 ± 1°C) were

obtained. (N found 6.12%, calculated 6.27%). The reagent is soluble in solvents like ethanol, carbon tetrachloride, acetone etc.

Stock solution of Fe(III) (0.05 M) has been prepared by dissolving ferric chloride (anhydrous) in distilled water containing few drops of HCl acid. The amount of Fe(III) in this solution was determined gravimetrically as ferric oxide and volumetically with EDTA.[7] Stock solution of HIPPO (0.05 M) was prepared by dissolving oxime in 70% aqueous ethanol.

Preparation of Fe(III)-HIPPO complex: A series of buffer solutions with pH values ranging from 2.0–4.0 were prepared using hydrochloric acid and sodium acetate. To 1.0 mL of 0.005 M Fe(III) solution, 5 mL buffer solution and 3 mL of 0.02 M ethanolic solution of HIPPO were added and the solution was diluted upto 25 mL keeping final concentration of alcohol 75%. The appearance of purple colour indicated complex formation. The spectra of the above solutions were recorded from 360 nm to 600 nm at different pH.

RESULTS AND DISCUSSION

Selection of wavelength: The absorbance measurement of Fe (III)-HIPPO complex showed that the absorbance of coloured solution of the complex increases continuously towards the shorter wavelength. The spectrum has a shoulder at 490 nm. A wavelength of 490 nm is selected for the present work.

Effect of pH: The colour of the complex was purple between the pH range 2.0–3.0. Above pH 3.0 the colour of the complex was reddish brown and was highly unstable. The complex was quite stable below pH 3.0. Therefore all the measurements were done at pH 2.5.

Stoichiometry and stability constant of the complex: The method of Vosburgh and Copper[8] showed that only one complex is formed. The stoichiometry of

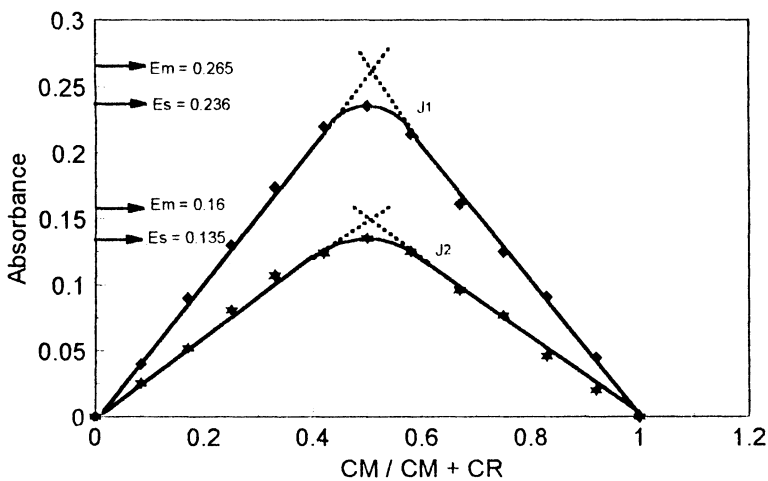

Fig. 1 Job's method of continuous variation
Plots of Job's method of continous variation (J_1, J_2) for determination of M : L ratio
(i) J_1 : 0.002 M Fe(III), 0.002 M HIPPO (ii) J_2 : 0.001 M Fe(III), 0.001 M HIPPO
pH = 2.5; λ = 490 nm

Fe(III)-HIPPO complex was studied by Job's method of continuous variation[9] and Yoe and Jone's mole ratio method.[10] Both the methods gave the metal-ligand ratio of 1 : 1.

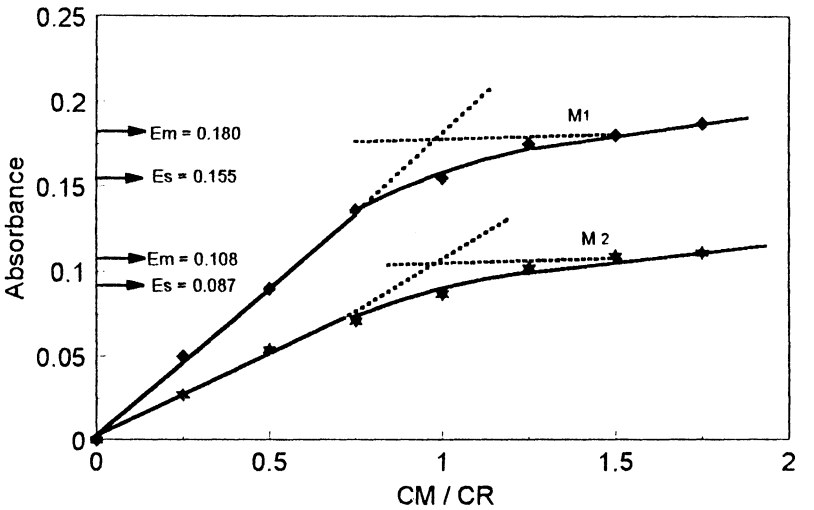

Fig. 2 Yoe and Jone's mole ratio method
Plots of Job's method of continuous variation (J_1, J_2) for determination of M : L ratio (i) M_1 : 0.002 M Fe(III), 0.002 M HIPPO (ii) M_2 : 0.001 M Fe(III), 0.001 M HIPPO pH = 2.5; λ = 490 nm

Stability constants were calculated from both methods using the formula

$$K_s = \frac{1-\alpha}{\alpha^2 C}$$

where $\alpha = \frac{E_m - E_s}{E_m}$ (E_m and E_s found from graph as shown).

TABLE-1
STABILITY CONSTANT OF Fe(III)-HIPPO COMPLEX AT 27°C

Method employed		E_m	E_s	α	K_s (n = 1)
Job's ratio method	J_1	0.265	0.236	0.1094	1.50×10^5
	J_2	0.160	0.135	0.1562	1.44×10^5
Mole ratio method	M_1	0.180	0.155	0.1388	1.39×10^5
	M_2	0.108	0.087	0.1940	1.33×10^5
Mean K_s					1.41×10^5

From K_s value, $\Delta G°$ for the complex formation at 27°C was calculated using the formula $\Delta G° = -RT \ln K_c$. This was found to be –7.06 Kcal/mole.

Validity of Beer's law: The Fe(III)-HIPPO complex obeys the Beer's law up to 7.84 ppm of Fe(III) ion. The molar absorptivity calculated from the Beer's law plot is found to be 1.21×10^3 lit mol^{-1} cm^{-1} at 490 nm. Sandell's sensitivity was calculated and found to be 0.046 $\mu g/cm^2$.

Determination of Iron in medicinal samples: Medicinal sample tablets were treated with nitric acid and the mixture was evaporated to dryness. Similar treatment was given 3 to 4 times. Finally the residue was dissolved in distilled water containing few drops of nitric acid and filtered. The filtrate was diluted to 100 mL. 10 mL of the above solution was further diluted to 100 mL and suitable aliquot portion was taken for analysis in 25 mL volumetric flask. The complex was formed by adding suitable buffer, excess reagent and diluting it to the mark. Absorbance was measured and mg of iron was determined from Beer's law calibration plot.

TABLE-2
DETERMINATION OF IRON IN MEDICINAL SAMPLES

Sample	Iron content (mg)		Relative error %
	Expected	Found	
lberol	105.00	104.63	–0.35
Fesovit	55.26	55.88	+1.12
Fecontin-f-continus	100.00	101.06	+1.06
Fefol	55.26	54.69	–1.03

Determination of Iron in Dolomite Ore: An exact amount of dolomite ore (*i.e.*, 2 g) was weighed and transferred to a 250 mL beaker. 50 mL 1 : 1 HCl was added to it and heated gently to dissolve the ore. It was evaporated to almost dryness. The procedure was repeated using three, 50 mL portions of 1 : 1 HCl and finally the solution obtained on dissolving the residue in 1 : 1 HCl was filtered through whatman filter paper to remove the insoluble silica. The residue on filter paper was washed thoroughly with distilled water and this filtrate was taken in a beaker and 2 mL conc. HNO_3 was added to it. It was then heated to oxidise all iron to Fe(III) state. This filtrate was diluted to 100 mL with distilled water. 5 mL aliquot from the filtrate was taken. 5 mL, 0.02 M solution of HIPPO, 5 mL ethanol and 5 mL buffer solution of pH 2.5 was added. The contents were diluted to 25 mL with ethanol. Absorbance of the solution was measured at 490 nm. Iron was found to be 0.466% [average of three determinations]. The iron(III) in the same dolomite determined using 1,10-phenanthroline was found to be 0.470%. Thus, the reagent gives results in iron determination, which are comparable with the established method.

Photometric determination of Fe(III) with EDTA using HIPPO as an Indicator: Ferric(III)-EDTA is more stable than purple coloured Fe(III)-HIPPO complex and hence on addition of EDTA solution, the colour goes on disappearing slowing.Therefore Fe(III) iron could be determined by photometric titration with EDTA using 2-hydroxy-4-isopropoxypropiophenone oxime as an indicator.

An aliquot of 50 mL of 0.025 M $FeCl_3$ solution was taken in a beaker. 10 mL buffer of pH 2.5 was added to it. 2 mL, 1% solution of 2-hydroxy-4-isopropoxy propiophenone oxime in 95% ethanol was added to it. This solution was titrated against 0.05 M EDTA solution from the burette. After each addition, the absorbance of the solution was measured at 490 nm. The absorbance went on decreasing and at the equivalence point it attained constant value. Volume corrections for absorbance values were made. The end point was obtained by extrapolating a straight line segment of the volume-absorbance curve. The iron content determined agrees well with the iron determined using standard method.

ACKNOWLEDGEMENT

The authors are thankful to Head, Chemistry Department, South Gujarat University, Surat, for the facilities and co-operation in the work.

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(*Received:* 6 April 1998; *Accepted:* 9 June 1998) AJC-1512