www.sphinxsai.com

ChemTech

International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.1, No.4, pp 868-872, Oct-Dec 2009

2-Hydroxy-4-Isobutoxy Acetophenone Oxime as spectrophotomeric reagent for Manganese

J.R.SHUKLA* & S.S.SHAH
Department of Chemistry
Shri U.P.Arts, Smt.M.G.Panchal Science and V.L.Shah Commerce College,
Pilvai-382 850 (India)
Corres.author : jrshukla@yahoo.co.in

ABSTRACT: 2-Hydroxy-4-isobutoxy acetophenone oxime(HIBAO) has been used for the spectrophotometric determination for Mn(II) at pH range 10.5 to 11.5 in chloroform medium. Job's method for continuous variation, Yoe and Jones' mole ratio method, the slope ratio method shows metal ligand ratio in complex to be 1:2. The stability constant of the complex is found to be 7.09×10^9. The Greenish Brown coloured complex obeys Beer's law in the concentration range 2.75ppm to 43.95ppm for Mn(II) ion, while the optimum concentration range from Ringbom plot is found to be 10.99ppm to 32.96ppm. The photometric sensitivity and molar absorptivity at the 600nm are found to be 0.040µg/cm^2 and 1360 L.mol^{-1}cm^{-1} respectively. The standard free energy of formation of complex is -13.63 kcal/mole at 30^{o}C. The complex is stable for One week. The reagent has also been found to give quite satisfactory results for Mn(II) present in synthetic mixtures. The antimicrobial Activity of HIBAO and Mn-HIBAO complex have also been checked.

INTRODUCTION

Various o-hydroxy phenones, phenone oximes, phenyl hydrozones, chalknoneoximes, etc, have been used as an analytical reagent for the spectrophotometric and gravimetric determination of Manganese and other transition metal ions[1-5]. In the present work the use of 2-hydroxy-4-isobutoxy acetophenone oxime (HIBAO) as photometric reagent for Mn(II) has been described.

EXPERIMENTAL

A 0.1M stock solution of Mn(II) has been prepared by dissolving Manganese Chloride (A.R) in distilled water. The amount of Mn(II) in this solution was determined following standard procedures[6].

Preparation of 2-Hydroxy-4-isobutoxy acetophenone oxime (HIBAO):

Resacetophenone was prepared from resorcinol by standard methods[7].2-Hydroxy-4-isobutoxyacetophenone(HIBA) has been prepared by refluxing resacetophenone and isobutylbromide in suitable solvent for 4 hrs. 2-Hydroxy-4-isobutoxyacetophenoneoxime (HIBAO)[8] has been prepared by refluxing HIBA with hydroxyl amine hydrochloride in the presence of sodium acetate in ethanol medium for 4 hrs. The reagent when recrystallized from ethanol was obtained in the colourless, needle like crystals (m.p. 102^{o}C ± 1^{o}C), with M.W 223.40gm. (calcd. for $C_{12}H_{17}NO_3$=223.27gm). The reagent is insoluble in water but soluble in alcohol, acetone benzene chloroform, carbon tetrachloride, etc. The elemental analysis, IR spectra and Mass spectra of the compound confirm its structure.

Preparation of Mn(II)-HIBAO complex and selection of solvent :

When an alcoholic solution of HIBAO was added to 0.01M aqueous metal ion solution, greenish Brown precipitates of complex were obtained in the pH range 10.5-11.5. The complex was found to be insoluble in polar solvents like water, methanol or ethanol but soluble in non-polar solvents like chloroform, benzene, CCl_4 etc. As Mn-HIBAO complex was more soluble in chloroform, it was selected as a solvent for extractive spectrophotometric determination of Mn(II).

Apparatus :

Spectrophotometric measurements were made with a Systronics UV/VIS spectrophotometer (model-118) using 10mm glass cells. All pH measurements were made with Systronic pH meter (model-324).

RESULTS AND DISCUSSION

Results are given in Fig. I-IV and Table I-II.

Optimum pH and Selection of Wavelength :

The pH of the solution has pronounced effect on the reaction between Mn(II) and HIBAO and the stability of the complex. on the other hand the absorbance is dependant upon the wavelength used. Both the

parameters were therefore controlled to give maximum absorbance. Absorbance measurements of the reagent in chloroform show maxima at 240nm, 268nm and 301nm with negligible absorbance beyond 400nm. The absorbance measurements of Mn(II)-HIBAO complex show a maxima at 400nm and 600nm. As the interference due to the reagent appeared to be negligible at wavelength of 600 nm was selected for the present work.

To determine the optimum pH for complex formation series of buffer solutions with pH values ranging from 8.0 to 11.5 were prepared. To above buffer solutions, 1.0 ml of 0.005M Mn(II) solution and 10 ml 0.005M HIBAO solution in chloroform were added. After shaking the mixture for two minutes, the greenish brown coloured complex was extracted. The absorbance of organic layer containing complex was measured at 600nm against a blank. From the results given in Fig. I, it may be generalized that maximum absorbance takes place at pH range 10.5 to 11.5. Hence a pH of 11.0 and wavelength of 600nm have been selected for the present work.

Reproducibility :

Absorbance measurements of a set of six solution prepared in a similar way and containing the same concentrations of all the reagents show that the reproducibility of measurements are quite good with a standard deviation of $\pm$ 0.434 Units, i.e., 0.26%.

Effect of time and temperature :

To determine the effect of time and temperature on the basis intensity of colour and the stability of the Mn(II)-HIBAO complex, absorbance was measured at room temperature (30^{o}C) at regular intervals of time up to two week and also at temperatures of 30^{o}C to 55^{o}C. The results show that complex is stable ($\pm$ 2% deviation) for one weeks and up to 45^{o}C.

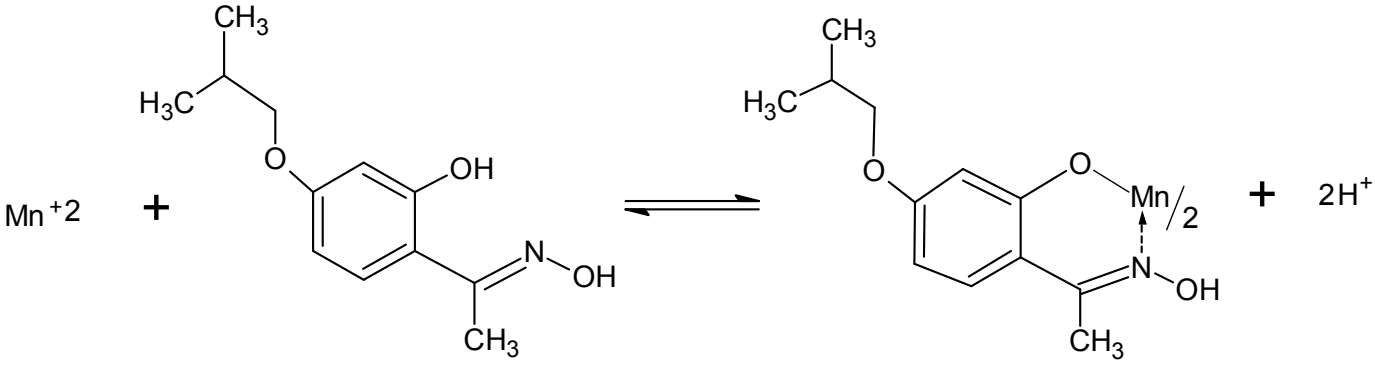
Stoichiometry and Stability Constant of the Complex :

The method of Vosbourgh and Cooper[9] showed that one complex is formed. To determine the stoichiometry of complex, Yoe and Jones mole ratio method[10] the slope ratio method[11] and Job's method of continuous variation[12] were employed (Fig. II-IV). All the three methods indicates that a metal:ligand ratio is 1:2 in the metalcomplex.

The value of the stability constants calMnlated from the job's method as well as from the mole ratio method are given in Table-I. From the table the average value of stability constant may be taken as 7.09×10^{9}. The standard free energy of formation of the complex, ΔG^{o}, is -13.63 kcal/mole at 30^{o}C.

The IR spectras of reagent and complex revealed that the –OH (stretch) band of 3393cm^{-1} for the reagent disappears when the complex is formed i.e., the complex formation takes place through the N of oximino group and O- of the 2-hydroxy group. Based on above data the Mn(II)-HIBAO complex can be assigned the following structure. The structure is also assigned by the data of magnetic susceptibility of the complex

.



Conformity to Beer's law and the optimum concentration range :

Beer's law is obeyed between the range 2.75ppm to 43.95ppm of Mn(II). At higher concentrations negative deviations occur. The optimum concentration range for determination of Mn(II) in solution, as deduced from the Ringbom plot[13], is found to be 10.99ppm to 32.96ppm. The molar absorptivity (ε) of the complex is 1360 L.mol^{-1}cm^{-1} and the photometric sensitivity as per Sendell's definition[14] is found to be 0.040μg/cm^{2} at 600nm.

Effect of diverse ions :

The effect of foreign ions on the spectrophotometric determination of Manganese was studied by adding these ions in quantities ranging from 1,00,000 to 10 μg to a solution containing 109.88 μg of Manganese. After adjusting the pH of the solution at 11.0, Mn(II) was exctracted as Mn(II)-HIBAO complex in the usual manner and the absorbance of the organic layer was measured. A difference of + 2% in the absorbance is taken as tolerance limit. The limit for various ions expressed in micrograms are as follows

up to 100000 µg : Na^{+}, K^{+}, NH_4^{+}
up to 10000 µg : Ca^{+2}, Ba^{+2}, Sr^{+2}, Mg^{+2}, Al^{+3}, Zn^{+2}, Cd^{+2}, Citrate, Cl^{-}, Br^{-}, tartrate, acetate, nitrate.
up to 1000 µg : Ag^{+},$Cr^{+3,}$ $UO2^{+2}$, Pd^{+2}
up to 100 µg : V^{+5}, Cu^{+2}, Ni^{+2}, Fe^{+3}, Co^{+2}.
up to 10 µg : EDTA

Determination of Manganese from various samples :
To determine the usefulness of the reagent in estimation of manganese from various samples containing manganese were taken and estimated by HIBAO. For this purpose, The synthetic mixtures containing manganese metal were also taken for analysis. Aliquot of this sample solution was pipeted out and its spectrophotomatic determination was carried out by the proposed method. The result are given in Table-II.

Antimicrobial Activity :
HIBAO and Mn-HIBAO were screened for their antibacterial activity against Gram positive bacteria i.e. *Bacillus subtilis* and Gram negative bacteria i.e. *Psudomonas aeruginosa* using Cup-plate agar diffusion method[15]. The Fungi *Aspergillus niger* was used for antifungal activity of above compound using Mnp-plate agar diffusion method. HIBAO exhibit good antibacterial activity and excellent antifungal activity with respect to standard drugs while the Mn-HIBAO complex found quit good antibacterial and antifungal activity.

Table I: **Stability Constant of Mn(II) –HIBAO Complex at 30°C**

Method employed	Em	Es	α	K (n=1)
Mole ratio method				
Set-I	0.678	0.645	0.04867	8.25×10^{9}
Set-II	0.340	0..312	0.08235	6.57×10^{9}
Job's Method				
Set-I	0.272	0.246	0.09559	6.47×10^{9}
Set-II	0.540	0.508	0.05926	7.06×10^{9}
Mean K Stab				**7.09×10^{9}**

Table II: **Analysis of Manganese in various samples**

Sample	"Mn" taken		Absorbance	"Mn" found		Relative error (%)
	µg	%		µg	%	
Synthetic mixture No. 1	172.3	-	0.431	174.5	-	0.81
			0.418	169.3		
			0.438	177.4		
			Avg.	173.7		
Synthetic mixture No. 2	136.8	-	0.330	133.6	-	1.63
			0.346	140.1		
			0.354	143.4		
			Avg.	139.03		
Synthetic mixture No. 3	226.1	-	0.579	222.3	-	0.79
			0.567	229.6		
			0.572	231.6		
			Avg.	227.8		

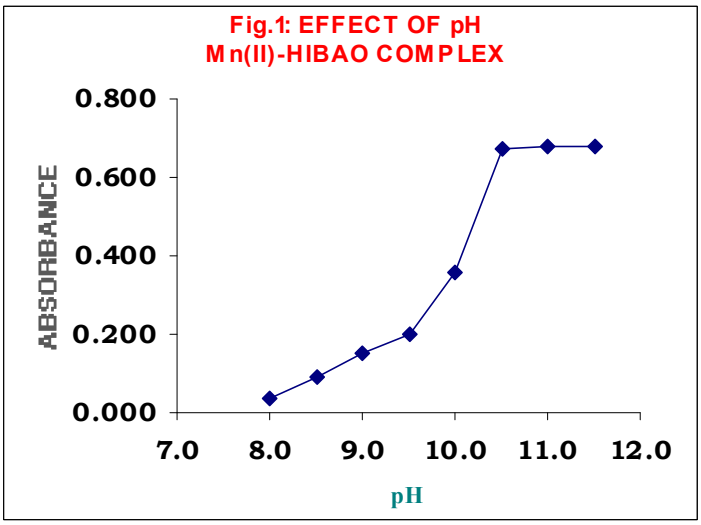


Fig : I : Effect of pH

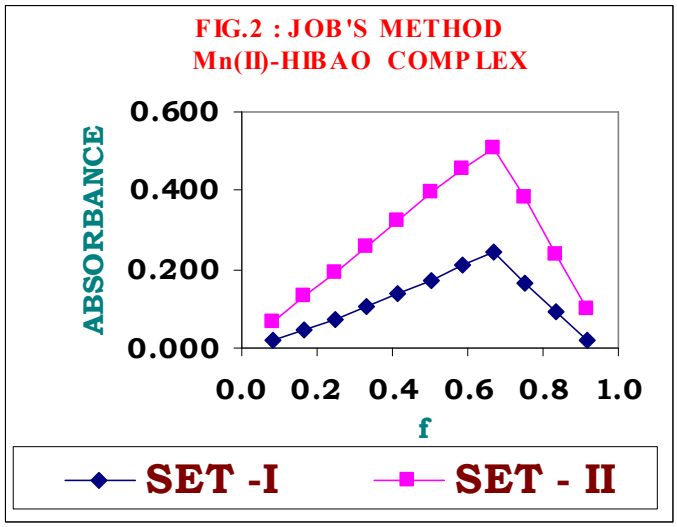


Fig : II : Job's method of continuous variation
Set-I : 0.001 M Mn(II) and 0.001 M HIBAO
Set-II : 0.002 M Mn(II) and 0.002 M HIBAO

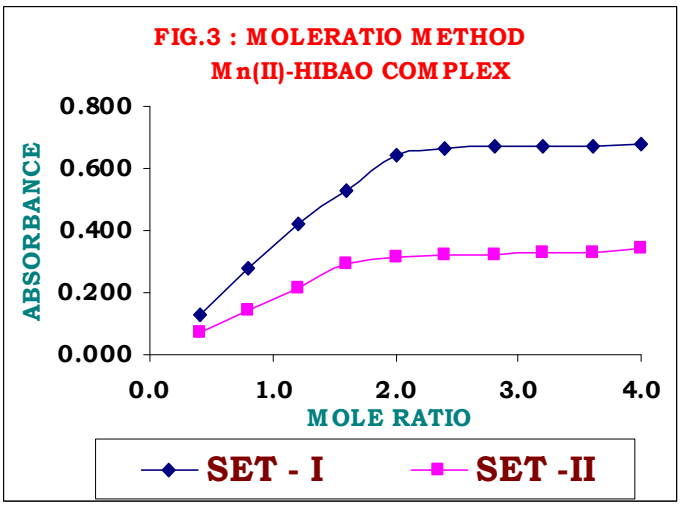


Fig : III : Yoe and Jones mole ratio method
Set-I :0.001M Mn(II) and 0.002M HIBAO,
Set-II :0.0005M Mn(II) and 0.001M HIBAO

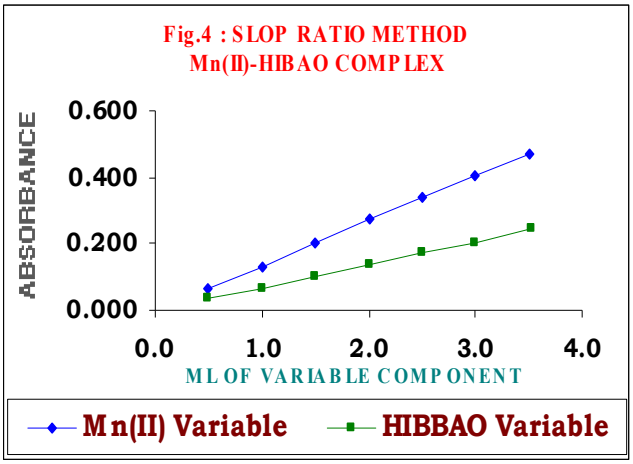


Fig: IV : Slope ratio method.
10 ml 0.001 M HIBAO ; 0.001M Mn(II) (variable)
10 ml 0.001 M Mn(II) ; 0.001M HIBAO (variable)

ACKNOWLEDGEMENTS

The authors are thankful to Uttar-Purva Gujarat Uchcha Kelvani Mandal, Pilvai, for providing laboratory facilities. The authros are also thankful to SICART, V.V Nagar, for providing elemental analysis and Bombay Tablets, Ganndhinagar for spectral analysis.

REFERENCES

1. J.D.Talati, and K.S.Parikh, *"Anarta"*, *J. North Gujarat Uni.,* **3**, 93, (1992).
2. J.D.Talati, and K.S.Parikh, *J. Inst. Chemists (INDIA),* **65**, 84, (1993).
3. J.D.Talati, and K.S.Parikh, *Asin J. Chem*., **6**,581, (1994).
4. J.A.Dave and S.S.Shah, Asian J. Chem., **20**, 4141,(2008).
5. Suketu I. Desai, Vikas A. Desai and H.B.Niak, Asian J. Chem., **20**, 4919,(2008).
6. A.I.Vogel, *"A Text Book of Quantitative Inorganic Analysis",* 4th Ed., (Longaman, London), 322, 1978,.
7. Brewster, C.M. and J.C.Harris, *J.Amer Chem Soc*., **52**, 4866 (1930).
8. A.I.Vogel, "*A Text Book of Practical Organic Chemistry,* 3rd Ed., (Longaman, London), 341, (1966).
9. W.C.Vosburgh and G.R.Cooper, J.Amer.Chem.Soc., **63**, 473 (1941).
10. J.H.Yoe and A.L.Jones, *Ind.Eng.Chem., Anal. Ed*., **16**, 111 (1944).
11. Harvey, A.E. and D.L.Manning, *J.Amer.Chem.Soc*., **72**, 4488 (1950).
12. P.Job, *Ann. Chem*., **9**, 113 (1928).
13. Ringbom, *Anal. Chem*., **115**, 332 (1938).
14. E.B.Sandell, *"Colorimetric determination of traces of metals"*, 3rd Ed., (inderscience, New York), pp.83, (1959).
15. A. L. Barry, Procedure and Theoretical Consideration for testing anti microbial agents in Agar media, 5th edition William and wilkins Baltimore,(1991).

*****