Spectrophotometric Determination of Vanadium using 2-Hydroxy-4-Isobutoxy Acetophenone Oxime

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ABSTRACT

2-Hydroxy-4-isobutoxy acetophenone oxime (HIBAO) has been used for the spectrophotometric determination for V(v) at pH range 2 to 3 in chloroform medium. Job's method for continuous variation, Yoe and Jones' mole ratio method, the slope ratio method show metal ligand ratio in complex to be 1:2. The stability constant of the complex is found to be 3.39×10^8. The yellow coloured complex obeys Beer's law in the concentration range 25.47 µg/ml to 203.76 µg/ml for V(v) ion, while the optimum concentration range from Ringbom plot is found to be 76.41 to 203.76 ppm. The photometric sensitivity and molar absorptivity at the 580nm are found to be 0.361 µg/cm^2 and 161 mol^{-1}cm^{-1} respectively. The standard free energy of formation of complex is   -11.82 kcal/mole at 30°C. The complex is stable for 48 hrs. The reagent has also been found to give quite satisfactory results for V(v) present in alloy like brass, bronze and synthetic mixtures. The antimicrobial Activity of HIBAO and V-HIBAO complex have also been checked.

Keywords: HIBAO, CCl, UV/VIS

I.   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 Vanadium 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 V(v) has been described.

II. METHODS AND MATERIAL

A 0.1M stock solution of V(v) has been prepared by dissolving Ammonium meta Vanadate (A.R) in minimum quantity of dilute sodium hydroxide solution and then diluted with distilled water. The amount of V(v) 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 isobutyl bromide 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°C $\pm$ 1°C), with M.W 223.40 (calcd. for $C_{12}H_{17}NO_3$ = 223.27). The reagent is insoluble in water but soluble in alcohol, acetone benzene chloroform, carbon tetrachloride, etc. The elemental analysis

and spectral analysis of the compound confirm its structure.

Preparation of V(v)-HIBAO complex and selection of solvent : When an alcoholic solution of HIBAO was added to 0.01 M aqueous metal ion solution, yellow precipitates of complex were obtained in the pH range 2.0 - 3.0. 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 V-HIBAO complex was more soluble in chloroform, it was selected as a solvent for extractive spectrophotometric determination of V(v).

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).

III. RESULTS AND DISCUSSION

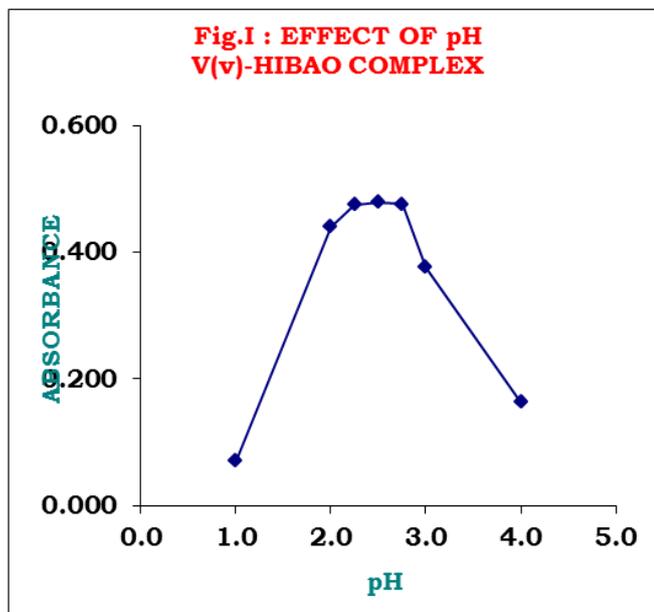Results are given in Fig. I-IV and Table I-II.
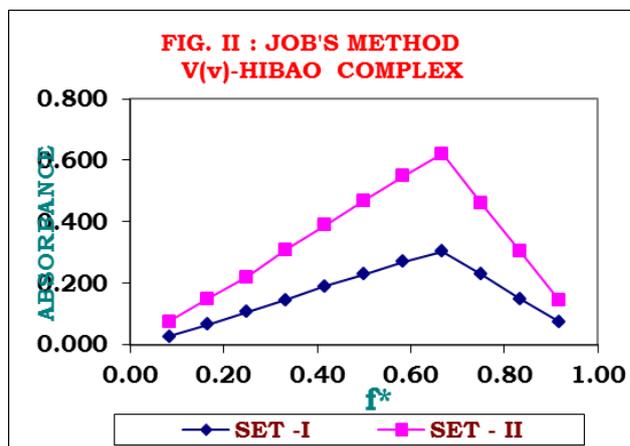

Figure I: Effect of pH

Figure II : Job's method of continuous variation
Set-I   : 0.01 M V(v) and 0.01 M HIBAO
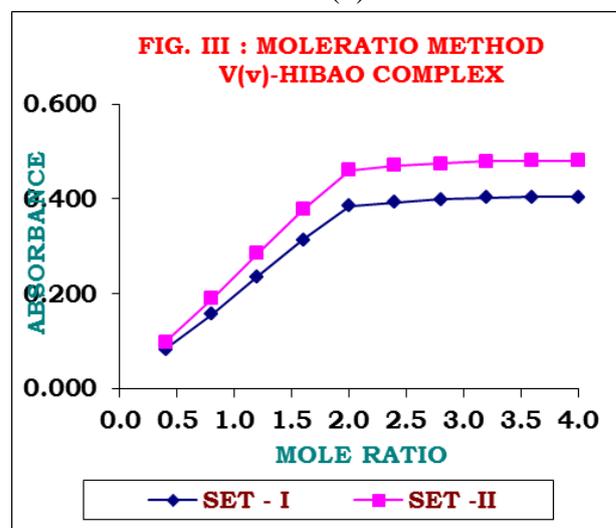Set-II   : 0.02 M V(v) and 0.02 M HIBAO

Figure III : Yoe and Jones mole ratio method
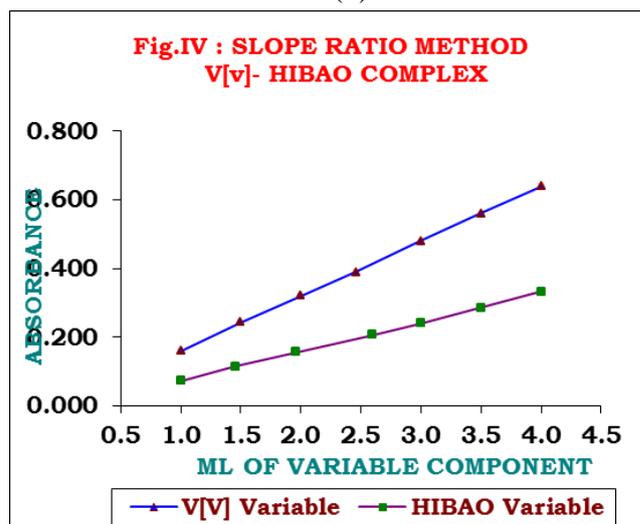Set-I :0.005M V(v) and 0.010M HIBAO,
Set-II :0.0025M V(v) and 0.005M HIBAO

Figure IV : Slope ratio method.
10 ml 0.01 M HIBAO ; 0.01M V(v) (variable)
10 ml 0.01 M V(v)   ; 0.01 M HIBAO (variable)

Table I: Stability Constant of V(v) –HIBAO Complex at 30°C

Method employed	Em	Es	α	K (n=1)
Mole ratio method				
Set-I	0.405	0.385	0.04938	3.16×10^8
Set-II	0.481	0.461	0.04158	3.70×10^8
Job's Method				
Set-I	0.322	0.304	0.05590	3.38×10^8
Set-II	0.644	0.621	0.03571	3.31×10^8
Mean K Stab				$\mathbf{3.39 \times 10^8}$

Table II: Analysis of Vanadium in various samples

Sample	"V" taken		Absorbance	"V" found		Relative error (%)
	μg	%		μg	%	
Synthetic mixture No. 1	382.1	-	0.117	367.9	-	1.24
			0.124	389.9		
			0.128	402.5		
			Avg.	386.8		
Synthetic mixture No. 2	764.1	-	0.236	745.2	-	0.67
			0.244	760.3		
			0.254	802.0		
			Avg.	769.2		
Synthetic mixture No. 3	1018.8	-	0.310	980.8	-	0.41
			0.336	1063.1		
			0.324	1025.1		
			Avg.	1023.0		

Optimum pH and Selection of Wavelength : The pH of the solution has pronounced effect on the reaction between V(v) 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 390 nm and 580 nm with negligible absorbance beyond 390 nm. The absorbance measurements of V(v)-HIBAO complex show a maxima at 390 nm and 580 nm. As the interference due to the reagent appeared to be negligible a wavelength of 580 nm was selected for the present work.

To determine the optimum pH for complex formation series of buffer solutions with pH values ranging from 2.0 to 3.0 were prepared. To above buffer solutions, 2.0 ml of 0.01 M V(v) solution and 10 ml 0.01 HIBAO solution in chloroform were added. After shaking the mixture for two minutes, the yellow complex was extracted. The absorbance of organic layer containing complex was measured at 580nm against a blank. From the results given in Fig. I, it may be generalized that maximum absorbance takes place at pH range 2.25 to 2.75. Hence a pH of 2.50 and wavelength of 580 nm have been selected for the present work.
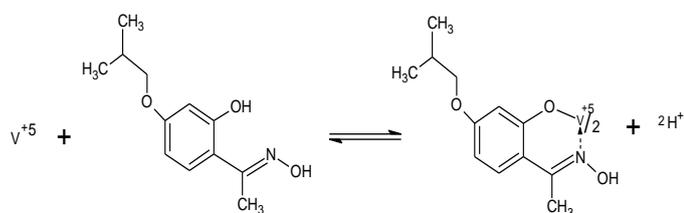
Reproducibility : Absorbance measurements of a set of ten solution prepared in a similar way and containing the same concentrations of all the reagents show that the reproducibility of measurements are quite good with a standard deviation of ± 3.729 Units, i.e., 0.37%.

Effect of time and temperature : To determine the effect of time and temperature on the intensity of colour and the stability of the V(v)- HIBAO complex, absorbance was measured at room temperature (30^oC) at regular intervals of time up to 48 hrs and also at temperatures of 30^oC to 55^oC. The results show that complex is stable (± 2% deviation) for two weeks and up to 45^oC.

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 show a 1:2 metal:ligand ratio in the complex.

The value of the stability constants calculated 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 3.39×10^8. The standard free energy of formation of the complex, ΔG^o, is -11.82 kcal/mole at 30^oC.

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 V(v)-HIBAO complex can be assigned the following structure.

Conformity to Beer's law and the optimum concentration range : Beer's law is obeyed between the range 25.47 to 203.76 ppm of V(v). At higher concentrations negative deviations occur.

The optimum concentration range for determination of V(v) in solution, as deduced from the Ringbom plot[13], is found to be 76.41 to 203.76 ppm. The molar absorptivity (ε) of the complex is $161 \ mol^{-1}cm^{-1}$ and the photometric sensitivity as per Sendell's definition[14] is found to be $0.361 \mu g/cm^2$ at 580nm.

Effect of diverse ions : The interference due to the presence of other ions on the determination Vanadium ions as V(v)-HIBAO complex has also been studied. A difference of more than ± 2 % in the absorbance value has been considered as interference. According to this criterion, the tolerance limits of various ions, expressed in μg, for a solution containing $509.40 \ \mu g$ (V(v)) are as follows.

up to 100000 μg : Na^+, K^+, NH_4^+.

up to 10000 μg : F^{--}, Cl^{--}, NO_3^{--}, SO_4^{--2}, BO_3^{--3}. : Perchlorate, tartrate,

up to 1000 μg : Ca^{+2}, Ba^{+2}, Sr^{+2}, Pb^{+2}, Mo^{+6}, I^{--}, Thiocynate.

up to 100 μg : Mn^{+2}, Al^{+3}, Zn^{+2}, Sb^{+3}, Sn^{+2}, Bi^{+3}, Cr^{+3}.

up to 10 μg : EDTA, Mg^{+2}, Ni^{+2}, Co^{+2}, Cu^{+2}.

Determination of Vanadium from various samples

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

Antimicrobial Activity :

HIBAO and V-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. The Fungi *Aspergillus niger* was used for antifungal activity of above compound using Cup-plate agar diffusion method. HIBAO exhibit good antibacterial activity and excellent antifungal activity with respect to standard drugs while the V-HIBAO complex found quit good antibacterial and antifungal activity.

IV. ACKNOWLEDGEMENTS

V. REFERENCES

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