
Spectrophotometric Microdetermination of Fe(III) and V(V) Using Schiff Base Derived from Salicylhydroxamic Acid

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Abstract: *A simple, rapid, accurate, precise and sensitive spectrophotometric method for determination of Fe^{+3} and V^{5+} in bulk sample using Schiff base derived from salicylhydroxamic acid is described. The method is based on the formation of coloured complexes in weak acidic medium. The coloured products have showed absorption band at λ_{max} 460 nm for Fe^{+3} – complex and also absorption band at λ_{max} 632 nm for V^{5+} –complex, respectively . The apparent molar ratio of complexes are (1:1) and (1:2) M : L in 20 % (v/v) ethanol solution as well as the formation constants for Fe^{+3} -complexes are 4.29 and 8.2, and for V^{5+} -complexes are 5.33 and 8.54, respectively. Beer's law is obeyed in the concentration ranges 0.11-2.80 $\mu g\ ml^{-1}$ for Fe^{+3} and 1.34 – 6.69 $\mu g\ ml^{-1}$ for V^{5+} . The apparent molar absorptivity , relative standard deviations and recoveries are calculated and the effect of foreign ions is also discussed.*

Keywords: Salicyl hydroxamic acid Schiff base , spectrophotometry, ferric chloride and ammonium vanadate, universal buffer solution.

1. INTRODUCTION

A considerable amount of work has been done in the analytical applications involving colour formation of metal ions with hydroxamic acid derivatives [1]. Salicylhydroxamic acid is known as Schiff base [2] used as a constituent of growth factors, food additives, antibiotics, antifungal agents and cell- division factors, N-pentafluoro-benzoyl-N- phenylhydroxamic acid (p-FBPFA) has been investigated [3] at ionic strength of 0.2 and 25°C. The solid state complexes of Fe^{+3} , Co^{+2} , Cu^{+2} and Ni^{+2} with monohydroxamic acid is studied [4] . Spectrophotometric determination of Fe^{+3} and V^{+5} ions using N-furoyl –N-phenyl hydroxyl amine and its Schiff bases are investigated [5]. Several methods have been reported for the quantitative determination of Fe^{+3} and V^{+5} , including titrimetry [6] an electroanalytical method [7], liquid chromatography [8,9], gas liquid chromatography [10,11]. The coordination phenomena occurring with hydroxamic acid compounds have been investigated by many authors [12, 13].

The present work describes spectrophotometric method which is superior to the reported ones for rapidity and high sensitivity. Also, different spectrophotometric methods are used for the micro determination of Fe^{+3} and V^{+5} ions and their stability constants of their complexes in universal buffer solution [12].

2. EXPERIMENTAL

2.1 Apparatus

All the absorption spectral measurements are made using Jasco V- 530 UV /Visible spectrophotometer, with equipped 10mm matched quartz cell. A pH –meter of type Hanna glass electrode with calomel electrode as a reference with pH \pm 0.005 unit is used for pH measurements.

IR spectra are recorded using spectrometer model (Bomem ; model MB 1575) from 4000 to 400 cm^{-1} at room temperature.

The 1H NMR spectra are also measured with a varian EML 390 spectrometer at 200 MHZ using TMS as a reference in DmsO – d_6 solvent. The two pervious apparatous (IR and 1H NMR are performed in micro analytical centre of cairo university

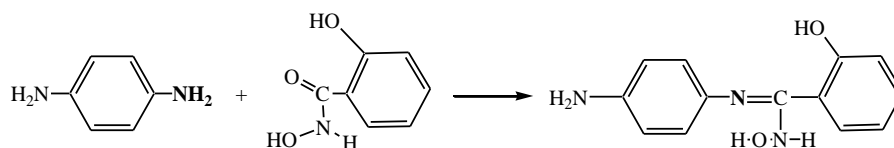
2.2 Reagents and standard solution

All chemicals are of analytical reagent grade, unless otherwise stated. Stock solution of (2×10^{-3} M) of both FeCl_3 and VO_3NH_4 salts are obtained from El-Nasr chemical company (ADWIC) and prepared by dissolving a known weight in bidistilled water and completed to 100 ml measuring flask as recommended [14]. A $100 \mu\text{g ml}^{-1}$ as a stock solutions of both V^{+5} and Fe^{+3} ions are prepared, as well as universal buffer solutions of the required pH are also prepared [14].

2.3 Preparation of the ligand

1.0814 gm of 1, 4-phenylene diamine are dissolved in (25 ml of ethanol) and added to 1.531 gm salicylhydroxamic acid in (15 ml of ethanol) dropwisly, the mixture is refluxed on water bath for 4 hrs. After that it is cooled at room temperature. The product is filtered and washed with ethanol, then recrystallised.

Scheme 1: preparation of the ligand



1, 4- phenylene diamine

salicylhydroxamic acid

Schiff base of salicylhydroxamic

3. RESULTS AND DISCUSSION

3.1 Analysis of the ligand

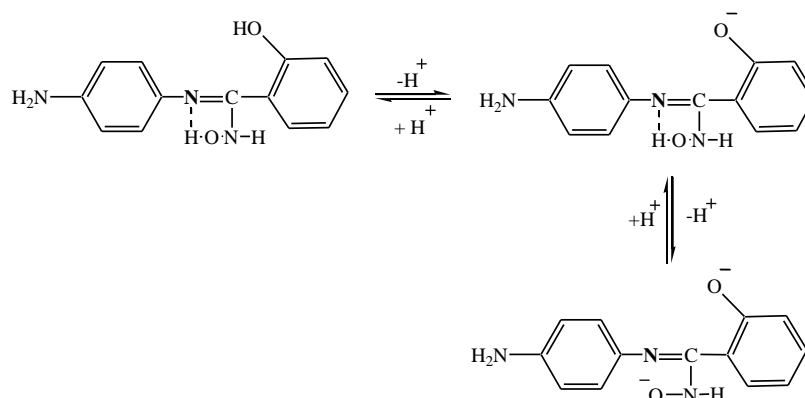
Elemental analysis (C, H, N), IR spectra and ^1H NMR of the ligand are determined. The empirical formula ($\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_2$) indicated that %C calc (60) found (55.92), %H calc (6) found (5.93), %N calc (13) found (12.61) and the yield is found to be 80%. ^1H NMR is performed and showed strong signals appearing in the ranges 6.8 and 6.5 chemical shift which may be attributed to the hydrogen of both NH or OH groups, respectively. Also, signals appearing at the ranges 7.5- 9.0 chemical shift are due to the hydrogen of both phenyl group and Ar-C=N rings.

The bands assigned at 3350 cm^{-1} is attributed to ν_{OH} group, also the band appeared at 1618 cm^{-1} (s) is related to $\nu_{\text{C=N}}$. The bands appeared at 1350, 1249 (s) and 1030 are due to $\delta_{\text{C-H}}$ and $\delta_{\text{C-N}}$ of aromatic ring. Further more, the assigned bands at 823 and 745 cm^{-1} are due to aromatic symmetric and asymmetric $\delta_{\text{C-H}}$ [9,10] as detected in Table (1) .

3.2 Spectra in aqueous buffer solution

The spectra of the ligand displays some interesting changes in accordance with pH values. The ionization of the proton starts with an increase in the pH of the medium. Thus the spectra in acid solution have bands at 425 nm and 320 nm, the absorption increases with increasing of pH values till pH reached to 7.3, and after that the absorption decreases in basic medium till reached to 11.2. The ionization constant of the ligand is calculated [15] and found to be $\text{p}K_{a1}$ 5.5 and $\text{p}K_{a2}$ 9.5

Scheme 2: Ionization of the ligand



3.3 Effect of pH on the complex formation

The optimum pH value that favors the formation of metal-ligand complex (maximum color intensity) in the required universal buffer solutions from pH's (1.8-12) are carried out. At slight acidic medium the color intensity of the complex is increased, but in alkaline medium it decreases due to hydrolysis of the formed complex as a result of proton displacement through metal ions [16].

3.4 Effect of sequence of addition and organic solvent ratio

It has taken about 2 ml (1×10^{-3} M) of metal solution in 10 ml measuring flask and 2 ml of the required universal buffer is added keeping (20% v/v) ethanol solution, during the measurements. From 2-2.5 ml (1×10^{-3} M) of the ligand is added, and completed to the mark with bidistilled water and the sequence of (metal – ligand – buffer) is found to be the best one for the high color intensity of the complex. The blank is prepared by the same manner without addition of metal solution.

3.5 Stoichiometry of the complexes in solution

The stoichiometry of the complexes is determined in solution by using the conventional molar ratio and Job's continuous variation methods. It was found that Fe^{+3} – ligand complexes are measured at λ_{max} 460 nm and pH 5.5, while V^{+5} – ligand complexes are measured at λ_{max} 632 nm and pH 4. The complexes have molar ratios of (1:1) and (1:2) M: L and the values of formation constants are calculated using Harvey-Manning equation [17]. This is listed in Table (1). The formed complexes indicate a red shift in comparison to the bands of the ligand as shown in Fig (1).

3.6 Calibration graph and reproducibility

Under the favorable conditions cited above a linear calibration graph for Fe^{+3} and V^{+5} ligand systems are obtained up to a concentration ranges which is permitted for calibration curve Fig(2). The determination of Fe^{+3} was in the range of 0.112- 2.8 $\mu\text{g ml}^{-1}$ with standard deviation 0.35 and relative standard deviation 0.96%. Also, the determination of V^{+5} is in the range of 1.34- 6.69 $\mu\text{g ml}^{-1}$ with standard deviation 0.28 and relative standard deviation 0.87 %. Precision and accuracy of the proposed method is tested by analyzing six replicate samples containing 0.8 to 4 $\mu\text{g ml}^{-1}$ of metal ions and the relative standard (RSD), the relative error (RE) and confidence limits are measured and listed in Table (2).

3.7 Effect of foreign ions

A systematic quantitative studies of foreign ions effect, by measuring the absorbance of a solution containing 2 ml (1×10^{-3} M) of the ligand with 2 ml (1×10^{-3} M) of either Fe^{+3} or V^{+5} solution. Adjusting the pH by universal buffer to the recommended value of the optimum pH. Different concentration of cations K^{+1} , Na^{+1} , Mg^{+2} , Cu^{+2} , Ca^{+2} , Ni^{+2} Mn^{+2} and Cr^{+3} are added, also another series of anions like CO_3^{-3} , NO_3^{-1} and PO_4^{-3} are tested. It is found that cations do not interfere up to 20 fold excess more than the concentration of Fe^{+3} and V^{+5} . On the other hand, the anions do not interfere till 10 fold excess than the recommended concentration, while oxalate, citrate and EDTA are interfered with the complex solution up to two fold excess of the metal concentration.

REFERENCES

- [1] Tandon, S.G. and Bhatta chrga, S.C. J of indian chem. Soc No 47, 583, 1970
- [2] Kehl, H. (Ed) chemistry and biology of hydroxamic acid karger, N., 1982
- [3] Odashima, T., Hidaka, K and Sakakura, K. J of solvent extraction and ion exchange, 14, 603-616, 1996
- [4] Mohamed, G., Ikhlas, A., Mansour, Y. and El-sayed, S. A. Spectrochimica acta part A Molecular and biomolecular spectroscopy 68, 305-311, 2007
- [5] Bass, V.C and Yoe, J.H. J. of Anal Chem Acta 35, 337, 1966
- [6] Mohamed, M.G, Aboul Enien, H.Y, Gadjarien E A, Anal Lett 16:45, 1983
- [7] Sudarat, S., Jatiporn, W., Kochakriangkrai, S., Kanlayanee K, Sanchai p Sensors and Actuators B Chemical 166-167, 772-776, 2012

- [8] Jain R , Jain CL . Indian Drugs;28,380, 1991
 [9] Cavrini V , Gatti R , Di – Pietra AM , Raggi MA .Chromatographia;23,680, 1987
 [10] Ito T . Mastuki Y , Kurihara H , Nambara T . J Chromatographia;417,79, 1987
 [11] Mirza T , Tan HIS . J pharm biomed Anal;25(1) 39-52, 2001
 [12] Mohan , M., Tandon , P . Gupta . N.S. J. of inorg . Nucl . Chem , 43 ,1223, 1981
 [13] Moustafa M M , Mohamed T Y ,El–shahat M.F . ,Egypt J chem., 43(3) , 259-265, 2000
 [14] Britton , H.T.S. Hydrogen ions 4 th ED .London Chapman and Hall, 1952
 [15] Amin ,A and Mohamed T. Y, J Annali di chimica , no 90, 389, 2000
 [16] El- Tabl , A.S. Kasher , T.I., El-Bahnasawy, R.M., Ibrahim , A.E., Pol. J. Chem. 73,245(1999)
 [17] L Mishra ,A.Jha ,and A.K.adaw ,Trans .Met .Chem. 22,406, 1999
 [18] R.M Issa ,F.A.Aly , M.Gaber , M.I .Ayad , Egypt J.Chem 29,49, 1986
 [19] A. E. Harvey ,D. L.Manning , J. Am .Chem . Soc. 71,4488, 1950

Table 1. Spectral characteristic of the coloured products of ligand with Fe⁺³ and V⁺⁵ metal ions

Parameter	Ligand		Fe ⁺³ - complex	V ⁺⁵ - complex
	a	b		
$\lambda_{max} (nm)$	302	423	460	632
Optimum pH	7.4	-	5.5	4.0
$\epsilon (Lmol^{-1} cm^{-1})$	0.764x10 ⁴	-	2.5x10 ⁴	1.13x10 ⁴
Log K _n (stability)	5.5, 9.5	-	(4.29, 8.2)	(5.33,8.54)
Colour intensity	pale yellow	-	red	green
Conc. range μgml^{-1}	nil	-	0.11- 2.8	1.34- 6.69
RSD%	-	-	0.96	0.870
Recovery %	-	-	98.1	97.2
Correlation coeff. (r)	-	-	0.9953	0.9968
Slope (b)	-	-	0.446	0.3
Intercept (a)	0.0393	-	-	0.0069

A= a+bC is the regression equation

Where **A** is the absorbance

a is the intercept

b is the slop

C is the concentration

Table 2. Evaluation of the accuracy and precision of the proposed procedure for determination Fe^{3+} and V^{5+} .

Metal	Taken ($\mu\text{g ml}^{-1}$)	Recovery (%)	RSD ^a (%)	RE ^b (%)	Confidence limits ^c
Fe^{3+}	0.8	100.5	1.00	1.05	0.804 ± 0.0033
	1.5	100.4	0.88	0.92	1.507 ± 0.0388
	2.0	101.0	0.63	0.67	2.02 ± 0.0419
V^{5+}	1.5	100.6	1.11	1.18	1.51 ± 0.0420
	2.0	101.5	0.88	0.91	2.03 ± 0.0536
	4.0	101.2	0.63	0.81	4.05 ± 0.0327

a Relative standard deviation for six determination.

b Relative Error RE

c 95 % confidence limits and five degree of freedom

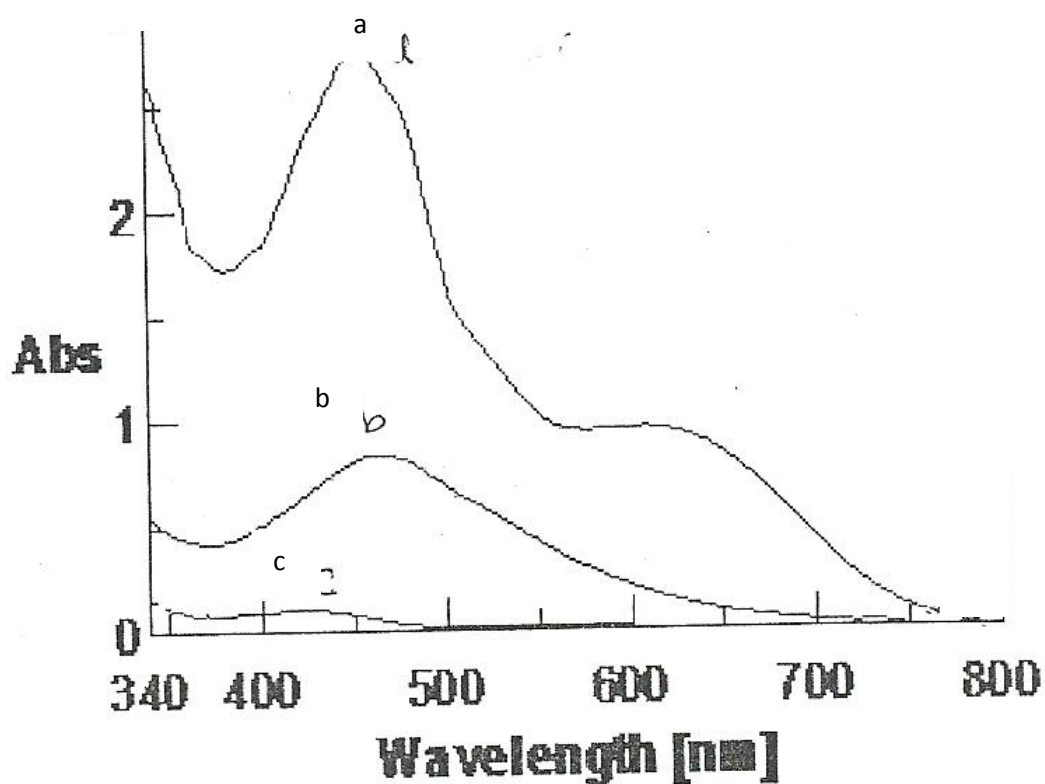


Fig.1 Absorption spectra of the coloured complexes

- a-** V^{5+} - ligand complex against blank ligand
- b-** Fe^{3+} - ligand complex against blank ligand
- c-** Ligand only against buffer

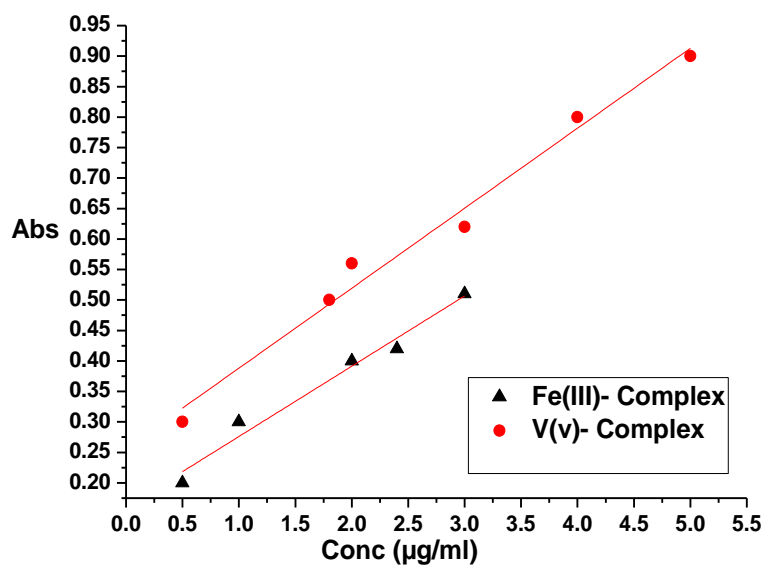


Fig.2 *Validity of Beer's law for Fe (III) and V (V) - complex*