CROATICA CHEMICA ACTA CCACAA 54 (4) 459—464 (1981)

YU ISSN 0011-1643
CCA-1304 UDC 546.881
Original Scientific Paper

Extractive Spectrophotometric Determination of Vanadium(V) with *N*-*p*-Chlorophenyl-2-naphthohydroxamic Acid and Investigation of Its Solid Complex[†]

V. C. Koshy and S. G. Tandon

Department of Chemistry, Ravishankar University, Raipur, 492.010, India

Received April 20, 1981

A simple, selective and sensitive method for the extractive spectrophotometric determination of vanadium(V) using *N*-*p*-chlorophenyl-2-naphthohydroxamic acid (CP-2-NHA) is described. Vanadium(V) is quantitatively extracted from 3—8.4 M HCl as a violet complex with CP-2-NHA into chloroform. Beer's law is applicable in the concentration range 34 and 224 μg of vanadium(V) per 25 ml of chloroform extract. The Sandell sensitivity of the system is 0.0089 μg/cm² at 530 nm. The method has been satisfactorily employed for the determination of vanadium in steel.

The solid complex, $VOCl(C_{17}H_{11}NO_2Cl)_2$, was prepared and characterised by melting point, elemental analysis, visible and infrared spectra.

INTRODUCTION

The years since the introduction of *N*-phenylbenzohydroxamic acid, PBHA, as a reagent for the detection and determination of vanadium(V)[1,2] have seen an explosive growth in this field. The upsurge of interest in the application of this method to a variety of problems[3-6] owes much of its impetus to the search for better reagents from the family of hydroxamic acids. A number of hydroxamic acids have been prepared by varying the nature and position of the substituent groups attached to the carbon and nitrogen atoms of —CON(OH)—, and their reaction with vanadium(V) in concentrated hydrochloric acid media studied[7-14]. In a further extension of this work, fourteen new *N*-arylhydroxamic acids with typical range of structural variations have been prepared[15]. Out of these, *N*-*p*-chlorophenyl-2-naphthohydroxamic acid has shown an encouraging combination of good sensitivity with better selectivity for vanadium(V). Hence, the optimum conditions for the colour reaction have been studied and the vanadium content in samples of B.C.S. analysed steels determined with satisfactory results.

Although a large number of hydroxamic acids have been reported as reagents for the spectrophotometric determination of vanadium(V), their solid complexes have not been isolated. In this work, the solid vanadium(V)-CP-2-NHA complex has been prepared and characterised by elemental analysis, melting point, visible and infrared spectra.

[†] Part of Ph. D. Thesis of V. C. K. Ravishankar University, Raipur, 1981.

EXPERIMENTAL

Apparatus

Absorption spectra were scanned on UV-VIS Carl Zeiss Jena SPECORD recording spectrophotometer, and fixed wavelength measurements made with E. C., India Model GS-865 spectrophotometer.

The infrared spectra were recorded as nujol mulls on Perkin Elmer Model-377 infrared spectrophotometer.

Reagents

CP-2-NHA was prepared as reported earlier[15]. Its 0.1% w/v solution in ethanol free chloroform[1] was used for extraction;[1] saturated solution in chloroform ($2.2 \times \times 10^{-2}$ M) was used for preparing solid vanadium(V) complex. A stock solution of ammonium metavanadate (AR, Hungary) was prepared[1] and diluted as required. For the preparation of the solid vanadium(V) complex of CP-2-NHA, a saturated solution of ammonium metavanadate in glass distilled water was used. Solutions of diverse ions, 20 mg/ml, were prepared from analytical grade salts.[16]

Procedure for Development of Colour

The procedure adopted here was the same as reported earlier[11]. The absorbance of the chloroform extract of $VOCl\ (C_{17}H_{11}NO_2Cl)_2$ was measured at 530 nm using chloroform as blank.

Procedure for Isolation of Solid Complex

To 100 ml of saturated solution of ammonium metavanadate in a 500 ml separatory funnel was added 55 ml of hydrochloric acid (11.4 M). To this was added 10 ml of saturated solution of CP-2-NHA in chloroform and 200 ml of *n*-hexane. On shaking for about two minutes, the solid vanadium(V) complex was obtained. It was filtered off, washed with water (5 × 15 ml) and dried in a vacuum over P_2O_5; m. p., 122—123 °C. The complex was analysed and the results are in agreement with the molecular formula, $VOCl\ (C_{17}H_{11}NO_2Cl)_2$. (Analysis: calculated for $VOCl\ (C_{17}H_{11}NO_2Cl)_2$; Mol. wt., 695.86; C, 58.69; H, 3.19; N, 4.03; Cl, 15.28; V, 7.32. Found: C, 58.26; H, 3.10; N, 4.10; Cl, 15.00; V, 7.25).

RESULTS AND DISCUSSION

Absorption Spectra and Solvents for Extraction

The solution of the $VOCl\ (C_{17}H_{11}NO_2Cl)_2$ in chloroform has a maximum absorbance of at 530 nm. The position of the absorption band remains intact on varying (i) the concentration of vanadium(V) or (ii) the acid concentration (2—10 M), thus indicating the presence of one type of complex. The coloured complex is extracted into benzene, chloroform, chlorobenzene, carbontetrachloride, o-dichlorobenzene, ethyl acetate, etc. readily, but chloroform is the most efficient solvent.

Effect of Acidity, Time of Shaking and Stability of Colour

Maximum colour develops if the acidity of the aqueous phase is maintained between 3.0 and 8.4 M HCl. Usually, measurements were made from 4 M HCl solutions. The colour is extracted into the chloroform layer in less than one minute and is stable for several days.

Volume of Aqueous Phase

The absorbance readings remain unchanged on varying the volume of the aqueous phase from 2 to 30 ml; however, a slight decrease in absorbance was observed thereafter. Usually the volume of the aqueous phase was 10 ml or smaller for 10 ml of organic phase.

TABLE I

etermination of Vanadium in the Presence of Diverse Ions. Fixed Amount of Vanadium(V) = 87.02 μg

Ion	Added as	Amount of ion added, mg	Error, %
I	II	III	IV
Al(III)	$Al(NO_3)_3 \cdot 9H_20$	40	0.0
		120	+ 2.5
Ba(II)	$Ba(NO_3)_2$	40	+ 1.3
		60	0.0
Bi(III)	$Bi(NO_3)_3 \cdot 5H_2O$	20	0.0
		40	− 4.8
Ce(IV)	$Ce(SO_4)_2$	40	+ 0.8
		60	− 1.3
Cd(II)	$3CdSO_4 \cdot 8H_2O$	40	+ 0.8
		60	0.0
Co(II)	$CoSO_4 \cdot 7H_2O$	40	− 1.3
		60	− 2.5
Cu(II)	$Cu(NO_3)_2 \cdot 3H_2O$	10	− 0.8
Fe(III)	$FeCl_3 \cdot 5H_2O$	13	− 2.8
		15	0.0
Li(I)	$(Li)_2SO_4 \cdot H_2O$	120	+ 2.5
		200	− 1.3
Mg(II)	$Mg(NO_3)_2 \cdot 6H_2O$	20	0.0
		40	0.0
		80	− 1.3
Mo(VI)	$(NH_4)_2MoO_4$	20	− 1.3
		30	− 8.9
		40	− 15.2
Ni(II)	$Ni(NO_3)_2 \cdot 6H_2O$	20	+ 0.8
Pb(II)	$Pb(NO_3)_2$	40	0.0
		60	− 0.8
Th(IV)	$Th(NO_3)_4 \cdot 6H_2O$	40	+ 1.3
		60	− 0.3
Ti(IV)	$K_2TiO(C_2O_4)_2$	5	0.0
		10	− 0.5
U(VI)	$UO_2(NO_3)_2 \cdot 6H_2O$	40	+ 0.8
		50	− 1.3
W(VI)	$Na_2WO_4 \cdot 2H_2O$	10	− 2.5
		20	− 39.2
		40	− 59.5
Zn(II)	$ZnSO_4 \cdot 7H_2O$	40	+ 0.8
		80	− 0.8
Zr(IV)	$Zr(NO_3)_4$	7	0.0
		10	− 1.8
		13	− 8.9
CH_3COO^-	CH_3COOH	3N	0.0
		5N	− 1.3
		7N	− 10.9
ClO_4^-	$HClO_4$	0.5N	− 1.3
		1N	− 5.6
		2N	− 12.9
NO_3^-	HNO_3	1N	0.0
		2N	− 4.1
PO_4^{3-}	H_3PO_4	2N	− 0.8
		3N	− 4.1
		4N	− 6.8
SO_4^{2-}	H_2SO_4	3N	0.0
		6N	− 4.1

Amount of Reagent

A 1 : 8 mole ratio of vanadium(V) to reagent ensures maximum colour. The reagent is colourless and its large excess is tolerated.

Beer's Law

Beer's law is obeyed in the concentration range 34 to 224 μg of vanadium(V) per 25 ml by Ringbom plot[17]. The molar absorptivity of the violet vanadium(V)-CP-2-NHA complex in chloroform is 5750 ± 100 litre mole^{-1} cm^{-1} at 530 nm. The Sandell sensitivity[18] of the system is 0.0089 μg/cm^2.

Effect of Diverse Ions

Fixed amounts of vanadium(V) were determined in the presence of varying amounts of diverse ions. Large amounts of Al(III), Ba(II), Bi(III), Cd(II), Co(II), Cu(II), Fe(III), Li(I), Mg(II), Ni(II), Pb(II), Th(IV), U(VI), Zn(II), acetate, perchlorate, nitrate, phosphate and sulphate are tolerated (Table I).

Tolerance of large amounts of sulphuric acid will permit the use of potassium pyrosulphate fusion of those vanadium bearing minerals which are not attacked satisfactorily by hydrofluoric acid. Ce(IV), Mo(VI), Ti(IV) and Zr(IV) form a light yellow chloroform extract with absorption bands at a shorter wavelength and having practically no absorption at 530 nm. Hence, relatively large quantities of these ions are tolerated. This explains the high selectivity of the vanadium(V) reaction with CP-2-NHA. Lead(II) and tungsten(VI) yield a precipitate with hydrochloric acid and are removed by repeated centrifuging and washing before the extraction of vanadium(V). Strong oxidising agents such as potassium dichromate and potassium permanganate interfered in the determination of vanadium(V); however, such interference could be easily eliminated by the ready conversion of these oxidants to noninterfering oxidation states, viz., Cr(VI) to Cr(III) and Mn(VII) to Mn(II).

Determination of Vanadium in Steel

The results obtained in the analysis of B.C.S. steels, using CP-2-NHA, are in excellent agreement with the certified values (Table — II). Thus, both the accuracy and the precision of the newly developed method are established.

TABLE II

Determination of Vanadium in B. C. S. Steels

B. C. S. Steels	Certified % of vanadium	% of vanadium found
241/1 High Speed Steel	1.570	1.564
Cr-V No. 224	0.242	0.241
Low Alloy Steel No. 252	0.460	0.458

Investigation of VOC1 $(C_{17}H_{11}NO_2Cl)_2$

The complex is a purple solid and is freely soluble in benzene, chlorobenzene, chloroform, o-dichlorobenzene, etc. It is sparingly soluble in water, *n*-hexane and cyclohexane. The solid complex is fairly stable if kept in a cool dark place. The molar absorptivity of the chloroform solution of the complex is exactly the same as that of its chloroform extract used for the spectrophotometric determination of vanadium. The purple solid complex gives a red colouration which gradually turns golden yellow and ultimately colourless with all alcohols.

The infrared spectrum of VOCl $(C_{17}H_{11}NO_2Cl)_2$ is compared with the spectrum of CP-2-NHA. The band of the free ligand at 3200 cm^{-1} is ascribed to O—H stretching vibration since it disappears in the spectrum of its vanadium(V) complex. The disappearance of this strong band indicates that the O—H bond has broken in the formation of the metal complex. The carbonyl stretching vibration in CP-2-NHA appears at 1615 cm^{-1}, as a very strong band, and on complexation with vanadium, this is shifted to 1600 cm^{-1}. A band of medium intensity at 905 cm^{-1} in CP-2-NHA has been assigned to N—O stretching vibration. In the spectrum of its vanadium(V) complex, this is transformed to two very close bands of medium intensity at 900 and 930 cm^{-1}, respectively.

The appearance of a strong band around 975 cm^{-1} in the VOCl $(C_{17}H_{11}NO_2Cl)_2$ indicates the presence of a V=O bond, since in structurally analogous complexes, (19—22), it has been observed in the range 965 ± 50 cm^{-1}.

Acknowledgement. — The authors are grateful to the authorities of the University Grants Commission, New Delhi for awarding a Junior Research Fellowship to one of them (V. C. K.).

REFERENCES

1. U. Priyadarshini, S. G. Tandon, *Anal. Chem.* **33** (1961) 435.
2. D. E. Ryan, *Analyst,* **85** (1960) 569.
3. E. M. Donaldson, *Talanta,* **17** (1970) 583.
4. A. A. Shahid, *Analyst,* **101** (1979) 209.
5. M. Uhrova and L. Kabrt, *Sb. Vys. Sk. Chem. Technol. Praze. Anal. Chem.,* **H11** (1976) 91.
6. R. R. Nanewar, Usha Tandon, *Talanta,* **25** (1978) 352.
7. S. G. Tandon and S. C. Bhattacharya, *J. Ind. Chem. Soc.* **47** (1970) 583.
8. U. Tandon and S. G. Tandon, *J. Ind. Chem. Soc.,* **46** (1969) 983.
9. D. C. Bhura and S. G. Tandon, *Anal. Chim. Acta,* **53** (1971) 379.
10. V. K. Gupta and S. G. Tandon, *Anal. Chim. Acta,* **66** (1973) 39.
11. Rama Pande and S. G. Tandon, *Croat. Chem. Acta,* **51** (1978) 353.
12. E. K. Abdusalamova and B. G. Ostrobrod, *Tr. Task. Politekh. Inst.,* 119 (1974) 17.
13. A. A. Shahid, *Anal. Chem.,* **48** (1976) 714.
14. V. C. Bass and J. H. Yoe, *Talanta,* **13** (1966) 735.
15. V. C. Koshy and S. G. Tandon, *J. Chem. Eng. Data,* Accepted,
16. P. W. West, *J. Chem. Educ.,* **18** (1941) 528.
17. A. Ringbom, *Z. Anal. Chem.,* **115** (1939) 332.
18. E. B. Sandell, *Colorimetric Determination of Traces of Metals,* Intersience Publishers, Inc., New York, 3rd ed., p-83, 97, 217 (1959).
19. J. Selbin, *Coord. Chem. Rev.,* **1** (1966) 293.
20. A. Syamal and K. S. Kale, *Inorg. Chem.,* **18** (1979) 992.
21. R. L. Farmer and F. L. Urbach, *Inorg. Chem.,* **13** (1974) 587.
22. J. J. R. Frausto da Silva, R. Wotton, and R. D. Gillard, *J. Chem. Soc.,* (1970) 3369.

SAŽETAK

Ekstrakcijsko spektrofotometrijsko određivanje vanadija(V) primjenom *N*-*p*-klorofenil-2-naftohidroksamne kiseline i istraživanje njihovog krutog kompleksa

V. C. Koshy i S. G. Tandon

Opisana je selektivna i osjetljiva metoda za ekstrakcijsko spektrofotometrijsko određivanje vanadija(V) pomoću *N*-*p*-klorofenil-2-naftohidroksamne kiseline (CP-2--NHA). Vanadij(V) se kvantitativno ekstrahira s CP-2-NHA u kloroform u obliku ljubičastog kompleksa iz otopina koje su 3—8.4 mol dm^{-3} s obzirom na HCl. Sistem slijedi Beerov zakon u području koncentracija 34 do 224 μg vanadija u 25 cm^3 kloroformnog ekstrakta. Osjetljivost metode izražena Sandellovim indeksom iznosi 0.0089 μg cm^{-2} kod 530 nm. Postupak je uspješno primjenjen za određivanje vanadija u čelicima.

Kruti kompleks, $VOCl(C_{17}H_{11}NO_2Cl)_2$ je sintetiziran i karakteriziran talištem, elementarnom analizom i pomoću vidljivih i infracrvenih spektara.

DEPARTMENT OF CHEMISTRY,
RAVISHANKAR UNIVERSITY,
RAIPUR, 492010, INDIA

Prispjelo 20. travnja 1981