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Extraction-Spectrophotometric Determination of Vanadium(V) Employing N^1-Hydroxy-N^1,N^2-diarylbenzamidines and Various Adduct-forming Substances

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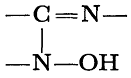
The reactions of 16 newly synthesized N^1-hydroxy-N^1,N^2-diarylbenzamidines with vanadium(V) in presence of various adduct-forming substances have been investigated photometrically in chloroform. The present study indicated the formation of 1:2:1 metal:reagent:acetic acid or phenol and 1:2:2 metal:reagent:thiocyanate complexes. On the basis of strong synergism, which is attributed to mixed-complex formation, simple, rapid, sensitive and selective methods for the spectrophotometric determination of microgram quantities of vanadium(V) have been developed. The influence of experimental variables on the procedures have been discussed.

A number of monobasic and bidentate chelating agents[1–15] react with vanadium(V) to form 1:2 (metal: ligand) complex having a basic V=O group and an acidic V–OH group in the same molecule. The basic V=O group reacts with acidic substances like carboxylic acids, hydrogen chloride, phenols *etc.* to produce hyper- and bathochromic effects. N^1-Hydroxy-N^1,N^2-diarylbenzamidines, a new type of monobasic and bidentate chelating agents possessing the function, I, react with

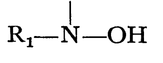


$$\begin{array}{l}-\mathrm{C}=\mathrm{N}-\\ \quad | \\ -\mathrm{N}-\mathrm{OH}\end{array}$$

Formula I.

vanadium(V) to form coloured 1 : 2 (metal : ligand) complexes. It is very likely that the basic V=O group of the complexes reacts with acidic substances such as acetic acid, phenol, *p*-chlorophenol and 2-naphthol to produce hyper- and bathochromic effects in chloroform solution, accompanied by synergism. The formation of both 1:2:1 (metal:ligand:acetic acid or phenol) and 1:2:2 (metal:ligand:thiocyanate) complexes is adaptable to the development of sensitive and selective methods for the spectrophotometric determination of traces of the metal.

The selectivity of the method for vanadium(V) employing N^1-hydroxy-N^1,N^2-diarylbenzamidines enables the direct determination of vanadium in steels and other materials.[16] This and other excellent qualities of *N*-hydroxyamidines as reagents for vanadium(V) gave us an encouragement to search for better reagents amongst the family of *N*-hydroxyamidines. A number of compounds of the general formula, II, have, therefore, been synthesized and examined as possible reagents for vanadium(V).



$$\begin{array}{l}\mathrm{R_3}-\mathrm{C}=\mathrm{N}-\mathrm{R_2}\\ \qquad | \\ \mathrm{R_1}-\mathrm{N}-\mathrm{OH}\end{array}$$

Formula II.

R_2 is phenyl, *p*-tolyl, *m*-tolyl, 2,5-dimethylphenyl, or 2-methyl-4-chlorophenyl; R_1 is phenyl, *p*-tolyl, *m*-tolyl, or *p*-chlorophenyl; R_3 is *p*-tolyl.

Of the 16 reagents examined in the present investigation N^1-hydroxy-N^1-(*p*-chlorophenyl)-N^2-(2-methyl-4-chlorophenyl)-*p*-toluamidine hydrochloride (HCPMCPTH), which has the largest molar absorptivity for its vanadium(V) complexes has been studied in detail.

Experimental

Apparatus and Solutions. A Carl Zeiss Specord recording ultraviolet-visible spectrophotometer and an ECIL UV-VIS spectrophotometer model GS-865 equipped with 1-cm quartz and silica cells were employed for recording spectra and absorbance measurements respectively. Systronic pH meter Type-322 was employed for the determination of pH values of the solutions. Twice distilled water and ethanol-free chloroform were used for solution preparations.

A stock solution of vanadium(V) was prepared by dissolving ammonium metavanadate in water and the solution standardized volumetrically with potassium permanganate.[20]

Solutions of cations were prepared from analytical reagent grade chlorides, sulfates or nitrates and those of anions were obtained by dissolving their sodium or potassium salts.

Reagents. N^1-Hydroxy-N^1,N^2-diarylbenzamidines were prepared by the condensation of equimolar quantities of *N*-aryl-*p*-toluimidoyl chloride and *N*-arylhydroxylamine in ether medium.[16,21] The resulting hydrochloride was filtered and crystallized from absolute alcohol. The free bases were obtained by treatment of hydrochlorides with dilute ammonia solution and crystallized from benzene:petroleum ether (2:1). All these compounds gave satisfactory C, H, and N analyses. 0.005 M (1 M=1 mol/dm^3) solutions of these reagents were used for extraction studies.

Procedure. Transfer an aliquot of vanadium(V) solution to a separatory funnel. Add suitable quantity of adduct-forming substance. Dilute to 25 ml with distilled water and add 10 ml of chloroform solution of the reagent. Shake the contents of the funnel vigorously for 2 min and allow the phases to separate. Dry the chloroform extract over anhydrous sodium sulfate and transfer to 25-ml volumetric flask. Dilute the extracts to 25 ml with chloroform and scan the absorption spectrum of the coloured extract against chloroform or reagent blank.

Results and Discussion

Absorption Spectra. The absorption spectra of vanadium–HCPMCPTH complex in the absence and presence of adduct-forming substances are shown in Fig. 1. When adduct-forming substances are added to chloroform solution of vanadium–HCPMCPTH complex, a hyper- and bathochromic effect is noticed which is attributed to mixed complex formation. The $\lambda_{\max}$ and ε depend on the nature of *N*-hydroxyamidine and the adduct-forming substance. The spectral characteristics of vanadium complexes of HCPMCPTH

Table 1. Spectral characteristics of vanadium-HCPMCPTH complex in the presence of acetic acid, thiocyanate, and phenols

Adduct-forming substance	Optimum acidity ranges of acetic acid / M	Color	$\lambda_{\max}$ / nm	ε / l mol^{-1} cm^{-1}	Optimum concn ranges from Beer's law (Optimum concn ranges from Ringbom plot) ppm of V	Sensitivity μg cm^{-2} of V	Relative standard deviation[a) / %
Acetic acid	1.0—10.0	BV	580	2900	1.0—16.0 (2.0—13.0)	0.017	±0.80
Thiocyanate	0—2.0	DG	610	6500	1.0—7.0 (1.5—6.0)	0.0080	±0.60
Phenol	0—3.0	B	590	6300	1.4—7.0 (1.6—6.5)	0.0085	±0.52
p-Chlorophenol	0—2.5	B	600	6800	1.0—7.0 (1.2—6.0)	0.0075	±0.74
2-Naphthol	0—3.0	GB	620	6500	1.2—7.0 (1.5—6.4)	0.0080	±0.50

BV, blue-violet; DG, deep-green; B, blue; GB, greenish-blue; ○, pH 3.0.

a) 10 measurement are made, each containing 4 ppm of V.

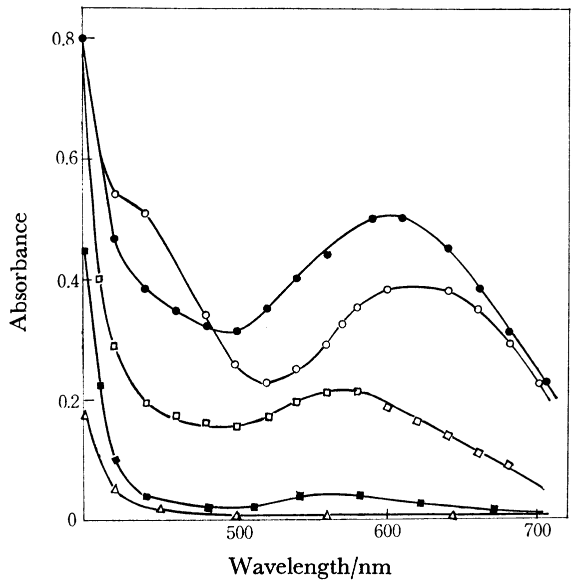


Fig. 1. Absorption spectra.

●: 7.35×10^{-5} M C_V + 0.003 M C_HCPMCPTH + 0.03 M *p*-chlorophenol, ○: 5.84×10^{-5} M C_V + 0.003 M C_HCPMCPTH + 0.01 M thiocyanate, □: 7.40×10^{-5} M C_V + 0.003 M C_HCPMCPTH + 1 M acetic acid, ■: 6.40×10^{-5} M C_V + 0.003 M C_HCPMCPTH, △: 0.003 M C_HCPMCPTH.

are recorded in Table 1.

Effect of Reagents Temperature and Time. For complete extraction of vanadium(V), acetic acid system requires a 12 fold molar excess of *N*-hydroxyamidine, whereas the optimal amount of *N*-hydroxyamidine required for quantitative transfer of the metal to organic phase following thiocyanate and phenol systems are 6 and 3 fold molar excess of the reagent respectively. The thiocyanate and phenol systems necessitate 8 and 250 fold molar excess of thiocyanate and phenols respectively for complete extraction of vanadium(V). Order of addition of reagents is not critical. Variation in temperature from 20 to 35 °C does not affect the $\lambda_{\max}$ and absorbance of coloured systems.

The extracts of acetic acid and thiocyanate systems are stable at least 50 and 35 h respectively. The HCPMCPTH–phenol–vanadium complexes are stable in chloroform for at least 30 h at 27±2 °C.

Nature of Adducts. The composition of the adducts were determined by various methods. The ratio of vanadium to *N*-hydroxyamidine was determined by mole ratio[22) and continuous variation methods,[23) and vanadium to adductant by curve fitting method.[24) In the thiocyanate system the ratio of vanadium to thiocyanate was determined by mole ratio method and slope ratio method.[25) The results indicate that V:HOAm:L (acetic acid or phenol) ratio in adduct is 1:2:1 and in thiocyanate system V:HOAm:SCN ratio is 1:2:2 as indicated in the V(V)–8-quinolinol–thiocyanate complex.[26)

N^1-*Hydroxy*-N^1,N^2-*diarylbenzamidines as Reagents for Vanadium(V).* All the 16 newly synthesized reagents were tested for their potentialities towards the spectrophotometric determination of vanadium(V). Beer's law was tested and confirmed for each system. All these compounds reacted with vanadium in presence of adduct-forming substances in a similar manner with only slight variation in the value of $\lambda_{\max}$ and ε. The vanadium–*N*-hydroxyamidine–acetic acid complexes possess $\lambda_{\max}$ in the range 570—585 nm with molar absorptivities in the range 2900—4300 l mol^{-1} cm^{-1}. The thiocyanato–vanadium complexes of these reagents show maximum absorption at 605—610 nm (ε=5100—6500). The vanadium complexes of the present reagents in the presence of phenol, *p*-chlorophenol and 2-naphthol have absorption maxima at 590—595 (ε=4600—6650), 595—600 (ε=4950—6800), and 590—620 nm (ε=4600—6650) respectively. The substitution of N^1-phenyl group(R_1) or N^2-phenyl group(R_2) with aryl groups has only slight bathochromic effect. Of the various group tested, *p*-chlorophenyl causes highest hyperchromic shift, when attached to hydroxylamine nitrogen atom. Substitution of R_2 with 2-methyl-4-chlorophenyl group results into the highest hyperchromic shift in the thiocyanate, *p*-chlorophenol and 2-naphthol complexes.

Effect of Diverse Ions. To evaluate the tolerance limits for different ions, solutions containing 4 ppm of vanadium(V) and varying amounts of other ions were analyzed as described above. Absorbance errors above 2% were considered to indicate interference.

In acetic acid system, tungsten(VI) seriously interfered. The system, however, tolerates the presence of the following ions, the tolerance limits of which are given in parentheses(ppm): citrate(500); tartrate(600); fluoride(500); chloride, bromide, nitrate, or sulfate (1500); phosphate(1000); arsenate(400); phthalate (800); triethanolamine or selenate(1000); alkali elements (1500); alkaline-earth elements(1000); lanthanoid elements(1000); Ni^{2+}, Zn^{2+}, Cd^{2+}, or Hg^{2+}(800); Cu^{2+}(600); Co^{2+}(700); Sb^{3+}(750); Bi^{3+}(600), Cr^{3+} (500); Th^{4+}(800); Tl^{3+}(1000); Pb^{2+}(800); Mn^{2+}(700); Fe^{3+}(800); Be^{2+}(1000); Ti^{4+}(20); Zr^{4+}(60), and Mo^{6+} (400).

In *p*-chlorophenol system iron(III) and tungsten(VI) interfered. However, the interference due to Fe^{3+} was eliminated by masking with trisodium phosphate. The tolerance limits for various ions are shown in parentheses(ppm): Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} Hg^{2+} (600); Pb^{2+}, UO_2^{2+}(500); Mo^{6+}(200); Zr^{4+}(100); Ti^{4+} (40); Cu^{2+}(200); Bi^{3+}, Fe^{3+}(800); Sb^{3+}(600); Al^{3+}, Cr^{3+}(500), and Th^{4+}(600). Alkali and alkaline-earth elements and lanthanoid elements, chloride, bromide, iodide, fluoride, nitrate, sulfate, citrate, tartrate, arsenate, phosphate, phthalate and borate have no interfering effect.

In thiocyanate system the interference due to Fe^{3+} was removed by masking with trisodium phosphate. The tolerance limits for other ions are indicated in parentheses(ppm): Cr^{3+}, Al^{3+}(500); UO_2^{2+}(400); Zr^{4+}(100); Mo^{6+}(300); Cu^{2+}(200); Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}(500); Ti^{4+}(60); W^{6+}(20); Fe^{3+}(800); Th^{4+} (800). Alkali metals, alkaline-earths, lanthanoid elements, chloride, bromide, fluoride, nitrate, sulfate, arsenate, phosphate, phthalate, borate, citrate and tartrate have no interfering effect on the determination.

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