

EXTRACTIVE PHOTOMETRIC DETERMINATION OF VANADIUM(V) AS AZIDO MIXED LIGAND COMPLEX WITH *N*-HYDROXY-*N*-*p*-CHLOROPHENYL-*N'*-(2-METHYL) PHENYL-*p*-TOLUAMIDINE HYDROCHLORIDE

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ABSTRACT

A simple, convenient and highly selective method for extractive photometric determination of microgram amounts of vanadium(V) has been developed. Chloroform solution of *N*-hydroxy-*N*-*p*-chlorophenyl-*N'*-(2-methyl)phenyl-*p*-toluamide hydrochloride (HCPMPTH) quantitatively extracts vanadium(V) as its azido mixed complex in the pH range between 0.7–5.3. The 1:2:2 (metal:reagent:azide) ternary complex shows an absorption maxima at 590–600 nm having the value for molar absorptivity $5670 \text{ l. mole}^{-1} \text{ cm}^{-1}$ with Sandell's sensitivity $0.0088 \mu\text{g}/\text{cm}^2$. Almost all common ions including Mn^{2+} , Cr^{3+} , Ti^{4+} , Zr^{4+} , Mo^{6+} and W^{6+} do not interfere.

INTRODUCTION

Literature survey reveals the use of a number of complexing agents to determine vanadium in the presence of other cations and anions. Of these *N*-hydroxy-*N,N'*-diaryl-benzamide has been claimed to be a convenient reagent for vanadium. It is now found that *N*-hydroxy-*N*-*p*-chlorophenyl-*N'*-(2-methyl)phenyl-*p*-toluamide hydrochloride may be used as a colorimetric reagent to determine vanadium(V) by taking advantage of the fact that the reagent reacts with vanadium(V) in the presence of azide forming a deep-green chloroform extractable mixed complex.

Various experimental factors such as time of standing, linearity of Beer's law, effect of reagent concentration, period of extraction, effect of diverse ions, etc., have been studied.

EXPERIMENTAL

Apparatus and reagents: An ECIL UV-VIS spectrophotometer model GS-865 with matched 1 cm cells and systronic pH meter Type-322 were used.

All the chemicals and reagents used were of BDH Analar grade. A stock solution of vanadium(V) was prepared by dissolving 1.765 g. ammonium metavanadate in double distilled water in a one litre volumetric flask and the solution was standardised volumetrically¹.

A 2% sodium azide solution was used throughout the experiment.

N-hydroxy-*N*-*p*-chlorophenyl-*N'*-(2-methyl)phenyl-*p*-toluamide hydrochloride was prepared by the method of Deb and Mishra² and a 0.1% w/v chloroform solution of the HCPMPTH was used for extraction purposes.

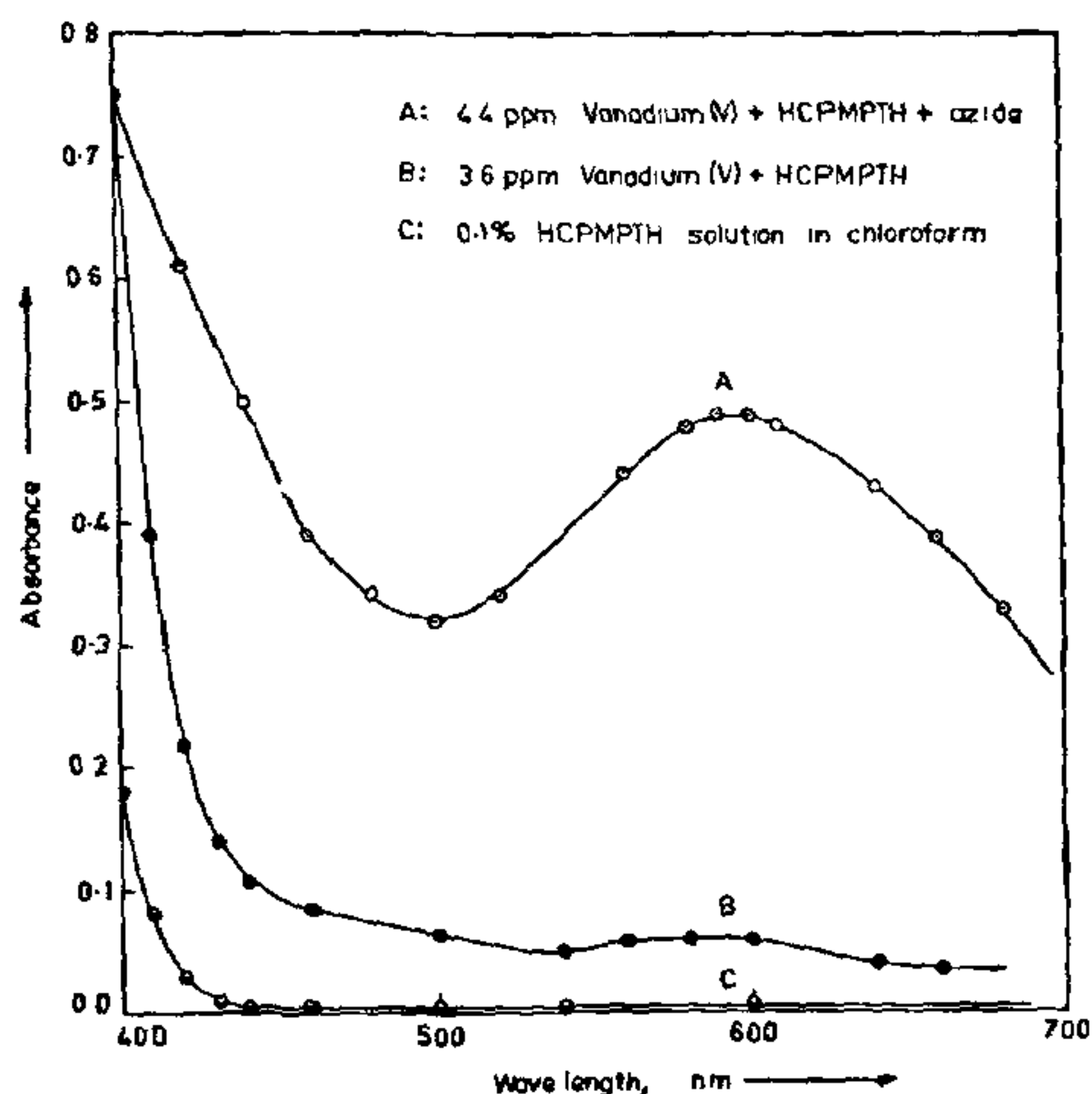
Procedure: A solution containing 100 μg of vanadium was transferred to a 125-ml separatory funnel, to which 5 ml of 2% aqueous solution of sodium azide was added and the pH was adjusted between 0.7–5.3 with 2 M hydrochloric acid and dilute ammonia in the final volume of 25 ml and extract with 10 ml of 0.1% chloroform solution of the HCPMPTH. The chloroform extract was dried over anhydrous sodium sulphate and transferred to 25 ml volumetric flask. The aqueous layer was washed with 2×5 ml portions of chloroform. The dried washings were mixed in the same volumetric flask and diluted to mark with chloroform. The absorbance was measured at the wavelength of maximum absorption against chloroform as the blank.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra of HCPMPTH and the vanadium(V)-HCPMPTH complex are shown in figure 1. The HCPMPTH shows negligible absorption in the region 450–700 nm. The vanadium(V)-HCPMPTH complex in the absence of azide shows a flat peak at 550–590 nm with ϵ , $850 \text{ l. mol}^{-1} \text{ cm}^{-1}$. In the presence of azide a dark-green ternary complex is developed having molar absorptivity $5670 \text{ l. mol}^{-1} \text{ cm}^{-1}$ at 595 nm.

Effect of variables Of the various organic solvents tested (benzene, toluene, xylene, chlorobenzene, *o*-dichlorobenzene, carbon tetrachloride and chloroform), chloroform was most suitable for extracting the vanadium complex. A 12 and 120-fold molar excess of HCPMPTH and azide was necessary for complete extraction.

Salting-out agents such as chlorides and nitrates of sodium, potassium and calcium (1 to 3 M) have no



significant effect on the extraction of vanadium(V). The extracts were stable for at least 30 hr at room temperature. The period of shaking was varied from 1 to 5 min and extraction was found to be quantitative after 1 min.

Beer's law, optimum concentration range, sensitivity and precision: Beer's law is valid between 1–9 ppm of vanadium(V). The optimum concentration range on the basis of Ringbom plot is found to be 1.5–7.6 ppm. The sensitivity of the colour reaction is $0.0040 \mu\text{g}/\text{cm}^2$ at 595 nm with molar absorptivity $5670 \text{ l. mole}^{-1} \text{ cm}^{-1}$. The precision of the method has been checked by measuring the absorbance values of 10 samples each containing a final concentration of 4.4 ppm of V/25 ml. The mean absorbance was 0.49 with standard deviation ± 0.0040 .

^a—in the presence of trisodium phosphate

^b—in the presence of thiourea

Composition: The ratio of vanadium(V) to HCPMPH was determined by the mole ratio³ and Job's method⁴ and the ratio of vanadium(V) to azide by a curve-fitting method⁵. The results show the formation of 1:2:2 (metal:reagent:azide) ternary complex.

Effect of diverse ions: To study the effect of diverse ions, a fixed amount of vanadium(V) (4 ppm at 2 ± 0.5 pH) was mixed with known quantity of foreign ion and vanadium was extracted according to the recommended procedure. The interference due to Fe^{3+} and Cu^{2+} could be eliminated by masking with trisodium phosphate and thiourea respectively.

Reasonable amounts of chloride, bromide, nitrate, sulphate, thiosulphate, urea, thiourea, phthalate, borate, citrate, tartrate, alkali and alkaline-earth metals did not interfere in the determination. The tolerance limits of other ions (in ppm) which caused an error less than $\pm 2\%$ are shown in parenthesis: Fe^{3+} (1200)^a; Ni^{2+} , Co^{2+} (2000); Cu^{2+} (500)^b; Zn^{2+} , Cd^{2+} (2400); Be^{2+} (1000); Al^{3+} (1500); Mn^{2+} (800); La^{3+} (1200); Ti^{4+} (180); Zr^{4+} (50); Mo^{6+} (500); W^{6+} (40); U^{6+} (1500); Rb^{+} (1200).

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