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Application of 1-(4-Tolyl)-2-methyl-3-hydroxy-4-pyridone to the Spectrophotometric Determination of Vanadium(V)

B. Tamhina, V. Vojković, and M. J. Herak

Laboratory of Analytical Chemistry, Faculty of Science, University of Zagreb, 41000 Zagreb, Strossmayerov trg 14, Croatia, Yugoslavia

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The application of 1-(4-tolyl)-2-methyl-3-hydroxy-4-pyridone (HY) for the spectrophotometric determination of V(V) by extraction into chloroform was investigated. It was found that depending on the extraction conditions three types of complexes are formed. At pH 1.2—2.5 an orange complex of the composition $VO_2Y \cdot HY$ with a maximum absorption at 500 nm is formed. However, at 1.2—2.0 M hydrogen ion concentration and in the presence of an excess of chloride ions a blue complex $VO_2Cl(HY)_2$ with maximum absorption at 625 nm was found. In the presence of an excess of perchlorate ions and at 0.2—1.0 M hydrogen ion concentration a blue complex $VO_2ClO_4(HY)_3$ with maximum absorption at 605 was found. Solutions of these complexes show great stability and they follow the Lambert-Beer's law. Procedures for the determination of vanadium at either 500 or 625 nm are very simple fast and selective. The compositions of the complexes have been characterized in chloroform solution. They were also isolated in crystalline form and indentified by elemental analysis and infrared spectroscopy.

INTRODUCTION

1-(4-tolyl)-2-methyl-3-hydroxy-4-pyridone (HY) has been utilized as a suitable reagent for extraction and separation of gallium(III)[1] and iron(III).[2] The organic extract of iron(III) formed with this reagent is suitable for its direct spectrophotometric determination[2].

This paper deals with the application of HY for the spectrophotometric determination of vanadium(V). The procedure is very simple, fast and selective.

The synthesis and physical properties of HY and its extraction efficiency have been described previously[3].

The application of 2-carbetoxy-5-hydroxy-1-(4-tolyl)-4 pyridone and 1--phenyl-2-methyl-3-hydroxy-4-pyridone to the spectrophotometric determination of vanadium(V) have also been studied[4,5].

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Beckman Spectrophotometer model DU-2. A pH-meter, Radiometer, model TTT 1 was used for the pH measurements.

Solutions and reagents

The synthesis of 1-(4-tolyl)-2-methyl-3-hydroxy-4-pyridone (HY) was described earlier[3]. Solutions of this reagent in chloroform served as the organic phase.

A standard solution of vanadium(V) (0.01 M) was prepared by dissolving 1.17 g ammonium vanadate in water and making up to a volume of 1 lit. The solution was standardized gravimetrically with cupferron[6].

All other chemicals used were of analytical reagent grade.

Procedure for measurement at 500 nm

An aqueous solution containing 10—100 μg of V(V) was adjusted to pH 2.0, diluted with water to about 10 ml and then extracted in a separatory funnel with 5 ml of a 0.005 M HY solution in chloroform. The solution was shaken for 2 min, the layer was separated and the organic phase transferred into a 10 ml volumetric flask. The aqueous phase was shaken again with 4 ml chloroform, which was transferred to the same volumetric flask and filled to the mark with chloroform. The absorbance was measured at 500 nm.

Procedure for measurement at 625 nm

To the solution (1 ml) containing 10—100 μg V(V), 1.6 ml of 10 M HCl was added and the volume made up with water to about 10 ml. The solution was extracted twice with 4 ml of 0.01 M HY in chloroform. After shaking for 2 min and separation the organic phases were transferred to a 10 ml volumetric flask and filled with chloroform to the mark. The absorbance was measured at 625 nm.

Isolation of vanadium(V) extracted species

The vanadium complexes were obtained by shaking a chloroform solution of the reagent (0.05 M) with an equal volume of ammonium vanadate dissolved in water. The orange $VO_2Y \cdot HY$ ($C_{26}H_{25}O_6N_2V$) complex was obtained at pH 2.0. The blue complexes $VO_2Cl(HY)_2$ ($C_{26}H_{26}O_6N_2VCl$) formed at an approximate acidity of 1.6 M HCl, and the $VO_2ClO_4(HY)_3$ ($C_{39}H_{39}O_{12}N_3VCl$) complex at an approximate acidity of 0.5 M $HClO_4$ and a concentration of 1.5 M $NaClO_4$. In all cases there was an excess of vanadium v. s. reagent. The organic phases were separated and the solvent evaporated in vacuo. The remaining solid products were recrystallized from chloroform-ligroin (1 : 2) and analyzed. The analytical results are shown in Table I.

TABLE I

Analytical data

Compound	%	C	H	N	Cl	V
$C_{26}H_{25}O_6N_2V$	calc'd	60.94	4.72	5.46		9.94
	found	60.67	5.20	5.22		9.76
$C_{26}H_{26}O_6N_2ClV$	calc'd	56.95	4.78	5.11	6.47	9.29
	found	56.99	4.98	4.97	6.20	8.98
$C_{39}H_{39}O_{12}N_3ClV$	calc'd	56.56	4.75	5.07	4.28	6.15
	found	56.30	4.83	5.02	4.25	5.91

RESULTS AND DISCUSSION

Optimal conditions for extraction of vanadium

At lower acidity, regardless of the kind of mineral acid used, vanadium(V) reacts with HY to give only an orange complex. It is soluble in chloroform and this solution has maximum absorption at 500 nm (Fig. 1). However, with

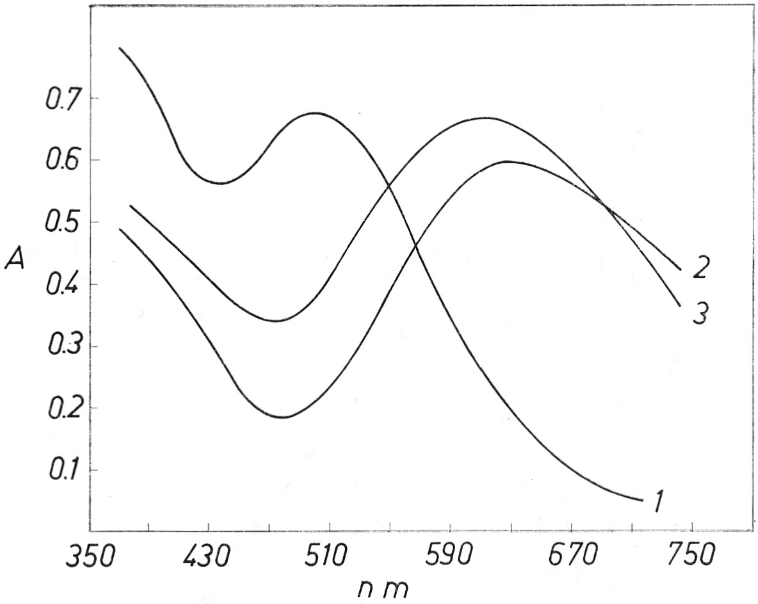

Figure 1. Absorption spectra of vanadium(V)-HY complexes in chloroform: (1) pH 2.0, (2) 1.6 M HCl, (3) 0.6 M $HClO_4$.

high conc. of HCl or $HClO_4$, a new blue coloured complex is obtained which was also soluble in chloroform. The complex formed in the presence of HCl shows a maximum absorption at 625 nm, and that with $HClO_4$ at 605 nm (Fig. 1). In order to investigate in more detail the conditions under which these complexes are formed, the dependency of the absorption on the concentration of HCl and $HClO_4$ has been determined. Measurements were carried out at 500, 625 and 605 nm. The results show that the optimal acidity for the formation of the orange complex is in the pH range of 1.2—2.5, for the blue chloro complex at a concentration of 1.2—2.0 M HCl, and for the blue perchlorato complex at a concentration of 0.2—1.0 M $HClO_4$. By varying the concentrations of H_2SO_4, CH_3COOH and H_3PO_4 only the formation of the orange complex was established, while the blue complexes were not obtained even at highest concentrations. However, if chloride or perchlorate ions were added the blue chloro and perchlorato complexes were formed regardless of the kind of mineral acid used.

The influence of the concentration of the reagent in the organic phase on the extraction of the complexes has also been established. It was found that, under the optimal conditions for the formation of both the orange and the perchlorato complex, the molar ratio of V : HY must be at least 1 : 15. For the chloro complex this ratio must be 1 : 70 in order to obtain constant absorbance readings.

Composition of the complexes

The composition of all the extracted complexes was determined by Job's method of continuous variations. The measurements were performed under the optimal conditions mentioned above. The results obtained (Fig. 2) indicate

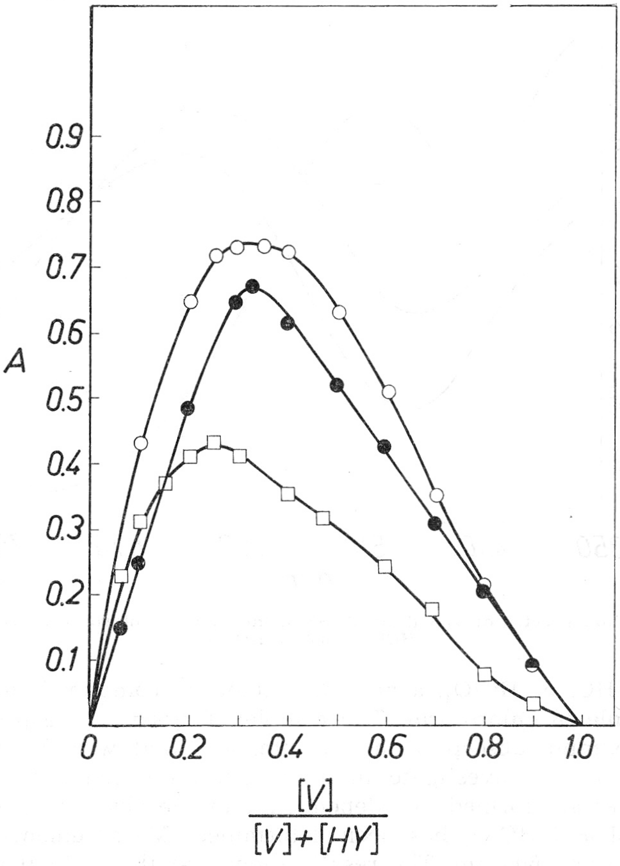

Figure 2. Determination of the complex composition by Job's method. (○) pH = 2.0, $C_V + C_{HY} = 6 \times 10^{-4}$ M, (●) 1.6 M HCl, $C_V + C_{HY} = 1.5 \times 10^{-3}$ M, (□) 0.6 M $HClO_4$, $C_V = C_{HY} = 6 \times 10^{-4}$ M.

that the molar ratio of V : HY in the orange complex and in chloro complex is 1 : 2, and in the perchlorato complex 1 : 3. Since V(IV) is stable in very acidic solutions, we have tried to investigate its extraction with HY. However, it has been found that vanadium(IV), without regard to the acidity of the solution, does not give any coloured complex with HY. In the aqueous solution, vanadium(V) exists as various ionic species depending on pH and its concentration. In diluted solutions, monomeric species of vanadium(V) prevail. At pH values smaller than 3, the cationic forms VO_2^+ and (to a smaller degree) VO^{3+} prevail in the solution[7,8]. Since for the extraction of vanadium, described here its concentration was low, and the concentrations of hydrogen ions was high, vanadium must be present in the solution as VO_2^+. For this reason, and on the basis of the results obtained, it can be assumed that the extraction mechanism is:

$$VO_2^+{}_{(aq)} + 2\,HY_{(o)} \rightleftarrows VO_2Y \cdot HY_{(o)} + H^+_{(aq)}$$

$$VO_2^+{}_{(aq)} + Cl^-_{(aq)} + 2\,HY_{(o)} \rightleftarrows VO_2Cl\,(HY)_{2(o)}$$

$$VO_2^+{}_{(aq)} + ClO_4^-{}_{(aq)} + 3\,HY_{(o)} \rightleftarrows VO_2ClO_4\,(HY)_{3(o)}$$

In order to confirm the formation of the extracted species shown in these equations, we have isolated these complexes in the solid form. Chemical analysis and IR spectra confirm that the complexes formed do have the stoichiometric formulae $VO_2Y \cdot HY$, $VO_2Cl(HY)_2$ and $VO_2ClO_4(HY)_3$. If the isolated complexes were again dissolved in $CHCl_3$, these solutions gave visible spectra identical to those obtained by direct extraction. This further proves that neither decomposition nor any change occured during the isolation.

Application to the spectrophotometric determination of vanadium

Linear standard curves were obtained for all these complexes and they obey the Lambert-Beer's law. The optimal concentration range for the determination of vanadium is 1—10 $\mu gVml^{-1}$. The molar absorptivity at 500 nm is 4100 1 $mole^{-1}$ cm^{-1}, at 625 nm 6000 1 $mole^{-1}$ cm^{-1} and at 605 nm 6750 1 $mole^{-1}$ cm^{-1}. The photometric sensitivity of the method, as defined by Sandell, is 0.0124 $\mu gVcm^{-2}$ at 500 nm, 0.0085 $\mu gVcm^{-2}$ at 625 nm and 0.0075 $\mu gVcm^{-2}$ at 605 nm. The reproducibility of the measurements, expressed as standard deviation, is 0.3—2%, depending on the vanadium concentration. The colour of all the complexes is stable for at least 24 hr.

Interference of foreign ions

The influence of various cations and anions was studied in the determination of both the orange and chloro complex. The perchlorato complex of vanadium is not recommended for the spectrophotometric determination because an excess of perchlorate, influences the absorbance. It was found that at pH 2.0 chloride, bromide, sulphate, phosphate and nitrate do not interfere in 7.000-fold amounts. Fluoride and acetate may be present in 1.000-fold, tartrate and oxalate in 50-fold excess, but citrate interferes in low concentration. At 1.6 M HCl acetate, nitrate, fluoride, bromide, sulphate and phosphate do not interfere in 4.000-fold amounts, tartrate, perchlorate and chloride in 2.000-fold amounts, but oxalate and citrate interfere in low concentration. Of the cations, ammonium, potassium, sodium, magnesium, calcium, barium, zinc, cadmium, aluminium, chromium(III), manganese(II), cobalt, nickel and copper do not interfere in 7.000-fold amounts at pH 2.0 and do not interfere in 4.000-fold amounts at 1.6 M HCl.

The cations which interfere at pH 2.0 are given in Table II. Uranyl(VI), gallium(III), niobium(V), zirconium(IV) and tantalum(V) react with HY giving colourless complexes but do not interfere if present in smaller quantities. If they are present in large quantities, an excess of the reagent should be added to eliminate their interference. Titanium(IV) decrease and iron(III) increase the absorbance. Titanium(IV) and zirconium(IV) can be masked by diaminocyclohexanetetraacetate (DCTA), but iron(III) interferes the determination of vanadium at pH 2.0. For the chloro complex, tantalum is the only metal that interferes seriously, while uranyl(VI), gallium(III), iron(III), niobium(V), zirconium(IV) and titanium(IV) can be present in 10-fold excess. If they are present in greater quantities, an excess of the reagent should be added to eliminate their interference.

TABLE II

Interfereing cations at pH 2.0
Concentration of vanadium 1×10^{-4} M, HY 2.5×10^{-3} M

Cation	Cation: V molar ratio	Absorbance at 500 nm
—	—	0.410
Uranyl(VI)	1	0.414
Titanium(IV)	1	0.034
	10	0.400[a]
Zirconium(IV)	10	0.405[a]
	1	0.413
Gallium(III)	1	0.412
Tantalum(V)	1	0.408
Niobium(V)	1	0.402
Iron(III)	2	1.445
	1	0.980

[a] Concentration of DCTA 1.0×10^{-2} M

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SAŽETAK

Primjena 1-(4-tolil)-2-metil-3-hidroksi-4-piridona za spektrofotometrijsko određivanje vanadija(V)

B. Tamhina, V. Vojković i M. J. Herak

Opisana je primjena ekstrakcije vanadija(V) s 1-(4-tolil)-2-metil-3-hidroksi-4-piridonom za spektrofotometrijsko određivanje vanadija. Utvrđeno je da nastaju tri vrste kompleksa ovisno o uvjetima ekstrakcije. U području pH 1.2—2.5 nastaje $VO_2Y \cdot HY$, kompleks narančaste boje s maksimumom apsorpcije kod 500 nm. U kiselijim otopinama (1.2—2.0 M H^+) uz prisustvo suviška klorid iona nastaje $VO_2Cl(HY)_2$, kompleks modre boje s maksimumom apsorpcije kod 625 nm, a uz suvišak perklorat iona i kod koncentracije vodikovih iona 0.2—1.0 M nastaje $VO_2ClO_4(HY)_3$, kompleks modre boje s maksimuom apsorpcije kod 605 nm. Nastajanje sva tri kompleksa slijedi Lambert-Beer-ov zakon, a otopine tih kompleksa u kloroformu su vrlo stabilne.

Postupak za određivanje vanadija kod 500 nm i 625 nm je vrlo jednostavan, brz i selektivan. Sastavi kompleksa su određeni mjerenjima u otopini i karakterizacijom izoliranih kompleksa u čvrstom stanju.

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PRIRODOSLOVNO-MATEMATIČKI FAKULTET,
ZAGREB

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