

Some Observations on the use of 2-Hydroxyacetophenone Thiosemicarbazone as a Spectrophotometric Reagent for the Determination of Vanadium(IV) and Vanadium(V)

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2-Hydroxyacetophenone thiosemicarbazone produce pale yellow coloured solutions with vanadium(IV) and vanadium(V) in acetic acid-sodium acetate buffer medium. The colour obtained has been used to develop spectrophotometric methods for the determination of vanadium(IV) and vanadium(V) in the concentration ranges 1.02-4.59 ppm and 0.2-4.6 ppm (λ_{\max} 360 nm) respectively.

INTRODUCTION

Thiosemicarbazones are selective and sensitive reagents for the spectrophotometric determination of metals^{1,2}. Only two spectrophotometric methods are reported for vanadium with thiosemicarbazones and each method has its own disadvantages like low sensitivity, poor selectivity and extraction etc. We report here the use and advantages of 2-hydroxyacetophenone thiosemicarbazone (HAPT) as a reagent for the spectrophotometric determination of vanadium(IV) and vanadium(V). In our earlier papers we have reported the synthesis and analytical properties of HAPT and its application to the spectrophotometric determination³ of palladium, copper, cobalt and nickel.

EXPERIMENTAL

A spectronic-21 Bausch-Lomb spectrophotometer equipped with glass or quartz cells was used for all absorbance measurements, and an ELICO pH meter of model LI-120 was used for pH measurements.

All solvents and reagents used were of analytical grade. HAPT was synthesized as described earlier³. A 5×10^{-2} M solution in DMF was used. Approximately 0.1 M solution of vanadium(IV) was prepared by the reduction of ammonium metavanadate with excess of sulphur dioxide⁴. The excess of sulphur dioxide was removed by bubbling with carbon dioxide and the solution was standardized potentiometrically⁵. For vanadium(V) solution, a 0.1 M stock solution of ammonium metavanadate was prepared in doubly distilled water and standardized titrimetrically⁴.

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Procedure

To an aliquot of the solution containing 1.02–4.59 ppm of vanadium(IV) or 0.2–4.6 ppm of vanadium(V), in a 25 ml calibrated flask, add 12.5 ml of buffer solution of pH 5.5, 3 ml of DMF and 1 ml of 5×10^2 M reagent solution. Dilute the mixture to the mark with distilled water and measure its absorbance at 360 nm against the reagent blank.

RESULTS AND DISCUSSION

HAPT gives yellowish green coloured solutions instantaneously with vanadium(IV) or vanadium(V) solutions in acetic acid-sodium acetate buffer of pH 5.5. The absorption spectra of these solutions show maximum at 360 nm. The absorbance vs pH plots reveal that the absorbance is maximum and unchanged in the pH ranges 5.0–6.5 and 5.0–7.5 for vanadium(IV) and vanadium(V) respectively. In both cases pH 5.5 was chosen for further studies.

Influence of Reagent Concentration

In both cases at least 40-fold excess is required for full colour development. Addition of excess of reagent has no adverse effect on the absorbance.

Influence of DMF Concentration

In both cases, the complexes are found to be soluble in DMF and 12% v/v of DMF is required to keep the complexes in solution. At lower concentrations of DMF the solutions are turbid.

Influence of Order of Addition

The order of addition has no influence on the absorbance. However, the sequence of buffer, DMF, metal ion solution and the reagent solution is followed for both the complexes.

Photometric Characteristics

Vanadium(IV): Beer's law is obeyed in the range 1.02–4.59 ppm. The optimum range as evaluated by Ringbom's method is 1.53–4.50 ppm. The molar absorptivity and Sandell's sensitivity of the method are $8500 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.0060 \mu\text{g cm}^{-2}$ respectively.

Vanadium(V): Beer's law is obeyed in the range 0.2–4.6 ppm. The optimum range is 0.61–4.60 ppm. The molar absorptivity and Sandell's sensitivity of the method are $8250 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.0061 \mu\text{g cm}^{-2}$ respectively.

Composition of the Complexes

In both the cases Vosburgh and Cooper's⁶ method indicated the formation of single complex species. Job's molar ratio and slope ratio methods showed that the metal to ligand ratio in each case is 1 : 1. The stability constants of the vanadium(IV) and vanadium(V) complexes are 2.4×10^4 and 6.05×10^5 respectively.

Effect of Foreign Ions

Various foreign ions are examined for their effect on the determination of vanadium(IV) or vanadium(V). The tolerance limits (in ppm) of these ions in the determination of 2.04 ppm of vanadium(IV) or vanadium(V) are as follows. An

error of $\pm 2\%$ in absorbance was considered to be tolerable. EDTA (1300, 39), tartrate (1185, 590), sulphate (960, 765), phosphate (78, 780), bromate (760, 255), citrate (755, 1520), bromide (800, 640), nitrate (620, 495), iodide (500, 500), thiourea (455, 455), chloride (320, 350), tetraborate (310, 930), thiosulphate (220, 90), perchlorate (200, 200), fluoride (190, 225), thiocyanate (115, 70), oxalate (70, interferes), ascorbic acid (14, 1), Pb (II) (330, 165 masked with thiosulphate), Cd(II) (135, 170), W(VI) (110, 100 masked with citrate), Th (IV) (90, 50) masked with fluoride, U(VI) (95, 150), Mo(VI) (58, 60), Zn(II) (50, 130), Fe(III) (45, 120 masked with fluoride), Mn(II) (35, 35), Ag(I) (25, 8), Al(III) (11, 45 masked with fluoride), Cr(III) (11, 11), Ce(IV) (6, 6), Ni(II) (5, 12), Pt(IV) (2, 2), Cu(II) (2 masked with citrate, 7 masked with thiosulphate), Co(II) (15, 15 masked with thiosulphate), Ru(III) and Au(III) (1 ppm each). In the case of V(IV) the tolerance limit of zinc(II) and iron(III) could be increased upto 250-fold and 100-fold excess by masking with citrate and phosphate respectively.

Application

The method developed for vanadium was applied to the determination of vanadium in steel sample (BCS 241/2). Steel sample was brought into solution by adopting standard procedure⁷. In the analysis fluoride (200 ppm) and citrate (500 ppm) were added to mask iron and tungsten respectively. The data are shown in Table 1.

TABLE 1
DETERMINATION OF VANADIUM IN ALLOY STEEL

| Composition of steel sample | Amount of vanadium (ppm) | | Error (%) |
|------------------------------|--------------------------|--------|-----------|
| | Taken | Found* | |
| BCS 241/2 (High speed steel) | | | |
| W 19.90; Cr 5.35; | 1.27 | 1.28 | 0.79 |
| V 1.59; Mo 0.53; | 2.54 | 2.52 | 0.79 |
| Co 5.70; C 0.84; | 3.82 | 3.78 | 1.05 |
| Si 0.21; S 0.025; | 4.58 | 4.59 | 0.22 |
| P 0.024; Mn 0.27; | | | |
| Ni 0.15; Cu 0.08; | | | |
| Sn 0.025 | | | |

*Average of five determinations.

TABLE 2
 $E_{1/2}$ VALUES OF THE POLAROGRAMS OF VANADIUM(IV),
VANADIUM(V) AND THE COMPLEXES

| Metal ion/Complex | $E_{1/2}(V)$ vs SCE $s = 0.08$ |
|---------------------------|-----------------------------------|
| HAPT | 0.345 |
| Vanadium(IV) | 0.240 |
| Vanadium(V) | 0.210 |
| Vanadium(IV)-HAPT complex | 0.705 |
| Vanadium(V)-HAPT complex | 0.660 |

Conditions: $[R] = 2.5$ ml of 5×10^{-2} M; $[M] = 1.0$ ml of 1×10^{-2} M;
pH = 5.5 12.5 ml; DMF = 5 ml; Total volume = 25 ml

Polarographic Study

Since the λ_{\max} in both the complex species is the same (360 nm), the polarograms of the vanadium (IV) and vanadium(V) complexes of HAPT are recorded (Table 2). The $E_{1/2}$ values of the polarograms of both the complexes are significantly different. This suggests that the oxidation state of vanadium is different in both the complexes.

Conclusions

The proposed methods are compared with the previously reported thiosemicarbazone reagents (Table 3).^{8,9} It is evident that HAPT is the most sensitive thiosemicarbazone for the spectrophotometric determination of vanadium. Further, the methods developed are simple rapid without the need for heating or extraction.

TABLE 3
COMPOSITION WITH OTHER THIOSEMICARBAZONE REAGENTS

| Compound | Species | λ_{\max} nm | pH | $l \text{ mol}^{-1} \text{ cm}^{-1}$ | Medium | Ref. |
|---------------------------|---------|---------------------|-------------|--------------------------------------|-------------------|--------------|
| Salicylaldehyde | V(V) | 370 | 5.0–6.5 | 6300 | Aqueous | 8 |
| thiosemicarbazone | V(V) | 375 | 0.06–0.08 M | 4300 | <i>n</i> -Butanol | 8 |
| 2-Acetylpyridine | V(V) | 400 | 3.5 | 5600 | Aqueous | 9 |
| thiosemicarbazone | | | | | | |
| 2-Hydroxyaceto phenone | V(IV) | 360 | 5.0–6.5 | 8500 | Aqueous | Present work |
| thiosemicarbazone | V(V) | 360 | 5.0–7.0 | 8250 | Aqueous | Present work |

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