



2-Hydroxy-4-*n*-propoxy-5-bromoacetophenone oxime as an Analytical Reagent for Gravimetric Determination of V(V)

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Received 1 August 2008; Accepted 1 October 2008

Abstract: 2-Hydroxy-4-*n*-propoxy-5-bromoacetophenone oxime (HnPBAO) was developed as a new analytical reagent for the gravimetric determination of pentavalent vanadium ion. In the pH range 4.0-6.0, the reagent gave a brown coloured precipitate with V(V). Job's method and Mole ratio method revealed that the stoichiometry of the complex is 1:1 (metal: ligand). Beer's law is obeyed up to 20.38 ppm of V(V). Molar absorptivity and Sandells sensitivity at 450 nm were found to be 10.22×10^2 L/mol/cm and $0.049 \mu\text{g}/\text{cm}^2$ respectively. The stability constant of V(V)-HnPBAO complex is found to be 1.195×10^6 . Gibb's free energy change for complex formation reaction was found to be -8.34 kcal/mol. The reagent can be used for the analysis of vanadium in ferro-vanadium alloys.

Keywords: Oxime, Analytical reagent, 2-Hydroxy-4-*n*-propoxy-5-bromoacetophenone

Introduction

A wide variety of reagents are available for the study of metal ions in analytical chemistry. They include thiosemicarbazones^{1,2}, oximes^{3,4}, *o*-hydroxy ketoximes⁵ etc. These reagents are generally used for the determination of transition metal ions using gravimetric and spectrophotometric techniques. In the present work, the use of 2-Hydroxy-4-*n*-propoxy-5-bromoacetophenone oxime (HnPBAO) as a gravimetric reagent for V(V) has been reported. Spectrophotometric methods have been used to confirm the stoichiometry of the complex and to determine the stability constants of the complex. The reagent was used to determine vanadium in alloys.

Experimental

Schimadzu UV-Visible spectrophotometer (160A) was used for all absorbance measurements and pH of the solutions was measured on Equiptronics (EQ-614) and buffer solutions of required pH were obtained using acetic acid-sodium acetate solution of suitable concentrations.

Synthesis of 2-hydroxy-4-n-propoxy-5-bromoacetophenone oxime (HnPBAO)

Resacetophenone was prepared using resorcinol, acetic acid and anhydrous $ZnCl_2$. This was treated with bromine in acetic acid and poured on ice cold water. The product was crystallized from ethanol. 2,4-Dihydroxy-5-bromoacetophenone obtained was mixed with anhydrous potassium carbonate, *n*-propyl iodide in acetone and refluxed. Hydroxylamine hydrochloride and sodium acetate were added and solution was again refluxed on a water bath. The mixture was poured on ice and light green solid got precipitated which was crystallized from ethanol (m.p 172 ± 1 °C). The reagent was soluble in solvents like ethanol, DMF *etc.*

The elemental analysis of the reagent showed the percentage of carbon, hydrogen and nitrogen as 45.83, 4.83 and 4.86% respectively. (The calculated value was found to be 46.12, 4.72 and 4.68% for carbon, hydrogen and nitrogen respectively).

Stock solution

Ammonium metavanadate (0.05 M) solution was prepared by dissolving the requisite amount (1.426 g) of salt in double distilled water, little free acid was added and standardized titrimetrically. Solutions of required concentrations were prepared by diluting the above stock solution. Solution of the reagent HnPBAO (0.05 M) was prepared by dissolving oxime in pure ethanol.

Gravimetric procedure

A 0.05 M solution of the reagent in pure ethanol was used. Ammonium metavanadate solution (0.05 M, 10 mL) taken in a clean beaker was diluted to about 100 mL with distilled water and pH of the solution was adjusted between 3.0 to 4.0 using sodium acetate-acetic acid buffer. The solution was warmed to 60°C and a small excess of reagent (0.05 M, 22 mL) was added. The light brown precipitate obtained was digested on water bath for 60 min at 60-70 °C. The precipitate was filtered through a previously weighed sintered glass crucible (G4) and washed with warm water followed by ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115 °C in hot air oven, cooled and weighed.

Gravimetric determination of V(V)

To establish the applicability of the reagent for gravimetric estimation of V(V), the metal ion was determined in the pH range 4.0 to 6.0. The maximum error being $\pm 1.5\%$. Estimations were done at pH 5.0 using different aliquots of V(V). In all cases the error in V(V) content did not exceed $\pm 0.46\%$ (Table 1).

Table 1. Result of gravimetric estimation of V(V) at pH 5.0, V(V)-HnPBAO

Weight of V(V) taken in mg	Weight of V(V) complex in mg	Weight of V(V) ion found in mg	Relative Error	
			mg	%
25.47	169.85	25.57	+0.10	+0.39
38.20	254.86	38.38	+0.18	+0.46
50.94	339.78	51.17	+0.23	+0.44

Interferences

To study the effect of foreign ions on gravimetric determination of V(V), 8-10 mg of various cations were added to a solution containing 25.47 mg of V(V) at pH 5.0 and gravimetric estimations were done. It was observed that Ca(II), Mg(II), Ni(II), Sr(II), Cd(II), Ba(II), K(I) and Na(I) do not interfere at this pH but Cu(II), Fe(III) and Co(II) interfered seriously. Many common anions like chlorides, bromides, iodides, nitrates, nitrites and sulphates were not found to interfere.

Spectrophotometric study of V(V)-HnPBAO complex

For taking the absorbance spectra, a solution of metal ion (0.0025 M, 1 mL) and reagent (0.01 M, 6 mL) was taken in a beaker and the pH was adjusted to 5.0 with buffer and the volume was made up to 25 mL with DMF. The absorbance was measured in the range 300-800 nm.

On plotting the absorbance spectra it was observed that the absorbance of the complex increased continuously towards a shorter wavelength. The spectra showed a shoulder band at 450 nm and hence all the measurements were done at 450 nm.

The V(V)-HnPBAO complex was found to be insoluble in chloroform, dioxane, ethyl acetate *etc* but it was soluble in DMF. For spectrophotometric studies varying amounts of V(V) solution was taken and pH was adjusted to 5.0 with acetic acid - sodium acetate buffer and HnPBAO solution was added and made up to 25 mL using DMF and the absorbance measured against reagent blank.

Validity of Beer's law

The V(V)-HnPBAO complex in DMF obeys Beer's law up to 20.38 ppm. Beyond this concentration the absorbance plot showed deviation from linearity (Figure 1). Standard graph thus obtained may be used for the determination of vanadium in an unknown solution using HnPBAO. Molar absorptivity calculated from Beer's law plot was found to be 10.22×10^2 L/mol/cm for V(V)-HnPBAO at 450 nm and Sandell's sensitivity was calculated and found to be $0.049 \mu\text{g}/\text{cm}^2$ of V(V) at 450 nm.

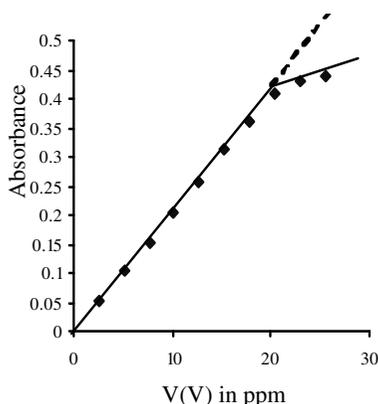


Figure 1. Beer's Law Plot for V(V)- HnPBAO Complex.

Plot of Job's method of continuous variation for determination of M: L ratio 0.001 M V(V), 0.001 M HnPBAO, pH = 5.0, $\lambda = 450$ nm

Stoichiometry of complex

The stoichiometry of V(V)-HnPBAO complex was determined by Job's method of continuous variation⁶ and Yoe and Jones's mole ratio method⁷ (Figure 2 and 3). Both the methods gave the metal:ligand ratio of the complex as 1:1. This is in agreement with the stoichiometry found from gravimetry.

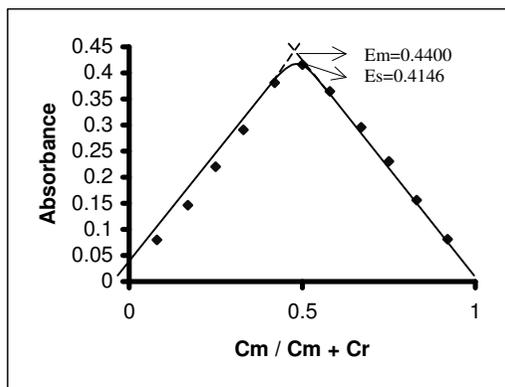


Figure 2. Job's Method for V(V)-HnPBAO Complex.
Plot of Job's method of continuous variation for determination of M:L ratio
0.001 M V(V), 0.001 M HnPBAO, pH = 5.0, $\lambda = 450$ nm.

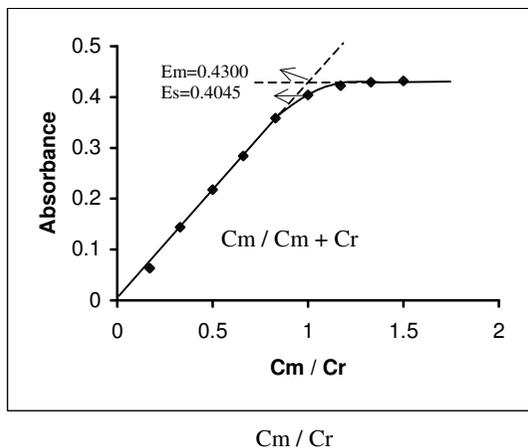


Figure 3. Mole-Ratio method for V(V)-HnPBAO Complex
Plot of Yoe and Jones method for determination of M:L ratio
0.001 M V(V), 0.001 M HnPBAO, pH = 5.0, $\lambda = 450$ nm

Stability constant of the complex

The stability constants of the complex were calculated using the formula $K_s = (1-\alpha)/4 \alpha^3 C^2$ where $\alpha = (E_m - E_s)/E_m$.

E_m = maximum absorbance obtained at the intersect of the two lines
 E_s = absorbance at the stoichiometric ratio of the metal to the reagent in complex.

The average stability constant found from two methods is 1.195×10^6 from K_s value. Gibb's free energy change for complex formation reaction was calculated and its value was found to be -8.34 kcal/mol at 27°C .

Determination of vanadium in ferro-vanadium alloy

The Ferro-vanadium alloy was obtained from National Metallurgical Laboratory, Jamshedpur. It was weighed exactly (156.70 mg) and dissolved in a mixture of concentrated nitric acid and hydrochloric acid (1:3) by heating on a sand bath. Excess nitric acid was evaporated and the solution was diluted to 100 mL with distilled water.

10 mL aliquot was taken and V(V) was determined gravimetrically using HnPBAO at pH 5.0. Fe(III) was masked by adding sodium fluoride. The experiment was repeated three times. Percentage vanadium found: 51.77%, Percentage vanadium reported: 52.10%.

Conclusion

2-Hydroxy-4-*n*-propoxy-5-bromoacetophenoneoxime (HnPBAO) is a suitable reagent for spectrophotometric determination of V(V). Many cations and anions were not found to interfere.

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