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NOTE

2-Hydroxy-4-Ethoxy Valerophenone Oxime as an Analytical Reagent for Molybdenum(VI)

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Molybdenum(VI) forms yellow coloured stable complex with 2-hydroxy-4-ethoxy valerophenone oxime at pH 3.0 in 50% aqueous ethanol medium. The complex absorbs maximum at 420 nm. The composition of the complex determined by Job's method was found to be 1 : 1 (metal : ligand). The stability constant of the complex is found to be 1.102×10^5. The standard free energy change for the formation of the complex is –6.98 kcal/mol at 30°C. Beer's law is obeyed up to 120.96 ppm of Mo(VI) ion. The molar absorptivity and Sandell's sensitivity at 420 nm are found to be 1.51×10^2 L/mol cm and 0.635 μg/cm^2, respectively. Interference due to presence of foreign ions in the spectrophotometric determination of Mo(VI) has been studied. The reagent has also been found to be give quite satisfactory results for the determination of molybdenum in ferro-molybdenum.

Key Words: Molybdenum(VI), 2-Hydroxy-4-ethoxy valerophenone oxime, Spectrophotometric determination.

Oximes[1–4] have been used as gravimetric and spectrophotometric reagents for a number of transition metal ions. In the present work, the use of 2-hydroxy-4-ethoxy valerophenone oxime (HEVOX) as spectrophotometric reagents for Mo(VI) is reported.

A 0.05 M stock solution of Mo(VI) was prepared by dissolving sodium molybdate [AR, BDH] in distilled water containing few drops of acid. It was standardized by the oxime method[5]. The solution was then diluted as per requirement.

Resvalerophenone[6] was prepared from resorcinol, *n*-valeric acid and anhydrous zinc chloride. 2-Hydroxy 4-ethoxy valerophenone was prepared by reported method[7]. Its oxime was prepared by refluxing its alcoholic solution with hydroxylamine hydrochloride in the presence of sodium acetate. It was crystallized from ethanol, colourless crystals were obtained. yield 85%, m.p. 80°C and elemental analysis (%), Found (Calcd.): C: 66.24 (65.82); H: 8.19 (8.01); N: 5.78 (5.90).

Preparation of Mo(VI)-HEVOX complex: A series of buffer solutions with pH values from 2.0–3.5 were prepared using hydrochloric acid and sodium acetate. To this 1.0 mL of Mo(VI) (0.01 M) solution of reagent HEVOX were added and the solution was diluted to 25 mL keeping final concentration of alcohol 50%. The appearance of yellow colour indicated complex formation. The coloured complex was formed instantaneously mixing the reagent and the order of addition of reagent had no effect on the reaction. The complex was stable for 24 h.

Spectrophotometric measurements were made on Bausch & Lomb spectrophotometer [Spectronics-20]. All the pH measurements were made with an Elico pH-meter [LI-10T].

Optimum pH and selection of wavelength: The absorbance is dependent upon the wavelength used. The absorbance measurement of Mo(VI)-HEVOX complex shows that the absorbance of coloured solution increases continuously towards the shorter wavelength; the absorbance shows a shoulder at 420 nm. A wavelength of 420 nm is selected for the present work. On studying the effect of pH, it was found that maximum complex formation takes place at pH 3.0. Hence, all the measurements were done at pH 3.0 and wavelength 420 nm.

Stoichiometry and stability constant of the complex: The method of Vosburgh and Copper[8] shows that only one complex is formed. To determine the stoichiometry of complex, Yoe and Jones mole ratio method[9] and Job's method of continuous variation[10] were used. These two methods show that the metal-ligand ratio in the complex is 1 : 1. The values of the stability constants calculated from Job's method as well as from the mole ratio method are given in Table-1. From the table, the average value of stability constant may be taken as 1.102×10^5. The standard free energy of formation of the complex ΔG° is –6.98 kcal/mol at 30°C.

TABLE-1
STABILITY CONSTANT OF Mo (VI)-HEVOX AT 30°C

Method employed	E_m	E_s	α	K (n = 1)
Mole ratio method	0.15	0.14	0.0660	1.070×10^5
Job's method	0.17	0.16	0.0588	1.134×10^5
Mean K_s	—	—	—	1.012×10^5

Validity of Beer's law: The Mo(VI)-HEVOX complex obeys the Beer's law up to 120.96 ppm of Mo(VI) ion. The molar absorptivity and Sandell's sensitivity calculated from the Beers's law plot are found to be 1.51×10^2 L mol^{-1} cm^{-1} and 0.635 μg cm^{-2}, respectively at 420 nm.

Effect of diverse ions: The influence of foreign ions on the spectrophotometric determination of Mo(VI) using HEVOX was also studied in the usual manner. A limit of 2.5% change in absorbance was taken as limiting concentration. It was observed in the solution of 86.4 ppm of Mo(VI) at pH 3. 0.1000 ppm concentration of Cd^{2+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, Sr^{2+}, Zn^{2+}, Zr^{4+}, Cl^-, ClO_4^-, NO_3^-, SO_4^{2-}; 750 ppm concentration of Co(II), bromide and 500 ppm concentration of iodide

could be tolerated. Phosphate, fluoride, citrate, oxalate interfere even when they are present in traces.

Determination of molybdenumin ferro-molybdenum: The pre-analyzed sample of ferro-molybdenum 0.5574 g was dissolved in a mixture of concentrated nitric acid and hydrochloric acid (1 : 3) by heating on a sand bath. Excess of nitric acid was evaporated and the solution was diluted to 250 mL. A 2.0 mL aliquot was taken. Fe^{3+} was masked by adding sodium fluoride. The pH was adjusted to 3.0 and the complex was formed by adding the reagent HEVOX. The final volume was adjusted to 25 mL with 50% aqueous ethanol and the absorbance was measured at 420 nm. The percentage of Mo(VI) found in ferro-molybdenum sample is 65.03% (theoretical value 64.55%).

REFERENCES

1. J. Singh and S.P. Gupta, *Curr. Sci. (India)*, **44**, 612 (1975); *Indian J. Chem.*, **14A**, 710 (1976).
2. S. Prakash, Y. Dutt and R.P. Singh, *Indian J. Chem.*, **8**, 460 (1970).
3. K.K. Desai and H.B. Naik, *Indian J. Chem.*, **25A**, 297 (1986).
4. A. Desai and H.B. Naik, *Indian J. Chem.*, **62**, 165 (1990).
5. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 4th Edn., p. 212 (1978).
6. H. Nogami, *J. Pharm. Soc. (Japan)*, **61**, 46 (1941).
7. Eijkman, Bergema and Henrard, *Chem. Center*, **1**, 815 (1905).
8. W.C. Vosburgh and G.R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).
9. J.H. Yoe and A.L. Jones, *Ind. Eng. Chem. Anal. Ed.*, **16**, 111 (1944).
10. P. Job, *Ann. Chem.*, **9**, 133 (1928).

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