

NOTE

Spectrophotometric Study of U(VI) with 2-Hydroxy-4-Chloro-5-Methylpropiophenone Oxime

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In view of the growing importance of *o*-hydroxy ketoxime as analytical reagent, we have applied 2-hydroxy-4-chloro-5-methylpropiophenone oxime (HCMPOX) for determination of U(VI) spectrophotometrically. Stoichiometry of the complex was studied by continuous variation, the mole ratio and the slope ratio methods which comes out to be 1 : 2 (metal : ligand). Absence isobestic point shows that single complex species exists. The stability constant of the complex is found to be 1.64×10^6 . The structure of the complex was also studied by infrared spectra and magnetic susceptible data.

The present communication deals with the spectrophotometric study of uranium(VI) with 2-hydroxy-4-chloro-5-methylpropiophenone oxime HCMPOX.¹ Earlier we used present oxime for Mo(VI) also.² The proposed method is simple rapid and more selective than the methods reported earlier.² HCMPOX was found to be specific and selective for the determination of U(VI). The orange yellow coloured water-soluble complex was found to be stable in the pH range 7.5–11.00 with maximum colour intensity between pH 8.5–10.0. Subsequent studies were carried out at pH 9.0–9.5. 15-fold excess of the reagent was necessary to attain the constant and maximum colour intensity. The colour development was quite rapid and remained unchanged for at least 3 h and the sequence of reagent addition had no significant effect on absorbance.

The solutions containing varying concentrations of U(VI) ions were added to 25 mL volumetric flasks containing 15-fold excess of reagent and 5 mL of buffer solution. Requisite amount of alcohol was added to maintain its 50–60% proportion in final dilution. All the absorbances were measured at 430 nm with the reagent solution as blank. On plotting absorbances against metal content, a straight line passing through the origin was obtained up to 47.6 ppm of U(VI) ions indicating obeyance of Beer's law. The value of the molar absorptivity came out to be 2.13×10^3 lit mole⁻¹ cm⁻¹. The influence of foreign ions was studied and it was observed that Ba²⁺, Be²⁺, Ca²⁺, Sr²⁺, K⁺, Na⁺, NH₄⁺, Cl⁻, Br⁻, I⁻,

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NO_3^{2-} , SO_4^{2-} , OAc^- , $\text{C}_2\text{O}_4^{2-}$, did not interfere but Cr^{3+} , Al^{3+} , Mn^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} could not be tolerated even when present in traces.

The composition of the complex was determined by Job's method of continuous variation³ the mole ratio method⁴ and the slope ratio method.⁵ The results from all these methods indicated the formation of 1 : 2 (metal : ligand) complex. The value of the stability constant calculated from the mole ratio method comes out to be 1.64×10^6 indicating the high stability of the complex.

For magnetic and infrared spectral studies the solid complex was isolated by simple evaporation method. The stoichiometry mixture of metal solution, reagent and buffer was kept in an evaporating dish for days and the solid complex left at the bottom was washed with ethanol and dried.

IR spectrum of the ligand shows two bands at 3380 and 3000 cm^{-1} in the —OH stretch region assigned to two different types of hydroxyl group present in the ligand. Only the band at 3380 cm^{-1} disappears in the complex showing the replacement of phenolic hydrogen by the metal. The coordination of the oximino group through nitrogen and not hydroxy group is indicated by the lowering of (C=N) frequency. This indicates that chelation takes place through the oxygen of —OH group and nitrogen of =N—OH group. Presence of characteristic frequency in the region 950–890 cm^{-1} is clear indication for the development of UO_2^{2+} in bonding^{6,7} Magnetic study claims octahedral diamagnetic character.

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