RESEARCHERID
THOMSON REUTERS
[COTII 2019]
ISSN 2348 – 8034
Impact Factor- 5.070

GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES

SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

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ABSTRACT

Osmium (VIII) forms chocolate colored complex with Phenenthraquinone monothiosemicarbazone (PTS) in the pH range 6.8- 8.5. Though the complex is soluble in common organic solvents however 50% methanol has been used to dissolve it during the investigation. The maximum absorbance of the complex is at 530nm. The molar composition of the complex has been found to be 1:3. The optimum range of concentration of osmium for its accurate determination, has been found to be 2.0 – 11 .0 ppm. The sensitivity of the reaction is 0. 0124 µg / $cm^{-2}$for Iog I_0/I = 0.001, with molar extinction coefficient of 15280 l $mole^{-1}$ cm^{-1} .

I. INTRODUCTION

Phenenthraquinonemonothiosemicarbazone (PTS) forms a chocolate colored complex with osmium (VIII), which is soluble in common organic solvents. In the present method, attempts have been made to utilise this color reaction for the spectrophotometric determination of osmium. Masking agents have been used to make the method more selective.

II. EXPERIMENTAL

Preparation of PTS:
PTS was prepared by oxidation of phenanthrene (Fluka, AG) to phenanthraquinone by the method of Schultz and was purified. Then equimolar amounts of phenanthraquinone and thiosemicarbazide (E.Merck GR) were dissolved separately in minimum amounts of methanol and then mixed. After mixing, the solution was refluxed for three hours on a boiling water bath. The hot solution was filtered under suction and cooled. Red crystals of PTS were obtained which were recrystallised from methanol (m,p, 191-192). The purity of the ligand has been checked by elemental analysis and thin layer chromatography. The wavelength of maximum absorption of PTS IS at pH 0.7,6.5 and11.9 is at 250,254 and 207 nm respectively. PTS solution was prepared by dissolving it in dimethyl formamide (DMF) because its greater solubility in this solvent. The solution is stable for two days.

Osmium (VIII) solution
Standard solution of osmium (VIII) was prepared by dissolving osmium tetroxide (1 g ampoule) in about 100 ml of 0. 2N sodium hydroxide contained in a glass – stoppered flask as described by Ayres and Wells. The orange red solution was washed into a one litre volumetric flask and the solution was made up to the mark with double distilled water. The solution was further standardized by the method of Klobbie. To 25 ml of stock solution was added 15 ml of 6M sulphuric acid and 2 g of KI. The liberated iodine was titrated with standard sodium thiouslphate solution. The difficulty in determining the end point on account of green colour of the reduced osmium was circumvented by taking iodine benzene and titrating with standard sodium thiosulphate until colorless layer of benzene was obtained. The titrations were repeated until same results were obtained. Working solutions were obtained from this stock solution. The oxidation state of osmium is eight, $K_2O_SO_4(OH)_2$and not six ($K_2O_SO_4$) as was formerly believed.

Solubility of the complex and its stability
The complex was found to be soluble in common organic solvents. It was further observed that atleast 40% methanol is needed for complete solubility of the complex. However, 50% methanol medium was maintained in subsequent studies. The absorbance of the solution remains constant for atleast 6 hours.

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Absorption spectra
To an aliquot containing 47.6 µ g of osmium, was added 1 ml of 2.5 x 10^{-3} M of the reagent in DMF and the pH was adjusted with dilute solutions of sodium hydroxide and hydrochloric acid. 5 ml of methanol was added and the volume of the solution was made up to 10 ml. The maximum absorbance of the complex has been found to be at 530 nm.

Effect of pH
The effect of pH on the complex was studied by preparing a series of solutions containing 1 ml of 2.5 x 10^{-4} M osmium (VIII) solution and an excess of the reagent. pH's were adjusted with dilute solutions of sodium hydroxide and hydrochloric acid. It has been found that absorbance is maximum and constant in the pH range 6.8-8.5. Subsequent work has been carried out within this pH range.

Effect of ligand concentration
Solutions containing 1 ml of 2.5 x 10^{-4}M osmium (VIII) were taken and reagent solution was added in increasing amounts. The pH, in each case was adjusted to 7.5 ± 0.1. The total volume was made to 10 ml, maintaining 50% methanol medium and absorbance were then measured at 530 nm against the reagent blanks prepared under identical conditions. The results show that at least 8 times molar excess of the ligand should be added for maximum absorbance. However, ten – fold molar excess was maintained in subsequent studies.

Physical constants of the complex
In order to study adherence to Beer's law, solutions containing varying amounts of osmium (VIII) and an excess of the reagent were prepared and the absorbance were measured against a reagent blank. It has been found that the system obeys Beer's law upto 12.85 ppm of osmium (VIII). The optimum range of concentration of osmium for accurate determination, as deduced from Ringbom plot has been found to be 2.0 – 11 .0 ppm. The sensitivity of the reaction is 0. 0124 µg / $cm^{-2}$for Iog I_0/I = 0.001, with molar extinction coefficient of 15280 1 $mole^{-1}$ cm^{-1}.

Recommended procedure
20. 0 – 110. 0 µg of osmium (VIII) is taken and ten – fold molar excess of the reagent is added. The pH is adjusted between 6.8 – 8.5 with dilute solutions of sodium hydroxide and hydrochloric acid. The solution is made up to 10 ml with double distilled water, keeping 50% methanol medium and the absorbance is measured against a reagent blank prepared under identical conditions. Knowing the absorbance the amount of osmium is deduced from the calibration curve.

Absorbance deviations
For a set of eight determinations containing 4.76 ppm of osmium, the mean absorbance was 0.382, with an average relative deviation of 0.47% and with standard deviation of 5.0 x 10^{-3}.

Molar composition of the complex

(i) By Job's method
A series of equimolar solutions of osmium (VIII) and the reagent were mixed in different ratios, while the sum of the molarities of the reactants was kept constant. The plot of absorbance vs mole fraction of osmium indicates the formation of 1:3 complex.

(ii) By mole ratio method
Solutions were prepared in which concentration of osmium was kept constant and that of the reagent was increased. The ratio of metal and the ligand in the complex, as deduced from the position of the break in the curve is 1:3, confirming the results obtained by Job's method.

Effect of foreign ions
Solutions containing fixed amounts of metal and varying amounts of foreign ions were prepared and analysed for the osmium content. The absorbance was measured at 530 nm against a reagent blank. The concentrations of different

ions (in ppm), which did not cause any interference in the determination of 4.76 ppm of osmium, are shown below. Masking agents, wherever, are given in parentheses :-

Chloride and nitrate (800 each), bromide (900), iodide (500), fluoride (100), phosphate (10), citrate and tartrate (400 each), thiosulphate(500), oxalate (150), EDTA (50), magnesium (II) and calcium (II) (80 each), barium (II) and strontium (II) (100 each), iron (II) (5, F^-), silver (I) (20 $C1^-$), zinc (II) (10, citrate), cadmium (II) (10, $S_2O_3^{-2}$), mercury (II) and palladium (II) (5 each, I^-), platinum (VI) (2, I^-), arsenic (III) (60), vanadium (V) (5), urany1 (II) (70), aluminium (III) (50), lead (II) (20, I^-).

However, nitrite, thiourea, nickel (II), copper (II), cobalt (II), ruthenium (III), rhodium (III) and iridium (III) interfere in the determination.

III. DISCUSSION

The simple but rather insensitive method using thiourea for the spectrophotometric determination of osmium is the best described method and is also popular. The main drawback with this method is that quantity of thiourea required for fixed amount of osmium depends on the volume of the solution. Out of the platinum metals palladium and ruthenium interfere.

The most sensitive reagent for osmium has been claimed to be 1,5 – diphenylcarbohydrazide. The color development is dependent on temperature, concentration of perchloric acid, time of standing in aqueous phase, period of extraction of the complex into chloroform and order of addition of reagents. Fe (III), Cu (II), Ru (III) and Au (III) interfere, as do larger quantities of Ni (II), Cr (VI), Mo (VI), and chloride.

2 – Amino – 8 – naphthol – 3, 6 – disulphonic acid is free from interference due to other platinum metals, but sensitivity is low. Quinistatin oxime method is simple but platinum and several base metals interfere. 3 – Nitroso – 2, 6 – pyridinediol forms a purple colored complex when heated to 100 ^oC for 30 minutes at pH 4.2-5.2. The method is sensitive but lacks selectivity.

Anthranilic acid gives color reactions with Os (IV), Os (VI) and Os (VIII). The reagent is sensitive, but the metal precipitates as the hydrated oxide on addition of the buffer when osmium is present is excess. The associated platinum and base metals interfere, but EDTA serves to mask some of the interferences. In case of acenaphthenequinone monoxime, complete complexation takes place only on heating the solution for about $1\frac{1}{2}$ hours and sensitivity is also low.

N – benzoyl – O– tolyl hydroxylamine, and hexamethylphosphoramide have been reported as sensitive reagents for osmium, but the pH range is narrow (11 – 11 .2) in case of N – benzoyl – 0 – tolylhydroxylamine and hexamethylphosphoramide is less selective.

In the present investigation, PTS has been found to be a suitable reagent for the determination of osmium. No heating is necessary for the development of color as is required in most of the well know methods. The method is simple, rapid and quite sensitive.