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Spectrophotometric Determination of Iridium(III) with Phenanthrenequinonemonosemicarbazone

H.C. RAI* and I. CHAKRABORTI

Department of Chemistry
L.S. College, Muzaffarpur-842 001, India

When phenanthrenequinonemonosemicarbazone (PQSC) reacts with iridium(III) a brown precipitate is formed on heating. The precipitate is partially soluble in ethanol and chloroform and soluble in dimethylformamide. Because of the intensity and stability of the colour formed with iridium(III) this system has been studied in detail with a view to utilise this reaction for the spectrophotometric determination of the metal.

Key Words: Spectrophotometric determination, Ir(III), Phenanthrenequinonemonosemicarbazone.

INTRODUCTION

Very few spectrophotometric reagents are available for the determination of iridium. One of the most sensitive reagents is leuco crystal violet. Major objection in the case of this method is that it is dependent upon a specific composition of the dissolved iridium salt. Aged iridium solutions produce green solutions of lower absorbance than those which are freshly prepared. The method is relatively free of interferences from associated platinum metals and certain base metals. Palladium and nickel interfere least whereas rhodium provides greatest interference.

A simple and rapid method for the determination of iridium involves the use of *o*-dianisidine. Sulphuric acid solutions cannot be used and there is interference from associated metals and from oxidants. The absorbance is sensitive to amount of the reagent and to the acidity of the medium in which the colour is developed.

When an iridium salt solution is boiled with tin chloride, a yellow colour is developed in presence of hydrobromic acid solution. This method suffers from excessive interferences, the effects of which can, in some instances, be removed readily. But in general, a rather complete isolation of iridium is a necessity. There is some value in the tolerance for sulphuric acid. In case if tin bromide, the sensitivity is more, but there is a decrease in stability. Unfortunately, the method is particularly sensitive to variations in procedure such as time of contact, temperature, quantity of reagent and hydrobromic acid. Beer's law is not obeyed. On the other hand there is an advantage in the short time required for determination. Tin(II) iodide forms a stable complex with maximum absorbance at 446 nm. Beer's law is not obeyed but reproducible results may be obtained over the range 0.8–11.7 ppm of iridium. Associated platinum metals and base metals interface.

In the present case, the determination has been carried out using PQSC. The advantage of the method is that the determination has been made possible in presence of various metal ions which are successfully removed by extraction with chloroform in cold solution.

Preliminary tests showed that phenanthrenequinonemonosemicarbazone (PQSC) forms water-insoluble coloured complex with Ir(III). The complex was found to get dissolved in DMF. Based on this property the present work was undertaken to develop a method for spectrophotometric determination of Ir(III).

EXPERIMENTAL

Preliminary investigations

Addition of PQSC solution in ethanol to iridium(III) solution results in the formation of a brown complex on heating the contents for 2 h on a boiling water bath. The complex could not be extracted in water immiscible organic solvents. However, it was found to dissolve in DMF. Varying amounts of DMF were added and it was observed that 60% DMF gives reproducible results above which the optical density remains constant.

RESULTS AND DISCUSSION

Absorption spectra of the complex

Absorption spectra of a series of solutions containing a fixed amount of iridium(III) (2 mL of 1×10^{-3} M) and an excess of the reagent (4 mL of 5×10^{-3} M) at different pH values, were recorded against corresponding reagents blank. The curve shows an absorption maximum at 460 nm (Fig. 1) and this wavelength was chosen for subsequent measurement.

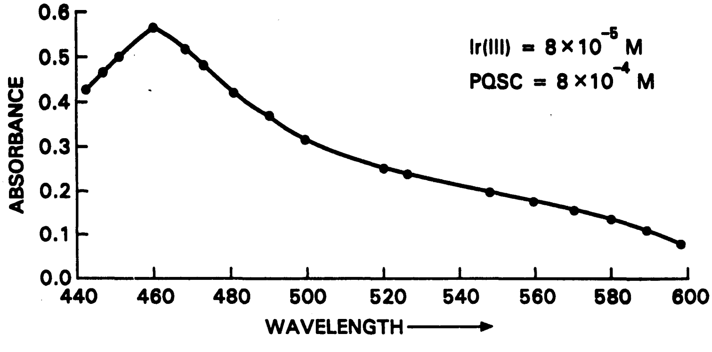

Fig. 1

Effect of heating

A study of the rate of colour development was made by heating the reaction mixtures for different intervals of time on a steam bath. The absorbance was found to become constant after heating for about 2 h. The results are recorded in Table-1. In the subsequent studies the reaction mixtures were treated for about 2 h.

TABLE-1
EFFECT OF HEATING TIME Ir(III)-PQSC COMPLEX

Heating time (min.)	Absorbance at 460 nm
0.0	0.010
10	0.083
20	0.149
40	0.298
60	0.420
100	0.525
120	0.552
150	0.552

Effect of pH

In order to investigate the role of pH on the formation of complex, a series of solutions containing 2 mL of 1×10^{-3} M iridium and 4 mL of 5×10^{-3} M reagent in ethanol were mixed. The pH of the solutions were adjusted between 5.0 and 10.5 with acetate buffers. For higher pH's, dilute sodium hydroxide was added. The solutions were raised to approximately 10 mL with water and heated on a boiling water bath for 2 h, cooled to room temperature and dissolved in DMF in a total volume of 25 mL so that the percentage of DMF in the final solution is sixty. The absorbance of these solutions is found to remain constant in the pH range 7.5–9.5. The results are shown in Fig. 2. Subsequent studies have been carried out at pH 8.5.

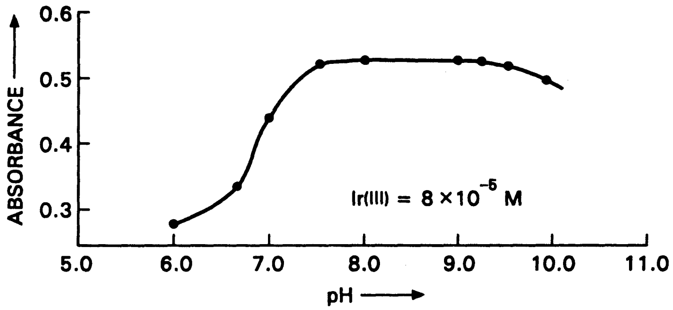

Fig. 2

Effect of excess of reagent

The effect of reagent concentration on the complex formation was studied by mixing solutions containing a fixed amount of iridium (2 mL of 1×10^{-3} M) and varying amounts of reagent till a large excess was present. 4.0 to 0.2 M sodium acetate and dilute sodium hydroxide were added to bring the pH to 8.5 and the volume was raised to approximately 10 mL with water. The contents were heated for 2 h on a water bath, cooled to room temperature and dissolved in dimethylformamide. The absorbance measurements were prepared at 460 nm against the corresponding reagent blanks prepared under identical conditions. A plot between absorbance and mole of ligand, Fig. 3, shows that at least 7 times excess of the reagent should be added for maximum absorbance. During the course of subsequent studies, ten-fold molar excess of reagent was used.

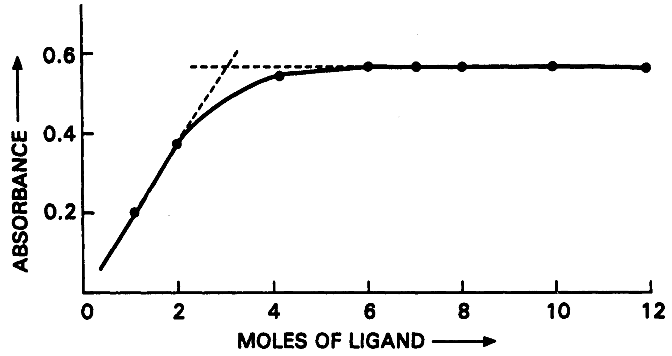

Fig. 3

Stability of the complex

To study the effect of time on the stability of chelate, the absorbance was measured at different time intervals and it was found to remain constant for 36 h.

Adherence to Beer's law, optimum range and sensitivity

Beer's law is obeyed up to 26.9 ppm of iridium (Fig. 4). while the optimum concentration range for accurate determination, as determined from Ringbom plot

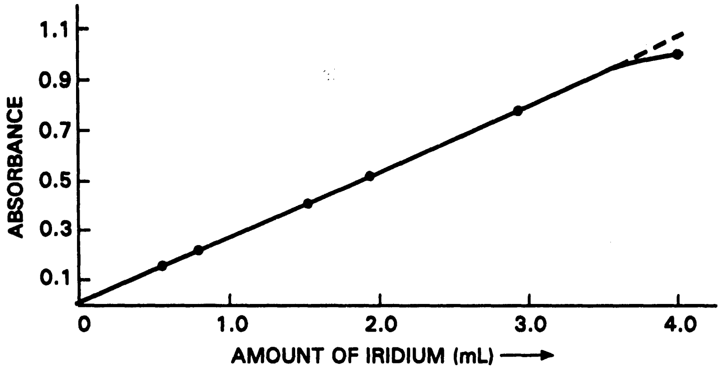

Fig. 4

(Fig. 5) is from 4.4 to 24.0 ppm of iridium at 460 nm. The sensitivity of the reaction has been found to be 0.027 $\mu g/cm^2$ for 0.001 absorbance and the value of molar extinction coefficients comes out to be 6.9×10^3 mole cm^{-1}.

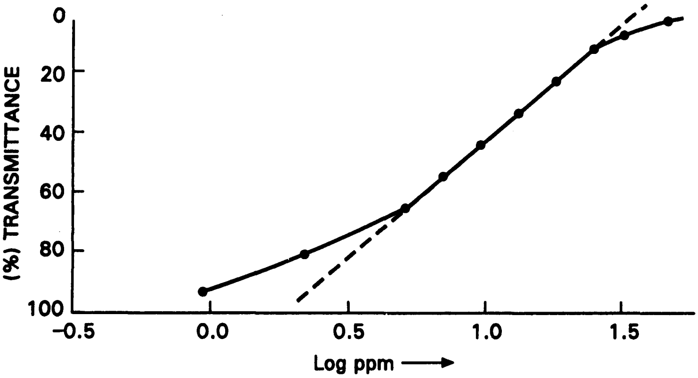

Fig. 5

Recommended procedure for the determination of iridium

A suitable aliquot containing 10g–600 μg of iridium is taken, 4 mL of 5×10^{-3} M reagent solution in ethanol is added and the pH is adjusted beween 7.5–9.5 with 4 mL of 0.2 M sodium acetate and sodium hydroxide. The contents are diluted to approximately 10 mL with water and heated for 2 h on boiling water bath cooled to room temperature and dissolved in DMF in a total volume of 25 mL so that the percentage of DMF in the final solution is 60–70. The absorbance is measured at 460 nm against a reagent blank prepared under identical conditions. From the absorbance, the iridium content is deduced from the calibration curve.

Absorbance deviations

To check the precision of the method absorbances of eight solutions each containing 15.4 ppm of iridium were measured at 460 nm. The mean absorbance was found to be 0.552 with standard deviation of 0.0026 and relative average deviation of ± 0.362%.

Molar composition

Molar composition was determined by the method of continuous variations[1,2] and the mole ratio method[3].

(i) Job's method

Equimolar solutions were analyzed for their stoichiometric ratio by Job's method. The maximum obtained at 0.25 mol fraction of metal in the Job's curve (Fig. 6) indicate that metal to ligand ratio in the complex is 1 : 3.

(ii) Mole ratio method

The absorbance of solutions containing 2 mL of 1×10^{-3} M iridium(III) and varying amounts of the ligand are plotted in Fig. 6. On extrapolation, a break in the curve is obtained, which shows the composition to be 1 : 3 (M : L), which is in agreement with that obtained by Job's method.

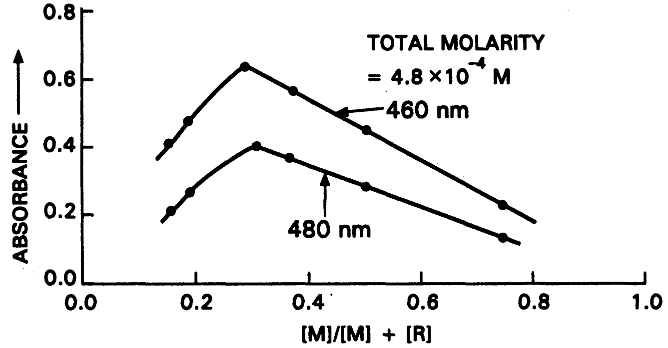

Fig. 6

On the basis of the molar composition the following tentative structure (Fig. 7) is assigned to the Ir-PQSC complex.

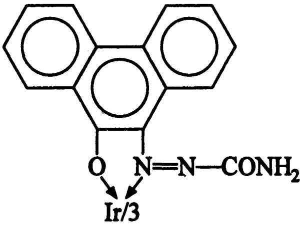

Fig. 7

Effect of foreign ions

For this study, a series of solutions containing 2 mL of 1 × 10^{-3} M iridium(III) were taken and a known amount of foreign ion was added to each one of them. Following the recommended procedure, the iridium content was determined in these solutions. Cobalt(II), nickel(II), copper(II), zinc(II), lead(II) and palladium(II) were removed by extraction with chloroform at room temperature as their PQSC complexes after which the determination of iridium(III) was carried out. Similarly, osmium is completely precipitated in 1 h at room temperature, hence removed by centrifugation. Silver(I) was precipitated as chloride while cadmium(II) and uranium(VI) were removed by centrifugation as their PQSC complexes at room temperature. The results of this study are summarized in Table-2.

TABLE-2
EFFECT OF FOREIGN IONS IN THE DETERMINATION OF IRIDIUM(III)

Amount of Iridium = 15.6 ppm

Diverse ions	Amount tolerated (in ppm)	Diverse ions	Amount tolerated (in ppm)
Chloride	1000	Aluminium(III)	200
Bromide	800	Barium(II)	400
Nitrite	500	Strontium(II)	400
Nitrate	1000	Calcium(II)	400
Sulphate	200	Uranium(VI)	50
Phosphate	400	Copper(II)	200
Fluoride	1500	Magnesium(II)	100
Perchlorate	1500	Cobalt(II)	200
Oxalate	200	Nickel(II)	200
Thiocyanate	300	Palladium(II)	100
Citrate	150	Lead(II)	100
Tartrate	500	Cadmium(II)	100
Borate	350	Zinc(II)	100
Sulphite	250	Silver(I)	50
Thiosulphate	20	Osmium(VIII)	20
Salicylate	500	Molybdenum	50

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