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Spectrophotometric Determination of Rhodium(III) and Iridium(III) with 3-Hydroxy-2-methyl-1,4-naphthoquinone 4-Oxime

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Rhodium(III) and iridium(III) form 1:3 and 1:2 (metal:ligand) complex, respectively with 3-hydroxy-2-methyl-1,4-naphthoquinone 4-oxime (HMNQM). The complexes are soluble in 20% ethanol. The reagent has been used for the spectrophotometric determination of Rh(III) and Ir(III). The optimum ranges of concentration for the determination of Rh(III) and Ir(III) are 0.27—5.24 and 1.51—15.85 over the pH range 5.0—7.5 and 5.3—8.0, respectively. The Sandell sensitivities for the determination of Rh(III) and Ir(III) are 0.0042 and 0.015 $\mu g\,cm^{-2}$, respectively. The determinations have also been carried out in the presence of foreign ions.

When ethanolic solution of 3-hydroxy-2-methyl-1,4-naphthoquinone 4-oxime was added to Rh(III) or Ir(III) solution, a yellow or orange brown colored complex was formed. The present study was undertaken to investigate the possibility of the use of HMNQM as a reagent for spectrophotometric determination of rhodium or iridium. Optimum conditions for the determination of rhodium(III) or iridium(III) alone or in presence of diverse ions have also been investigated.

Experimental

Reagents and Apparatus. Preparation of 3-hydroxy-2-methyl-1,4-naphthoquinone 4-oxime (HMNQM) has been reported earlier.[1] The 1×10^{-2} M (1 M=1 mol dm^{-3}) solution of HMNQM was prepared in ethanol (95%).

Buffer solutions were prepared by mixing 0.2 M sodium acetate and 0.2 M acetic acid in the required proportions. For higher pH, sodium hydroxide was added.

Rhodium(III) Solution. A standard solution of rhodium(III) was prepared by dissolving rhodium trichloride (Johnson Matthey) in double distilled water containing 1 M hydrochloric acid. The solution was standardized gravimetrically by precipitating rhodium as the sulfide, followed by ignition to the oxide and then reduction to the metal in an atmosphere of hydrogen and cooling in carbon dioxide. Subsequent dilutions were made by diluting the stock solution, maintaining acidity at 1 M.

Iridium(III) Solution. A standard solution of iridium was prepared by dissolving iridium(III) chloride (Johnson Matthey) in double distilled water containing 1 M hydrochloric acid. The iridium solution was standardized gravimetrically by precipitating iridium as the hydrated oxide, followed by careful ignition in air and then reduction to the metal in presence of hydrogen gas and cooling in an atmosphere of carbon dioxide. Subsequent dilutions were made by diluting the stock solution and keeping the acidity at 1 M.

Reagent grade chemicals were used in the study of interferences. Double distilled water was used throughout the work.

A Unicam SP 600 spectrophotometer was used for measuring absorbance and an ECIL expanded scale pH meter PH821A was used for pH measurements.

Absorption Spectra and Effect of pH. Both rhodium and iridium complexes show the maximum absorption at 470 and 480 nm respectively (Fig. 1). Subsequent studies have been carried out at this wavelength. A plot of absorbance *vs.* pH shows that the absorbances remain constant in the pH range 5.0—7.5 and 5.3—8.0 for Rh(III) and Ir(III),

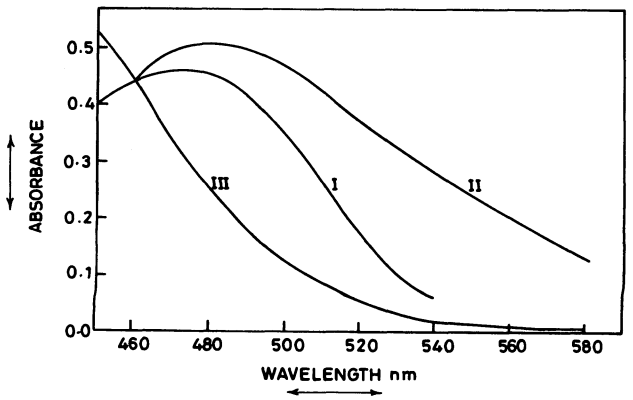

Fig. 1. Absorption spectra of I rhodium(III) complex *vs.* reagent, rhodium 2×10^{-5} M; II iridium(III) complex *vs.* reagent, iridium 4×10^{-5}M; III reagent *vs.* water, HMNQM 2×10^{-4} M.

respectively. Further studies have been carried out at pH 6.0 and 6.5 for rhodium and iridium, respectively.

Rate of Color Development and Stability of the Complexes. The rate of reaction between metal and HMNQM is slow at room temperature. The color intensity was found to increase when the solutions containing a fixed amount of Rh(III) or Ir(III) and excess of reagent were heated on a water bath for various intervals of time and absorbances were measured at 470 or 480 nm for Rh or Ir, respectively. Results of this study show that complete complex formation takes place on heating the contents for about 50 min and 3 h for rhodium and iridium, respectively.

The Rh-HMNQM and Ir-HMNQM complexes were found to be quite stable and absorbances were found to remain constant up to 48 and 24 h, respectively.

Effect of Ethanol Concentration. The precipitated complexes were found to be soluble in ethanol. It has been found that 20% (v/v) ethanol is sufficient to dissolve the precipitate completely. Subsequent studies for rhodium and iridium have been carried out in 20% ethanol medium.

Effect of Reagent Concentration. A plot of absorbance *vs.* moles of ligand shows that at least eight and five times molar excess of the reagent is required for maximum complex formation for rhodium and iridium, respectively (Fig. 2). In further studies ten times molar excess of the reagent was used for both metal.

Adherence to Beer's law, Optimum Range and Sensitivity. Beer's law is obeyed up to 5.97 and 17.68 ppm (1 ppm=1 $\mu g\,cm^{-1}$) while the optimum concentration ranges for accurate determination, as determined from Ringbom plot

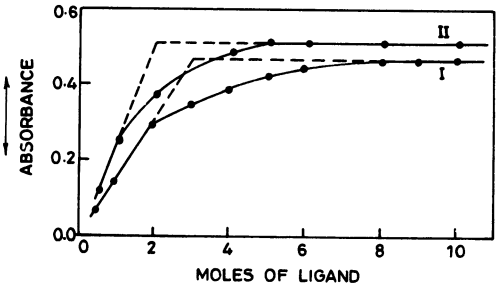

Fig. 2. Effect of reagent concentration, I: Rh(III)-complex Rh=2×10^{-5}M, II: Ir(III)-complex Ir=4×10^{-5}M.

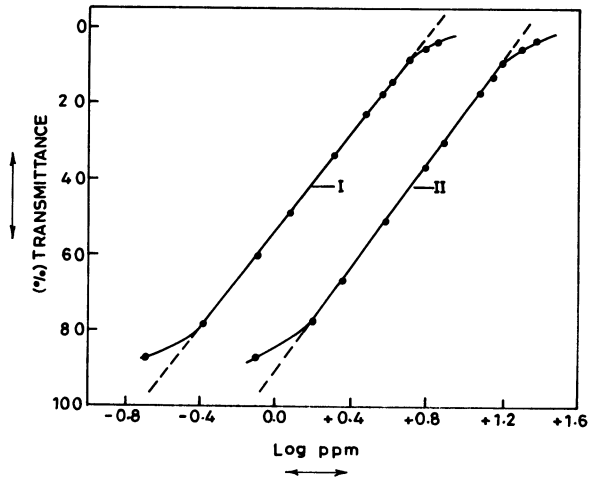

Fig. 3. Ringbom plot for I Rh(III)-HMNQM complex; II Ir(III)-HMNQM complex.

(Fig. 3), are 0.27—5.24 and 1.51—15.85 ppm for rhodium and iridium respectively. The sensitivity in terms of Sandell's definition, is 0.0044 μg Rh/cm^2 and 0.015 μg Ir/cm^2 for log I_0/I=0.001 with molar absorptivity 2.32×10^4 and 1.27×10^4 l mol^{-1} cm^{-1}, respectively.

Recommended Procedure. To a suitable aliquot containing 6.7—131.0 μg of Rh(III) or 37.7—396.2 μg of Ir(III) is added ten times molar excess of reagent. The pH is adjusted between 5.0—7.5 for rhodium and 5.3—8.0 for iridium with acetate buffer and dilute solution of sodium hydroxide. The contents are heated on a boiling water bath for 1 and 3 h, respectively for rhodium and iridium, cooled to room temperature (30±5 °C). The total volume is raised to 25 cm^3 with double distilled water, keeping 20% ethanol concentration. The absorbance of the solution is measured at 470 nm for rhodium and 480 nm for iridium against reagent blank prepared under similar conditions. Knowing the absorbance, the amount of rhodium or iridium is deduced from the calibration graph.

Molar Composition of the Complexes. The composition of the complexes were determined by Job's method of continuous variations[2,3] (Fig. 4) and mole ratio method[4] (Fig. 2). Both of these methods show that the stoichiometric ratio of metal to HMNQM in the complex is 1:3 (Rh:HNMQM) and 1:2 (Ir:HMNQM).

Absorbance Deviations. Measured under experimental conditions, absorbance of six solutions, each containing 2.06 ppm of rhodium, gave mean absorbance of 0.465 with average relative deviation of ±0.32% and maximum relative

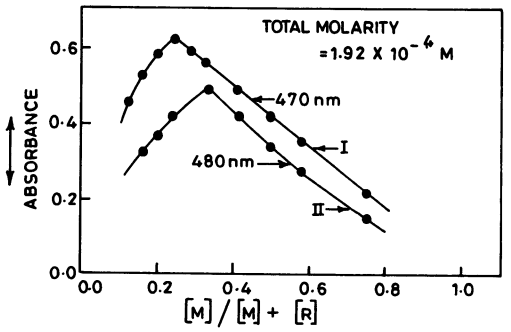

Fig. 4. Composition by Job's method, I: Rh(III)-complex, II: Ir(III)-complex.

deviation of ±0.64% with standard deviation of 0.002. Seven solutions each containing 7.68 ppm of iridium gave an average absorbance of 0.51 with standard deviation of 0.0026. The average relative deviation was found to be ±0.39% and average maximum deviation was ±0.78%.

Effect of Diverse Ions. The effect of diverse ions was studied in the determination of rhodium and iridium following the recommended procedure. The amounts (in ppm) of ions which do not cause any interference with 2.06 ppm of rhodium are given below in parentheses. Masking agents, wherever used, have been mentioned against each:

Chloride (700), bromide (300), iodide or nitrate or sulfate (200), fluoride (600), nitrite or phosphate (150), sulfite or oxalate or EDTA (100), tartrate (50), thiocyanate (80), Ca(II) (100), Ba(II) or Hg(II) (80), Mg(II) or Zn(II) or Cd(II) or Pb(II) (40), Al(III) (20), Mn(II) (30), Fe(II) or Co(II) or Ni(II) or Cu(II) (10, EDTA), Sn(II) (40, F^-), As(III) (50), $Ag^{\dagger}$(I) (20, Cl^-), Sb(III) (25), Pd(II) (2, I^-), Os(VIII) (2, SCN^-), V(IV) or Th(IV) (20, F^-), U(VI) (10, PO_4^{3-}). Thiourea, thiosulfate, citrate, Ru(III), Ir(III), and Pt(IV) interfere and attempts to mask the cations were unsuccessful.

For 7.68 ppm of iridium(III), the limits of tolerance are; chloride (100), bromide or nitrate (300), iodide or fluoride (400), nitrite (50), citrate (70), tartrate or oxalate or thiocyanate (100), phosphate, sulfite (150), EDTA (80), sulfate (200), Ca(II) (80), Ba(II) or Cd(II) or Cr(III) (70), Mg(II) or Zn(II) (50), Al(III) (10), Hg(II) or Mn(II) (100), Fe(II) or Co(II) or Ni(II) or Cu(II) (15, EDTA), Sn(II) (20, F^-), As(III) (20), $Ag^{\dagger}$(I) (40, Cl^-), Pd(II) (10, I^-), Os(VIII) (4, SCN^-), V(IV) (10, F^-), U(VI) (70, PO_4^{3-}). However, interference due to thiosulfate, thiourea and Ru(III), Rh(III), and Pt(IV) could not be avoided.

Discussion

Quite a few satisfactory reagents are known for the spectrophotometric determination of rhodium. Several methods for the spectrophotometric determination of Rh have been reviewed by Beamish.[5] Tin bromide[5] is a sensitive reagent for rhodium, though the method is not selective and stability of the complex is also low (3 h). The HMNQM method is more sensitive than *N,N'*-bis(3-dimethylaminopropyl)dithiooxamide,[5] *o*-mercaptobenzamide[6] and oximidobenzotetronic acid or α-isonitrosobenzotetronic acid.[7] Most of the associated metals interfere in the case of these reagents.

†Removed by centrifugation.

Table 1. Sensitivities of reagents for Rh and Ir

Reagent	Sensitivity μg Rh/cm²	Reagent	Sensitivity μg Ir/cm²
Tin(II) bromide	0.0035/427 nm	Leucocrystal Violet	0.004/590 nm
N,N-Dimethyl-*p*-nitrosoaniline	0.0015/510 nm	*o*-Dianisidine[a]	0.016/530 nm
Oximidobenzotetronic acid or α-isonitrosobenzotetronic acid	0.07/475 nm	*N,N*-Dimethyl-*p*-nitrosoaniline	0.010/530 nm
N,N'-bis(3-dimethylaminopropyl) dithiooxamide	0.012/420 nm	Oximidobenzotetronic acid or α-isonitrosobenzotetronic acid	0.020/480 nm
o-Mercaptobenzamide	0.014/377 nm	Cerium(IV) sulfate sulfuric acid	0.12/510 nm
Acenaphthenequinone monoxime	0.0036/390 nm	Acenaphthenequinone monoxime	0.021/385 nm
3-Hydroxy-2-methyl-1,4-naphthoquinone 4-oxime (Present method)	0.0044/470 nm	3-Hydroxy-2-methyl-1,4-naphthoquinone 4-oxime (Present method)	0.015/480 nm

a) 3,3'-Dimethoxybiphenyl-4,4'-diamine.

In *N,N*-dimethyl-*p*-nitrosoaniline[5] full color development takes place within 10 min of heating, but after 20 min absorbance begins to decrease and also the volume of the buffer solution used has a pronounced effect on the absorbance of the complex. In acenaphthenequinone monoxime[8] EDTA, NTA, SCN^-, $S_2O_3^{2-}$, Ir, Pt, Cu, Fe, and cerium(IV) cause serious interference. Recently 1-phenyl-3-(2-pyridyl)thiourea[9] has been successfully used for the determination of rhodium. The disadvantage is that the absorption maximum lies in UV region.

For the determination of iridium with Leucocrystal Violet,[10] Rh and Fe(III) interfere seriously. This method depends upon a specific composition of the dissolved iridium salt and aged iridium solutions give green solutions of lower absorbance than those which are freshly prepared. Tin bromide method[11,12] is not selective. This method is sensitive to certain variation in the procedure such as time of contact, temperature, quantity of reagent, and hydrobromic acid. In *o*-dianisidine[13] method, there is interference from associated metals and from oxidants and sulfuric acid solution cannot be used. The absorbance is sensitive to the amount of reagent and to the acidity of the medium. In *N,N*-dimethyl-*p*-nitrosoaniline[14] method, the composition of the complex is not known and the method offers no specificity among platinum metals and there is interference from nonvolatile acids. The method is sensitive to changes in the conditions. In acenaphthenequinone monoxime[15] method, most of the platinum metals interfere and prior separation of iridium is necessary and sensitivity is also low.

The present method, using 3-hydroxy-2-methyl-1,4-naphthoquinone 4-oxime involves simple technique. The method is quite sensitive and the complexes are stable for a long time. Other factors such as effect of buffer, pH, heating time, amount of reagent do not have any effect on the absorbance. Most of the associated metals do not interfere. The sensitivity is comparable (Table 1) with other methods known for the purpose.

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