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Spectrophotometric Determination of Osmium by Ternary Complex Formation with Thiocyanate and Rhodamine 6G

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Osmium in trace amounts is determined by use of its reaction with thiocyanate and Rhodamine 6G to form an ion-association complex at pH 3.0. Aided by stabilization with gelatin, measurement of absorbance at 565 nm permits the determination of osmium in the range 0.04—1.2 ppm. The colour system is very stable and provides a molar absorptivity of 6.84×10^4 l mol^{-1} cm^{-1}. A few elements interfere and methods are suggested for handling them except ruthenium and rhodium.

Although many spectrophotometric methods have been suggested for the determination of osmium in the literature, the most often used are based on its reaction with thiourea[1-2] or thiocyanate.[3-4] These methods, besides being insensitive, call for considerable skill on the part of analysts as they are unselective and hence subjected to many sources of errors.

A highly sensitive method based on reaction of osmium with diphenyl carbazide[5] ($\varepsilon = 1.5 \times 10^5$ l mol^{-1} cm^{-1}) has been described. This method lacks adequate selectivity and is not reliable because of its dependence on various experimental parameters such as acid concentration, temperature, and duration of heating. Prior extraction of OsO_4 into chloroform and subsequent colour development in the organic phase have been attempted to improve the selectivity,[6] but this caused considerable dimunition in the sensitivity ($\varepsilon = 3.1 \times 10^4$ l mol^{-1} cm^{-1}). We ourselves had examined the osmium-diphenyl carbazide reaction and found that the determination can be made highly selective by extracting the complex into isobutyl methyl ketone at pH 5.0.[7]

The investigation reported here is based on the interaction of Rhodamine 6G cation with the anionic osmium–thiocyanate complex. The introduction of Rhodamine 6G in the reaction medium resulted in formation of a new coloured species with a molar absorptivity of 6.84×10^4 l mol^{-1} cm^{-1}. A detailed study indicated that under certain conditions most other ions do not duplicate the colour reaction, concluding that the analytical method may facilitate the determination of osmium with high degree of selectivity.

Experimental

Reagents. *Osmium (VIII) Solution*: This solution was prepared by dissolving 1 g of osmium tetroxide in 250 cm^3 of water as described elsewhere.[2] A working solution containing 10 μg cm^{-3} of osmium was prepared by suitably diluting the stock solution with water.

Potassium Thiocyanate Solution (5%): This solution was prepared by dissolving 5 g of potassium thiocyanate in water and diluting the solution to 100 cm^3.

Rhodamine 6G Solution (0.005%): This solution was prepared by dissolving 0.05 g of the reagent (BDH) in water and diluting the solution to 1 dm^3 with water.

Buffer Solution: This solution was prepared by dissolving 34 g of sodium aecetate trihydrate in water, adding 15 cm^3 of glacial acetic acid, adjusting to pH 3.0 with dilute HCl, and diluting to 250 cm^3.

Gelatin Solution (1%): This solution was prepared by dissolving 1 g of gelatin in boiling water and diluting the solution to 100 cm^3.

Apparatus. A Carl Zeiss PMQ-II Spectrophotometer with 10 mm quartz cells was used.

Procedure. To an aliquot of sample solution upto 15 cm^3 containing not more than 30 μg of osmium were added 2.5 cm^3 each of the thiocyanate and buffer solutions. The solution was heated on a boiling water bath for 20 minutes and cooled. The solution was transferred to a 25 cm^3 volumetric flask, 5 cm^3 of Rhodamine 6G solution added, 1 cm^3 of gelatin mixed, and distilled water was added to the mark. Absorbence was measured at 565 nm with 10 mm cells against a reagent blank.

Results and Discussion

The addition of Rhodamine 6G to a weakly acidic solution of osmium containing excess thiocyanate resulted in formation of a pink coloured complex. Maximum intensity was developed about an hour after the addition. Further standing of the mixture caused the colour to begin to fade owing to gradual separation of the ion-associate as a precipitate. The addition of gelatin retarded the precipitation since, in its presence, the colour system was found to remain stable for at least 24 h. Later experiments showed that the reaction can be made to proceed rapidly by first heating the osmium solution with thiocyanate for about 20 min on a boiling water bath and then adding Rhodamine 6G and gelatin to the cooled so-

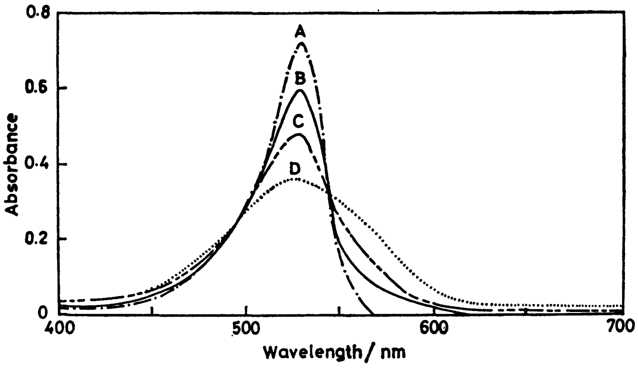

Fig. 1. Absorption spectra (2.5 cm^3 each of 1 mol dm^{-3} acetate buffer and 5% potassium thiocyanate, 1 cm^3 of 1% gelatin).
A: 2 cm^3 of 1.07×10^{-4} mol dm^{-3} Rhodamine 6G, total volume 25 cm^3, reference water 10 mm cells, B, C, and D: as in A with 0.5, 1.0, and 2 cm^3 of 1.07×10^{-4} mol dm^{-3} osmium.

lution. The resulting complex was characterised by its absorption maximum at 565 nm as taken against that of the reagent blank at 530 nm (Fig. 1).

Effect of Experimental Variables. Two sets of experiments were carried out to investigate the influence of acidity of the colour development in the range 2 mol dm^{-3} HCl to pH 9.0. In one set, solutions containing osmium and thiocyanate were adjusted to various acidities and then heated to expedite the formation of the binary complex. The solutions were then adjusted to pH 3.0 before treating with Rhodamine 6G and gelatin for colour development. In the other, the binary complex was first formed at pH 3.0 and then adjustment was made to varying acidities before the binary complex was brought into reaction with Rhodamine 6G. It is apparent from Fig. 2 that the interaction with Rhodamine 6G proceeds over a wide range of pH from 1 to 9, provided the binary complex is formed in the pH range 1—3.5. The most favourable pH for the colour development is 3.0.

Experiments were then made to ascertain the optimal concentrations of potassium thiocyanate and Rhodamine 6G for obtaining the maximum and constant absorbance. The results indicate that the absorbance increases with increasing concentration of potassium thiocyanate and Rhodamine 6G and that it reaches a limiting value when the concentrations are 2 cm^3 of 5% thiocyanate and 4 cm^3 of 0.005% Rhodamine 6G. The presence of the reagents in excess of the amounts indicated did not affect the absorbance.

The effect of temperature on the formation of the anionic thiocyanate complex was studied by thermostating reaction mixtures for 30 min at various temperatures ranging from 40 to 98 °C. Colour was developed after the solutions were cooled to room temperature. The results indicate that a constant and maximum absorbance is obtainable for the solutions that have been kept at 65 °C and above. Further studies using a boiling water bath showed that 15-min heating was sufficient to provide maximum absorbance and that prolonged heating upto 40 min did not affect the recovery of osmium.

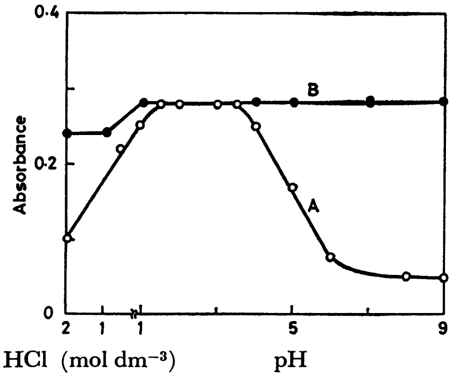

Fig. 2. Effect of pH/acidity (20 μg of osmium, 2.5 cm^3 each of 5% potassium thiocyanate and buffer, 5 cm^3 of 0.005% Rhodamine 6G, 1 cm^3 of 1% gelatin, final volume 25 cm^3, 565 nm, 10 mm cells).
A: Formation of Os–SCN$^-$ complex, B: association of SCN$^-$ with Rhodamine 6G.

With the above optimal conditions a linear calibration graph was obtained over the range of 0—30 μg of osmium. The molar absorptivity was calculated to be 6.84×10^4 l mol^{-1} cm^{-1} at 565 nm and the sensitivity of the reaction was 0.0028 μg cm^{-1}.

Ten replicate determinations of standard osmium solutions each containing 20 μg of osmium gave an average recovery of 100.4% with a relative standard deviation of 1.8%.

Nature of the Complex. Experiments were then conducted to find reaction ratios between osmium and Rhodamine 6G by the mole-ratio and continuous var-

TABLE 1. EFFECTS OF DIVERSE IONS
(Amount of osmium = 20 μg in 25 cm^3)

Diverse ion	Amount added/μg	Absorbance
None	—	0.285
Pt(IV)	20	0.550
	—a)	0.285
	250a)	0.285
	500a)	0.320
Pd(II)	20	0.580
	500a)	0.285
	1000a)	0.360
Rh(III)	1	0.310
	20	0.510
Ir(IV)	20	0.315
	—b)	0.280
	200b)	0.280
	500b)	0.500
Ru(III)	1	0.340
	20	0.570
Fe(III)	20	0.440
	1000b)	0.280
Co(II)	250	0.285
	500	0.315
	1000a)	0.280
Hg(II)	20	0.285
	100	0.390
	1000a)	0.290
Cu(II)	20	0.345
	50a)	0.285
	100a)	0.340
Zn(II)	50	0.285
	100	0.410
	—c)	0.285
	1000c)	0.280
Zr(IV)	100	0.285
	500	0.335
	—d)	0.285
	1000d)	0.285
W(VI)	100	0.285
	500	0.335
	1000d)	0.285

a) Two cm^3 of 2% thiourea added before addition of Rhodamine 6G. b) In the presence of 1 cm^3 of 5% ascorbic acid. c) One cm^3 of 0.1 mol dm^{-3} EDTA added before addition of Rhodamine 6G. d) In the presence of 2 cm^3 of 2% sodium fluoride.

iation methods. The equilibrium shift method was employed to establish combining ratios of osmium and thiocyanate. The results indicate the empirical formula of the complex as $R^+[Os^{II}(SCN)_3]^-$ where R^+ represents the Rhodamine 6G cation.

Though 0.5 cm^3 of 1% solution of gelatin was found to be sufficient to stabilize the system, a significant effect was observed when gelatin was added prior to the addition of Rhodamine 6G solution. In this instance the sensitivity of the colour reaction diminished considerably. It was also noticed that the ion-associate breaks down when heated to higher temperature or treated with miscible organic solvent like acetone. Since Rhodamine 6G is known to exist as aggregates in aqueous solution,[8] and from the fact that acetone raises the "critical micelle concentration" of the dye and that the addition of gelatin or increase in temperature can cause deaggregation of the dye,[9] it appeared reasonable to conclude that the resulting colour change was due to interaction of the thiocyanate complex of osmium with micelles of Rhodamine 6G. The addition of gelatin after the addition of Rhodamine 6G prevents further aggragation of ion-associates, thus stabilising the colour system. The observed spectral shift possibly arises due to short range electrostatic interaction of the π-cloud of the dye with the polarising anion or π-cloud of another dye molecule or both, which can lower the energy gap between the highest occupied and lowest unoccupied molecular orbitals.

Effects of Diverse Ion. The influence of amounts of several ions were studied on the determination of 20 μg of osmium. No interference was noticed in the presence of 1 mg amount of Br^-, NO_3^-, ClO_4^-, I^-, SeO_3^{2-}, $B_4O_7^{2-}$, AsO_4^{3-}, PO_4^{3-}, Li^+, Be^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, UO_2^{2+}, Cr^{3+}, Al^{3+}, Bi^{3+}, La^{3+}, Tl^{3+}, Th^{4+}, Ce^{4+}, or Sb^{5+}. Other metal ions, which interfered, were dealt with as summarised in Table 1. The data clearly show that only ruthenium and rhodium interfere seriously with the determination.

TABLE 2. ANALYSIS OF SYNTHETIC SAMPLES[a)]

	Absorbance
None	0.285
Pt^{4+}(0.25 mg) + Pd^{2+}(0.5 mg)	0.280
Pt^{4+}(0.25 mg) + Pd^{2+}(0.5 mg) + Ir^{4+}(0.2 mg)	0.285
Pt^{4+}(0.25 mg) + Fe^{3+}(1 mg) + Ni^{2+}(1 mg)	0.275
Pd^{2+}(0.5 mg) + Fe^{3+}(1 mg) + Cu^{2+}(0.05 mg)	0.285
Pd^{2+}(0.5 mg) + MoO_4^{2-}(1 mg) + La^{3+}(1 mg)	0.280
Fe^{3+}(1 mg) + Cu^{2+}(1 mg) + Ni^{2+}(1 mg)	0.285
WO_4^{2-}(1 mg) + Fe^{3+}(1 mg) + UO_2^{2+}(1 mg)	0.280

a) Determinations were carried out after adding appropriate masking agents as given in Table 1.

Analyses of several composite mixtures by the proposed method are given in Table 2.

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