

## Spectrophotometric Determination of Os(VIII, VI & IV) with 4- & 5-Sulphoanthranilic Acids

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4-Sulpho and 5-sulphoanthranilic acids have been studied for the spectrophotometric determination of Os(VIII, VI and IV). 4-Sulphoanthranilic acid gives a bluish violet complex with Os(VIII) at pH 1.0-5.2 (sensitivity  $0.014 \mu\text{g cm}^{-2}$ ), a reddish violet complex with Os(VI) at pH 1.5-5.0 (sensitivity  $0.015 \mu\text{g cm}^{-2}$ ), and a violet complex with Os(IV) between pH 4.5 and 8.7 (sensitivity  $0.009 \mu\text{g cm}^{-2}$ ). Interference of other ions can be avoided with EDTA and by prior distillation of osmium as tetroxide. 5-Sulphoanthranilic acid is not at all suitable for the spectrophotometric determination of Os(IV).

IN earlier communications<sup>1-4</sup>, the author reported some interesting effects due to the introduction of non-coordinating substituents on organic reagents having chelating groups and also successfully applied these for spectrophotometric determinations.

Anthranilic acid<sup>5</sup> as a spectrophotometric reagent for osmium is known. In a programme to develop efficient reagents for the spectrophotometric determination of osmium, the effect of introducing sulphonic acid group at different positions of anthranilic acid has now been studied. Thus the efficacy of 4-sulphoanthranilic acid and 5-sulphoanthranilic acid as spectrophotometric reagents for Os(VIII, VI and IV) has been investigated. Anthranilic acid<sup>5</sup> does not show any definite metal-ligand ratio with Os(VIII) or Os(VI); colour develops after a long time and the pH range is short. In contrast, 4-sulphoanthranilic acid forms complexes of definite stoichiometry with Os(VIII), (VI) and (IV). Colour develops immediately and has a wide pH range. However, 5-sulphoanthranilic acid does not give any complex of definite composition with Os(VIII) or (VI). While both anthranilic acid and 4-sulphoanthranilic acid develop complete colour with Os(IV) on heating for 10 min, 5-sulphoanthranilic acid does not develop colour in cold. Although on heating a pink colour develops, it never obeys Beer's law and possesses no definite pH range. Thus 5-sulphoanthranilic acid is totally unsuitable for spectrophotometric determination of Os(IV). The results show that 4-sulphoanthranilic acid is a better reagent for osmium than anthranilic acid and 5-sulphoanthranilic acid and in fact from many other known reagents used for spectrophotometric determination of osmium<sup>6</sup>. In this paper detailed spectrophotometric study of 4-sulphoanthranilic acid with osmium VIII, VI and IV have been reported while the results of 5-sulphoanthranilic acid are summarized below: With Os(VIII) at pH 1.3-3.7, 5 sulphoanthranilic acid forms reddish violet complex with maximum absorbance at 490 nm; obeys Beer's law from 1.0-16.0 ppm of Os(VIII); the optimum concentra-

tion range is 2.0-14.0 ppm. The sensitivity of the colour reaction is  $0.015 \mu\text{g cm}^{-2}$ .

The reddish complex of Os(VI)-5-sulphoanthranilic acid formed at pH 1.3-3.7 has maximum absorbance at 490 nm. It obeys Beer's law from 1.0 to 18.0 ppm with optimum concentration range 2.0 to 14.0 ppm of osmium(VI). The sensitivity of the system is  $0.018 \mu\text{g cm}^{-2}$ .

### Materials and Methods

A Hilger Uvispek spectrophotometer and a Cambridge pH-meter were used.

A standard solution of Os(IV) was prepared by dissolving weighed quantity of potassium chlorosmate ( $\text{K}_2\text{OsCl}_6$ ) (Johnson & Matthey) in 1N hydrochloric acid.

Os(VIII) solution (250 ml) in 0.02N caustic soda solution was prepared from 0.1 g ampoule of osmic acid ( $\text{OsO}_4$ ) as suggested by Ayres and Wells<sup>7</sup>; the solution was standardized iodometrically<sup>8</sup>. A standard Os(VI) solution was obtained by reducing the standard Os(VIII) solution with minimum quantity of 1:2 ethanol.

Solutions (0.5 and 0.2%) of 4-sulphoanthranilic acid were prepared in doubly distilled water.

All the metal solutions for interference studies were obtained by dissolving analytical grade chlorides, sulphates, nitrates or oxides in water or hydrochloric acids.

*Procedure: For Os(VIII or VI)* — An aliquot of the solution containing 200  $\mu\text{g}$  of Os(VIII or VI) was mixed with 5 ml of the reagent (0.2%, w/v) solution. One or two drops of conc. hydrochloric acid was added and allowed to stand for 10 min. After adjusting the pH to  $\sim 2$  with dil. hydrochloric acid or sodium hydroxide, it was diluted to 25 ml and the absorbance measured against reagent as blank.

*For Os(IV)* — To potassium chlorosmate solution [100  $\mu\text{g}$  of Os(IV)] was added the reagent solution (5 ml, 0.05%, w/v), and the pH adjusted to  $\sim 5$  with sodium hydroxide. It was then heated on a water-bath for 5-10 min. After heating it was cooled, volume adjusted to 25 ml with distilled water

and the absorbance measured against reagent blank.

All measurements for osmium(VI) were made at 530 nm.

The colour intensities of the systems remain unchanged in the pH ranges 1.0-5.2 for Os(VIII), 1.5-5.0 for Os(VI) and 4.5-8.7 for Os(IV).

For complete colour development, 8 ppm of each Os(VIII) and Os(VI) require 2 ml (0.2% w/v) of reagent solution. For 4 ppm of Os(IV) the amount of reagent required is 1 ml (0.5% w/v).

The colour is stable for 5 hr for Os(VIII), ~10 hr for Os(VI) and for more than 24 hr for Os(IV).

The systems follow Beer's law over the range 1.0-14.0 ppm for Os(VIII), 1.0-16.0 ppm for Os(VI) and 1.0-12.0 ppm for Os(IV). The optimum concentration ranges evaluated by Ringbom's method<sup>9</sup> are 2.0-12.0, 2.0-12.0 and 2.0-10.0 ppm for Os(VIII), Os(VI) and Os(IV) respectively.

The percentage relative errors per 1% absolute photometric error<sup>10</sup> for Os(VIII), Os(VI) and Os(IV) are 2.78, 2.75 and 2.72 respectively. The sensitivities ( $\log I_0/I = 0.001$ ) calculated as described by Sandell<sup>11</sup> are  $0.014 \mu\text{g cm}^{-2}$  for Os(VIII),  $0.015 \mu\text{g cm}^{-2}$  for Os(VI) and  $0.009 \mu\text{g cm}^{-2}$  for Os(IV).

**Composition of the complexes** — The compositions of Os(VIII), Os(VI) and Os(IV) complexes were determined by mole ratio method<sup>12</sup> and Job's method<sup>13</sup> of continuous variation. Os(VIII) forms both 1:1 and 1:2 (metal-ligand) complexes, Os(VI) forms 1:2 complex and Os(IV) forms 1:1 complex.

**Degree of dissociation and instability constant** — The degree of dissociation  $\alpha$ , was calculated from Harvey and Manning equation<sup>14</sup>. The instability constants evaluated from the equation  $K = (m \alpha c)^m \times (n \alpha c)^n / c(1-\alpha)$  where  $m = n = 1$ , for Os(IV) and  $m = 1$   $n = 2$  for Os(VI) are given in Table 1.

The dissociation constants of the complexes were also evaluated from a study of the absorbance of the complementary mixtures of non-equimolar solutions of metal ions and the reagent. The colour of the solutions were developed as described previously. The values calculated by literature method<sup>15</sup> are reported in Table 2.

**Effect of diverse ions** — With Os(IV), many of the common ions and the platinum metals interfered, forming a coloured product with the reagent. However in the presence of EDTA (disodium salt; 1 ml, 0.5%, w/v) the interfering ions can be tolerated. The tolerance limits (ppm) for the ions are given in the parentheses:  $\text{Ca}^{2+}$ (400),  $\text{Ba}^{2+}$ (200),  $\text{Zn}^{2+}$ (30),  $\text{Mg}^{2+}$ (200),  $\text{As}^{3+}$ (200),  $\text{VO}_3^-$ (50),  $\text{WO}_4^{2-}$ (50),  $\text{UO}_2^{2+}$ (20),  $\text{Hg}^{2+}$ (50),  $\text{Ni}^{2+}$ (50),  $\text{Co}^{2+}$ (50),  $\text{Fe}^{3+}$ (20),  $\text{Cr}^{3+}$ (20),  $\text{Mn}^{2+}$ (50),  $\text{Pd}^{2+}$ (20),  $\text{Pt}^{4+}$ (20),  $\text{Ir}^{4+}$ (20),  $\text{Rh}^{3+}$ (10),  $\text{Ru}^{3+}$ (10). Gold interferes.

For Os(VIII) or Os(VI), the following ions are found to interfere even in the ratio 1:1  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{4+}$ ,  $\text{Ru}^{3+}$ ,  $\text{Rh}^{3+}$ ,  $\text{Ir}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{W}^{6+}$ ,  $\text{U}^{6+}$ ,  $\text{Ag}^+$ ,  $\text{Au}^{3+}$ . As

TABLE 1 — STABILITY CONSTANTS OF 4-SULPHOANTHRANILIC ACID COMPLEXES

$E_m$	$E_s$	$C \times 10^3 M$	$\alpha$	$K$
		Os(VI)		
1.02	0.92	0.1	0.09	$3.1 \times 10^{-9}$
		Os(IV)		
0.295	0.255	5.0	0.135	$1.04 \times 10^{-5}$

TABLE 2 — DISSOCIATION CONSTANTS OF THE COMPLEXES

[Metal] $\times 10^4$ (M)	[Reagent] $\times 10^4$ (M)	$m$	$n$	$p$	$x$	$K$
Os(VI) 2.5	10.0	1	2	4	0.41	$2.2 \times 10^{-9}$
Os(IV) 2.5	7.5	1	1	3	0.33	$3.6 \times 10^{-5}$

EDTA considerably reduces the colour of the osmium tetroxide and osmate, it cannot be used, as has been done for Os(IV). However the interference from these ions may be avoided by prior distillation of osmium as tetroxide.

**Separation of osmium by distillation and subsequent determination** — In a distillation apparatus<sup>6</sup> solutions containing 8 ppm of osmium was mixed with solutions of the ions  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{V}^{5+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Ru}^{3+}$ ,  $\text{Pt}^{4+}$ ,  $\text{Ag}^+$ . The mixture was treated with 20 ml of 6M nitric acid and distilled slowly in a current of air for 20 min. The distillate was absorbed in 7 ml of 0.07M potassium hydroxide solution. In the distillate the colour was developed and measured as described before. Duplicate experiment showed that the average recovery of osmium was 98%.

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