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Trace Determination of Osmium (VIII) by Amperometric Titrations Using Thiodipropionic Acid

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Abstract

Amperometry is an electro-analytical technique which is being economic is very suitable technique for the estimation of various metal ions for developing country like India. In the present work Osmium (VIII) has been estimated using a sulphur containing organic ligand, thiodipropionic acid abbreviated as TDPA. TDPA has often been used as complexing agent and analytical reagent. This ligand has also been exploited earlier for the amperometric determination of manganese. The present work was undertaken with a view to extend the use of this ligand for the amperometric determination of osmium(VIII) in traces at d.m.e. The metal ion has been estimated with this ligand using 0.5 M NaOH medium as supporting electrolyte. Metal species as well as organic acid, both are polarographically active in this medium and give their characteristic cathodic and anodic wave respectively. Cathodic (using TDPA as titrant) as well as anodic (using Os(VIII) solution as titrant) titrations were carried out successfully for the trace determination of Os(VIII) metal ion. All these titrations have been carried out at room temperature using a manual Toshniwal Polarograph. Metal species- TDPA stoichiometry obtained was 1:1 in both types of titrations. Osmium solution as dilute as 6.00ppm for cathodic titrations and 10.00ppm for anodic titrations were estimated successfully with high degree of accuracy. Maximum error (±2%) was encountered in the case of most dilute solution. Studies of interference of foreign ions in the determination of Os(VIII) were also investigated. The technique has the added advantages in being relatively quick, economic and simple.

Keywords: Amperometry; Osmium (VIII); thiodipropionic acid; Interference.

1. Introduction

The six metals, named, ruthenium, rhodium, palladium, osmium, iridium, and platinum are called platinum group metals. Osmium metal is lustrous, bluish white, extremely hard, and brittle even at high temperatures. The tetroxide is highly toxic. Very low concentrations in air can cause lung congestion, skin damage or eye damage. Hence there should be some economic technique to estimate low concentration of this metal ions and amperometry is playing a good role in this aspect. Amperometric titration has also been used in past for trace determination of this metal with different ligands like ethanethioic acid, 2- mercapto and 3-mercaptopropanoic acid and thioglycolic acid (1-3).

2. Experimental

The author used a Toshniwal (India) manual polarograph of the type CLO2A, in association with a polyflex galvanometer of type PL50 for recording polarograms as well as variation in current during amperometric titrations. Osmium tetroxide, OsO_4 was used as a source compound for Os(VIII). Stock solution Os(VIII) (4) was standardized amperometrically. TDPA solution was prepared fresh daily and standardized. For maintaining the inert environment during the titration, purified nitrogen gas was employed. Titrations were carried out 3-4 times of metal solution of any concentration. Titration voltages were selected in the limiting region of cathodic wave of metal ions in case of both cathodic as well as anodic titrations as TDPA is not polarographically active. Titrating voltage during the titration of Os(VIII) was selected at -0.40 V and -1.00V for cathodic and anodic titrations respectively. The selected potential was kept constant throughout the experiment. Limiting current corrected for dilution by the titrant was recorded as a function of the volume of the titrant. Dilution correction was made with the help of equation: $i_{corr} = i_{obs}(V+v)/V$, where i_{corr}, is the corrected current, i_{obs} is the observed current, V is the volume of solution taken initially and v is the volume of titrant added. Null point was obtained graphically taking i_{corr} along y-axis Vs volume of titrant added along x-axis.

3. Result and Discussion

Os (VIII) has been reported by Meites (5) to give three well defined wave in 0.1M NaOH medium. Amperometric determination of OsO_4 solution (anodic titrations) or TDPA solution (cathodic titrations) as titrant were carried out at -0.40V and -1.00V. It may be mentioned that -0.40V fell in the limiting region of osmium (1st wave) and -1.00V fell in region of 2nd wave of osmium, any anodic current was totally absent. Null point always corresponded to the M:L molar reaction ratio of 1:1 (Figure. 1 and

Figure. 2). It has been reported that titrations of Os(VIII) with ETA (6) yielded 1:1 titrimetric ratio as in case of titrations of Os(VIII) with TDPA. The method enabled the estimation of Os(VIII) solution up to 5.71ppm (cathodic titrations) and 9.71ppm (anodic titrations) with maximum error (±2%) in the case of most dilute solutions only. The common thiourea method (7) (spectrophotometric) for determination of Os(VIII) is valid over much shorter range of 8-40 ppm only and also suffers, like these new amperometric methods, from interferences from other platinum metals significantly. The new amperometric methods thus have advantage over the spectrophotometric method as far as the determinable range of concentration is concerned.

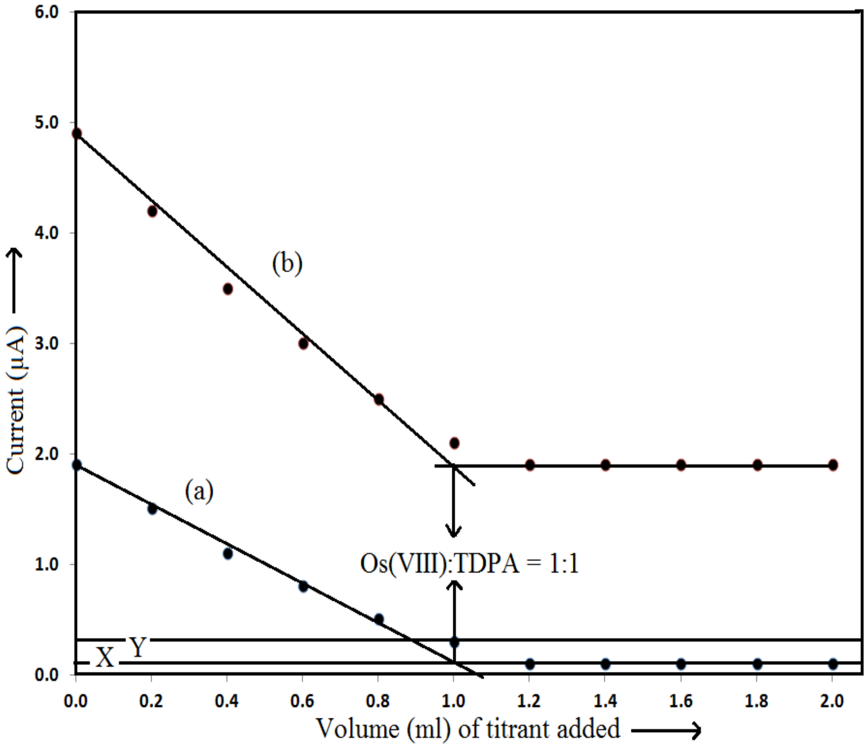

Figure 1: Amperometric titration curve of Os (VIII)- TDPA system in 0.1M NaOH medium (Cathodic titration).

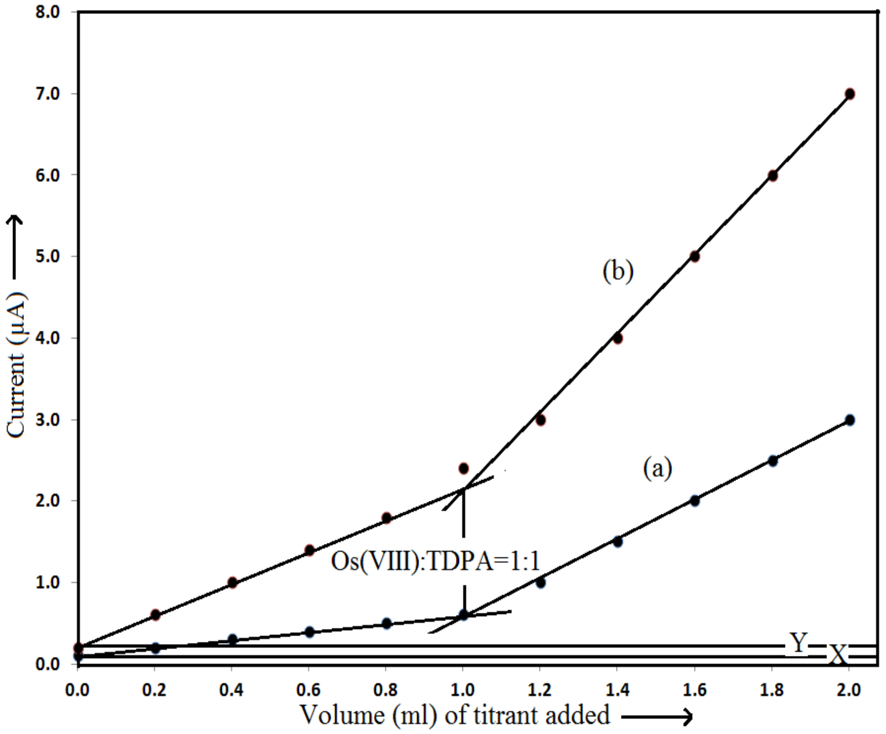

Figure 2: Amperometric titration curve of Os (VIII)- TDPA system in 0.1M NaOH medium (Anodic titration).

4. Checking of Interference of Foreign Ions and Selectivity

Study of interference of foreign ions in the new amperometric method was carried out for three concentrations of each metal species: 5.00 mM, 1.00 mM and 0.50 mM. Table-1 includes safe limits of foreign ions in the cell solution. Non-interfering species did not interfere even when present simultaneously in the cell solution. However, for these selectivity tests, the maximum concentration of each species taken was 0.25 mM to avoid super saturation.

5. Conclusion

The study shows that thioglycolic acid is suitable for the determination of trace quantities of Os (VIII). The methods give reproducibility with standard deviation of 0.05 only. The techniques have the added advantages for the developing country like India in being relatively quick, economic and simple.

Table 1: Safe limit of the concentration of foreign ions in the cell solution with respect to the concentration of the metal species.

Metal ion	**Os(VIII)**	
Medium	**0.5M NaOH**	
Foreign ion	**Cathodic titration**	**Anodic titration**
Cl-	B	B
NO3-	B	B
CH3COO-	B	B
Ox2-	B	B
WO42-	B	B
Mg(II)	B	B
Al(III)	B	B
V(V)	1/10	B
Cr(III)	B	B
Cr(VI)	Equal	Equal
Mn (II)	A	A
Mn (VII)	A	A
Fe(II)	1/5	1/5
Fe(III)	B	B
Co(II)	A	A
Ni(II)	1/10	1/5
Cu(II)	A	A
Zn(II)	A	A
Mo(VI)	1/10	5t
Cd(II)	equal	1/5
Hg(II)	1/10	1/5
Ru(III)	A	A
As(III)	1/20	1/10
SCN-	B	B

A = Serious interference even when the conc. of foreign ion is 1/20 of the metal.
B = No interference even when foreign ion is 20 times that of metal.
t = Times.

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