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Amperometric trace determination of rhodium(III) using thio-organic acid

Rajni Arora[a], Ritu Langyan[b], Dayawati[c] and S. P. Khatkar[a]

[a]Department of Chemistry, M. D. University, Rohtak, India.
[b]Department of Chemistry, Kurukshetra University, Kurukshetra, India
[c]Department of Chemistry, Govt. P.G. College, Jhajjar, India

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ABSTRACT

Amperometric determination of Rh(III) was accomplished in 0.1M NH_3 + 0.1M NH_4Cl medium with TDPA at d.m.e. (dropping mercury electrode). Both cathodic and anodic titrations were carried out successfully. Metal species-TDPA stoichiometry obtained was 1:1. The lowest concentration estimated by amperometric titrations were 5.00 ppm and 9.00 ppm for cathodic and anodic titrations respectively with high degree of accuracy. Maximum error (± 2%) was encountered in case of most dilute solutions. Interference of different foreign ions has also been studied.

Keywords: Amperometry, Rhodium(III), Thiodipropionic acid.

INTRODUCTION

Rhodium is one of the platinum group metals which is precious and rare element in the Earth's crust. The metal is found to be harmless if used in elemental form rather than as compounds [1]. Hence there should be some economic technique to estimate low concentration of this metal ion 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 [2,3], thioglycolic acid [4] and thiomalic acid [5]. Various reagents were used for the spectrophotometric determination of Rh (III) [6-7] and many sulphur containing organic ligands have been used in amperometry for the trace determination of metal ions. Thiodipropionic acid (TDPA) which contains hard oxygen donor atom of two carboxylate groups and a soft sulphur atom acts as mono, bi or tridentate ligand, has often been used as a complexing agent and analytical reagent. TDPA has often been used as complexing agent and analytical reagent. This ligand has also been exploited earlier for the amperometric determination of manganese (Mn). The present work was undertaken with a view to extend the use of this ligand for the amperometric trace determination of Rh(III) in 0.1M NH_3 + 0.1M NH_4Cl medium at d.m.e accomplishing both cathodic as well as anodic titrations. The interference of different foreign ions has also been investigated.

MATERIALS AND METHODS

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. Rhodium chloride, $RhCl_3.xH_2O$ was used as a source compound for Rh(III). Stock solution of Rh(III) [5] was standardized amperometrically. TDPA solution was prepared fresh daily and standardized. Purified nitrogen gas was employed for deaeration. Amperometric determination of metal solution of any particular concentration was carried out at least thrice. 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. Titration voltage for the amperometric titration of Rh(III) selected was -0.50V. The selected potential was kept constant throughout. Limiting current corrected for dilution by the addition of titrant and 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.

RESULTS AND DISCUSSION

Rh(III) was found to be polarographically active and gave cathodic wave in this medium with its limiting region spread over a short potential region from -0.40V through -0.60V with $E_{1/2}$= -0.24V (fig.1). TDPA did not give any wave in this medium. Titration voltage selected was -0.50V, which fell in the limiting region of Rh(III) alone as no anodic current due to TDPA was present here. The cathodic current of Rh(III) decreased linearly with the addition of TDPA and finally, titration curve shown in Fig. 2 was obtained. Anodic titration were performed at -0.50V. This voltage fell in the limiting region of cathodic wave of Rh(III) alone, no current due to TDPA was present here. Titration resulted in amperometric curves of the type shown in the Fig. 3. The null point corresponded to the Rh(III):TDPA molar ratio of 1:1 in both type of titrations.

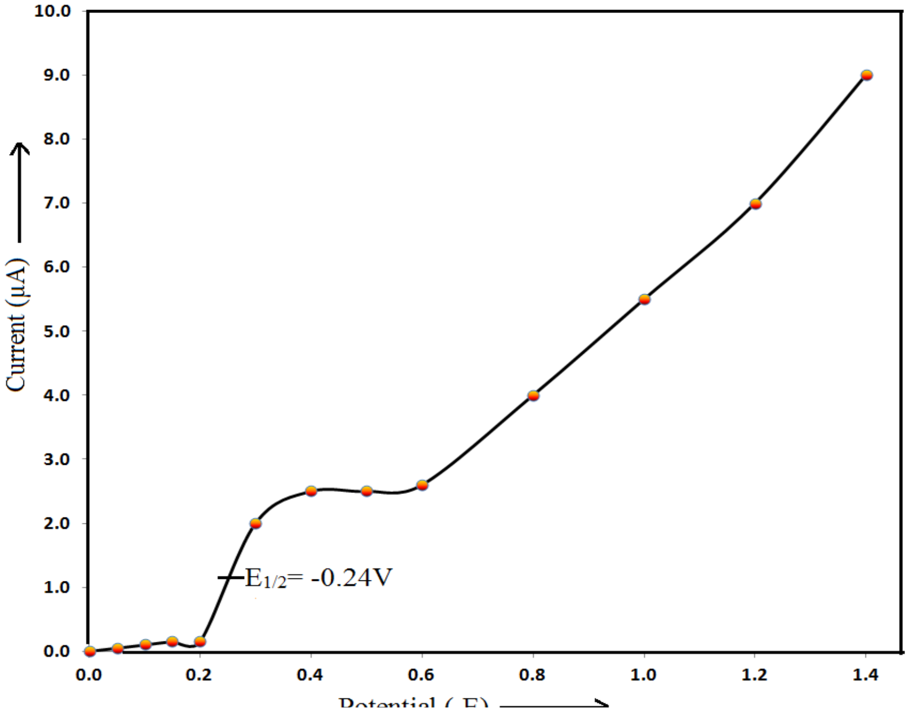

Fig. 1. Polarogram of 0.70 mM Rh(III) in 0.1M NH_3 + 0.1M NH_4Cl medium (Residual current excluded)

The new method is quite efficient as they enable estimation of even a 5.00ppm solution of Rh(III) for cathodic titration and 9.00ppm for anodic titration with high degree of accuracy. In this matter, this method proves to be somewhat superior to the older methods available in the literature [8].

However, all these (old and new methods) show a very low degree of tolerance for coinage and platinum metal ions. In between the old and new methods, interference of other foreign ions is lesser and accuracy of determination of most dilute solutions slightly better in case of new method employed in the present study. Also, the new method compares very well with the reported, $SnCl_2$ and NaOCl spectrophotometric methods for the determination of Rhodium[9]. However, new amperometric methods score a point over spectrophotometric methods as they are valid for a far greater range of concentrations of Rh(III) solutions.

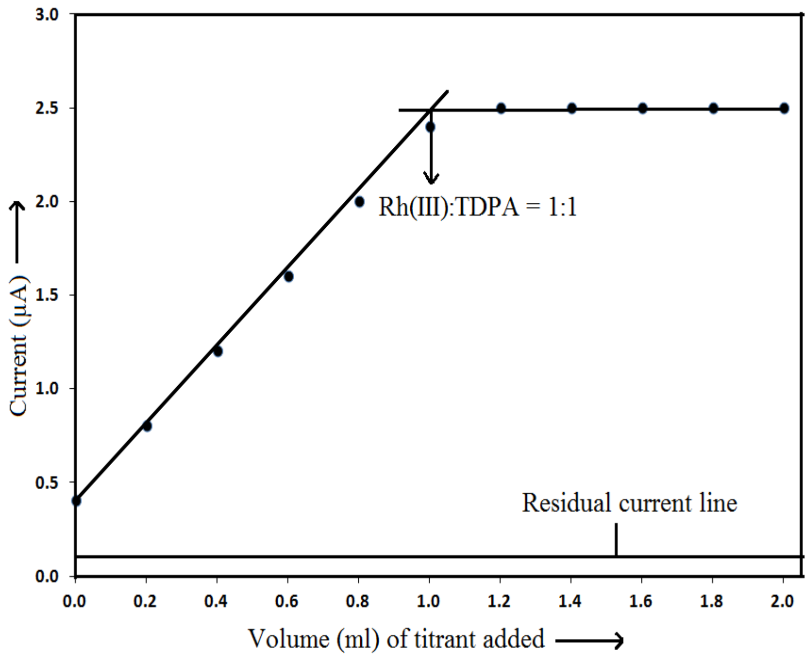

Fig. 2.Amperometric titration curve of Rh(III):TDPA system in 0.1M NH_3 + 0.1M NH_4Cl medium

Titration voltage	:	-0.50V
Conc. of TDPA	:	0.50mM
Conc. of Rh(III) in the titrant solution	:	5.00mM

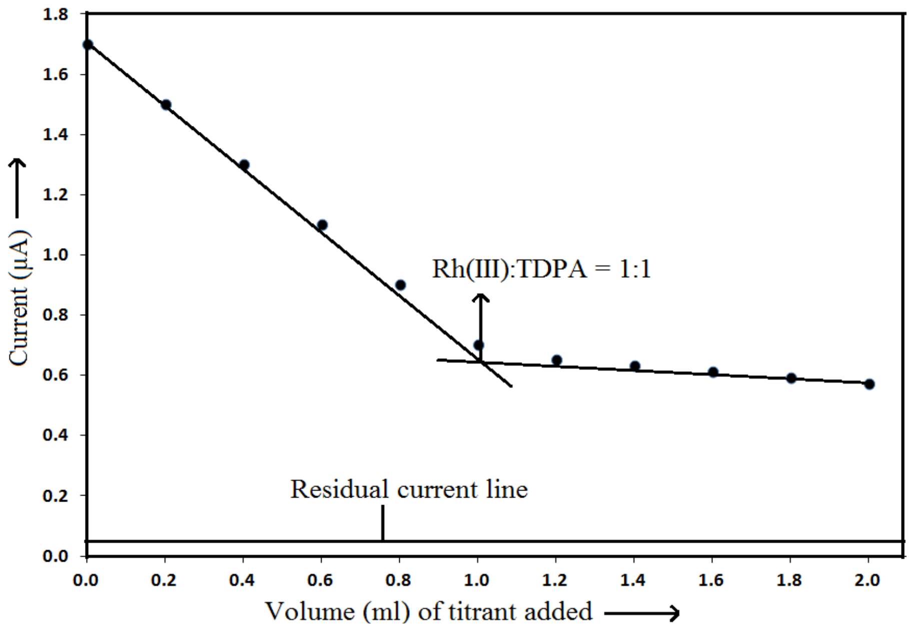

Fig. 3. Amperometric titration curve of Rh(III):TDPA system in 0.1M NH_3 + 0.1M NH_4Cl medium

Titration voltage	:	-0.50V
Conc. of Rh(III)	:	0.50mM
Conc. of TDPA in The titrant solution	:	5.00mM

The 1:1 complex with TDPA was not reported yet. This seems to form 1:1 complex with Rh(III) in this medium (table 1). This is much apparent from the nature of the amperometric curve shown in Fig. 2 and 3. However, 1:1 complex of Rh(III) with similar thio-ligand [9] has already been reported.

Table 1

Medium (0.1M NH_3 + 0.1M NH_4Cl)	Potential selected (V)	M:L ratio	Concentration range (ppm)
Cathodic titration	*-0.50*	*1:1*	*514.53 to 5.15*
Anodic titration	*-0.50*	*1:1*	*514.53 to 10.29*

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.

Table 2 Safe limit of the concentration of foreign ions in the cell solution with respect to the concentration of the metal species

Metal ion	Rh(III)	
Medium	0.1 M NH_3 + 0.1 M NH_4Cl	
Foreign ion	Cathodic titration	Anodic titration
Cl^-	B	B
NO_3^-	B	B
CH_3COO^-	B	B
Ox^{2-}	B	B
WO_4^{2-}	Equal	5t
Mg(II)	B	B
Al(III)	B	B
V(V)	1/5th	1/5th
Cr(III)	1/10th	1/10
Cr(VI)	1/20th	1/5th
Mn (II)	B	B
Mn (VII)	A	A
Fe(II)	Equal	Equal
Fe(III)	5t	Equal
Co(II)	Equal	Equal
Ni(II)	1/5th	1/20th
Cu(II)	A	A
Zn(II)	5t	5t
Mo(VI)	1/10	1/20th
Cd(II)	5t	Equal
Hg(II)	1/20th	1/5th
Au(III)	A	A
As(III)	1/5th	1/10th
SCN^-	B	B
Ag(I)	A	A
Pd(II)	A	A

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

CONCLUSION

The study shows that thiodipropionic acid is suitable for the determination of trace quantities of Rh(III). 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.

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