Amperometric Determination of Ru(III) Metal Ions in Solution at Trace Level with the Help of α – Mercaptopropionic Acid as a Ligand

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Abstract

New amperometric trace determination of Ru(III) with the help of α -mercaptopropionic acid (RSH) at dropping mercury electrode Vs S.C.E is reported in the medium consisting of 2.5 M KCl in 8% acetic acid. The two-stage cathodic reduction of Ru(III) in this medium has been reported in the literature. The organo-sulfur ligand RSH was also found to give its characteristic reversible, one-electron anodic wave with a Half-Wave Potential of -0.12V. The ligand RSH is used as a titrant in the titrations, carried out only at some constant voltage (here, -0.05 V) which falls in the common limiting region of ligand RSH as well as 1st cathodic wave of metal ions of Ru(III). However, a chemical reaction between the two species is not indicated and the basis of the new titrimetric method seems to be the current compensation phenomenon (the beauty of amperometric). Ru(III): RSH null point molar ratio is 1:0.67 and Ru(III) solutions up to 4 ppm can be estimated with a fair degree of accuracy. The study of various interfering cations and anions is also reported in this new method.

Keywords

Amperometry, -mercaptopropionic acid, Ruthenium, d.m.e., current compensation.

Introduction

Right at the beginning of civilization, scientists have a great interest in the analysis of metal ions at trace levels. Various trace analytical methods for estimation of transition metal ions in solution have been reported in literature like Polarography[1-10], Voltammetry, Amperometry etc. This new amperometric method is developed for the trace determination of Ru(III) metal ions with α-mercaptopropanoic acid (RSH) is carried out in a medium consisting of 2.5M KCl in 8% acetic acid (pH = 2.15).

Amperometric Determination of Ru(III) with RSH

This new amperometric determination of the metal species with RSH was carried out in a medium consisting of 2.5M KCl supporting electrolyte in 8% acetic acid employing the organic-sulfur compound as titrant in cathodic titrations. The metal species-RSH molar ratio obtained at the null point was 1:0.67. The titrations are solely based up on the phenomenon of current compensation and carried out only at some voltage in the common limiting region of both the species (metal ion & Ligand).

Polarographic Characteristics of the Metal Ions

Ru(III) has been reported[11] to give reduction waves in this medium. The first wave though started at a potential more positive than 0.00V, its limiting region stretched over the potential range of -0.04V through -0.20V; its $E_{1/2}$ and number of electrons involved in the electrode reaction could not be ascertained. Diffusion control and proportionality of the wave height to the concentration of Ru(III) in the cell solution (Table) were rechecked and found to be good.

Table -1 Proportionality checking of the diffusion current of Ru(III) to its concentration in the medium consisting of 2.5M KCl in 8% acetic acid; h=40 cms.

Concn. (c) of Ru(III) (mM)	i_d at -0.05V (μa)	i_d/c
5.000	7.920	1.564
1.000	1.704	1.604
0.15	0.884	1.648
0.250	0.410	1.560
0.100	0.169	1.590
0.050	0.092	1.640
0.040	0.072	1.630

Average i_d/c at -0.05V = 1.602

The second wave with its limiting region spread over the potential range of -0.30V through -0.60V has been described as ill-defined[11].

Polarographic characteristics of RSH

RSH was observed by the author to give its characteristic reversible, one-election anodic wave in this medium consisting of 2.5M KCl in 8% acetic acid with the short limiting region spread over the potential range of -0.2V through -0.08V (Fig.-1). The polarogram did not show any pre-wave[12]. The value of $E_{3/4}$-$E_{1/4}$ [(-0.100V)-(-0.155V)], was found to be 0.055V, $E_{1/2}$ being -0.12V. Diffusion control of the wave of RSH in the cell was checked (tables -2 and table-3) and found to be good.

Table -2 Diffusion control checking of RSH (0.50mM) wave in the medium consisting of 2.5M KCl in 8% acetic acid:

Height (h) of the mercury column (cm.)	i_1 (μa) at -0.05V (residual current excluded)	$i_1/\sqrt{h}$
30	1.039	0.1898
40	1.207	0.1907
50	1.12	0.1963
60	1.540	0.1960

Fig.-1

Polarogram of 0.50mM RSH in 2.5M KCl in 8% KCl soln. excluding residual current

Potential ▬○▬ at X-axis

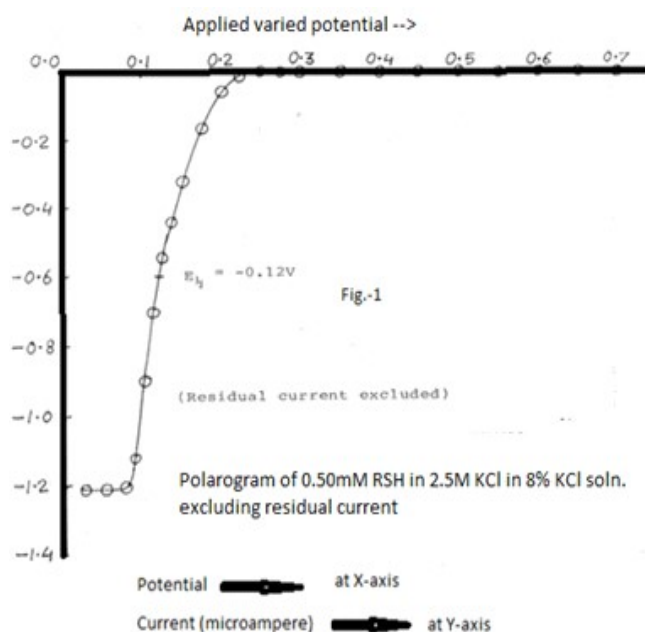Current (microampere) ▬○▬ at Y-axis

Table-3 Checking of proportionality of the diffusion current of RSH to its concentration in the medium consisting of 2.5M KCl in 8% acetic acid; h=40

| Concn. (c) of Ru(III) (mM)	i_d at -0.05V ($\Box$a)	i_d/c
5.000	12.208	2.442
1.000	2.420	2.420
0.15	1.204	2.408
0.250	0.606	2.424
0.100	0.242	2.420

Amperometric Studies

The first wave of Ru(III) was exploited for its amperometric determination at -0.05V which fell in the diffusion region of both the metal species and organic sulfur compound. On titrating Ru(III) solution with RSH, the cathodic current was progressively compensated by the anodic current of the acid. The titration curve reached the null point (i.e. intersected the residual current line) when the molar concentration ratio of Ru(III) and RSH was 1:0.67. The addition of more RSH led to the appearance of an anodic current with a slight change in the slope of the curve (Fig. 2). No color change occurred in the course of titrations. The results of the titrations are given in Table 4.

Table-4 Amperometric determination of Ru(III) with RSH in the medium consisting of 2.5M KCl in 8% acetic acid

Titrant	:	RUSH
Titration Voltage	:	-0.05V
Range of concern. of RSH used	:	50.00mM-0.50mM

Concn. of Ru(III) taken ppm	Concn. of Ru(III) obtained (Mean) ppm	%age error (Mean)	Standard deviation
505.35	505.35	0.00	0.00
101.07	101.07	0.00	0.00
50.54	50.54	0.00	0.00
25.27	25.27	0.00	0.00
10.11	10.11	0.00	0.11
7.58	7.64	0.79	0.06
5.05	5.17	2.32	0.11
2.53	2.41	4.74	-

Fig-2
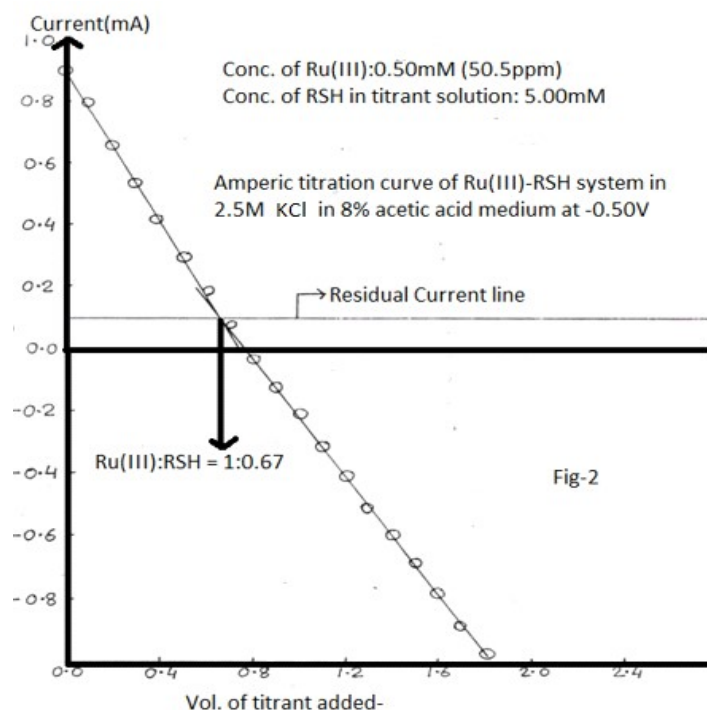
The RSH wave at -0.50V (2nd wave region of Ru^{III}) was totally absent, with absolutely no reduction in the cathodic current. This is basis of the titration is only the phenomenon of current compensation is indicated by the nature of the amperometric curve (Fig.-2) as well as the fact that the tirimetric Ru(III): RSH ratio (1:0.67) is in good agreement with the i_d/c(Rui-1wave) value of 1:0.62

The reverse titration, using Ru(III) as titrant, was also performed at -0.05V. Anodic current of RSH decreased with the advancing titration, finally yielding to the emergence and linear increase of the cathodic current. However, the Ru(III)-RSH ratio at the point of intersection of the residual current line was found to be different for different concentrations of metal species and hence, this form of titration cannot be recommended. Interestingly, the new method did not yield good results if the concentration of KCl or 1.0M KCl in 8% acetic acid, failed because no fixed titrimetric Metal-Ligand ratio could be obtained.

Interference and Selectivity Checking of Foreign Ions

Interference of various cations (Mg(II), Al(II), Cr(III), Mn(II), Co(II), Ni(II), Zn(II), Cd(II)) and anions (NO_3^-, SO_4^{2}, Cl^-, Ox^{2-}) in the cathodic titrations was checked.

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Concentrations of Ru(III), viz. 505.35 ppm, 101.07 ppm and 50.54 ppm were selected for such studies., These ions did not interfere in titrations even when 20 times in excess of that of Ru(III) in that solution but, some metal ions like V(V), Mn(VI), Fe(II), Fe(III), Cu(II), Rh(III), Pd(II), Os(VIII) and $S_2O_3^{2-}$ seriously interfered at all concentrations. The safe limit of other foreign ions in the cell solution, has been included in the table-5.

Table-5 The safe limit of the concentration of foreign ions in the cell solution with respect to the concentration of the metal species determined with RSH in a medium consisting of 2.5M KCl in 8% acetic acid.

Foreign Ion	Relative Safe Limit
Ir(III)	Equal
Au(II)	1/20
Pb(II)	1/2
MoO_4^{2-}	1/20
WO_4^{2-}	15

Discussiions

Amperometric determination of Ru(III) with the help of RSH was carried out in the medium consisting of 2.5M KCl solution in 8% acetic acid. The exact composition of this supporting electrolyte medium was established by trial and error method. The new methods required the use of organic acids as titrants. A method with MPSH is already available in the literature[14] and the author could not carry out any improvement over the same. The polarographic activity of RSH the medium was observed by the author and found to give its usual one-electron anodic wave with short diffusion regions spread over the potential range of -0.02V through -0.08V as shown in the Fig.-4.

Ru(III) gave two reduction waves in this medium [11]. The 1st wave started at a potential more positive than 0.00V and $E_{1/2}$ and the number of electrons involved in the electrode reaction could not be checked. The limiting region of this wave stretched over the potential range of -0.04 through -0.20V while that of the 2nd wave stretched from -0.30V through -0.60V. The 2nd wave was rather ill-defined and its $E_{1/2}$ also could not be ascertained[11]. The first wave was fully diffusion controlled while the 2nd wave was not. The proportionality of the height of the 1st wave to Ru(III) concentration in the cell was rechecked by the author (Table-1) and found good, while, as reported (loc.cit) it was not so in the case of the 2nd wave. O.P. Agrawal and S.P. Khatkar[13] have proposed the following electrode reaction for the two waves:

Ru(III) + e$^-$ $\rightarrow$ Ru(II). . . . . (First wave)
Ru(II) + 2e$^-$ $\rightarrow$ Ru(0). . . . . (2nd wave)
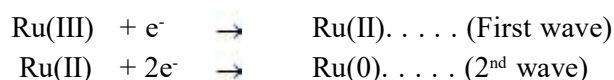
It seems the new amperometric methods like the MPSH method reported [14] do not entail any chemical interaction and are based solely on the phenomenon of compensation of the cathodic current of the 1st wave of Ru(III) by the anodic current of the organic sulfur compounds. It may be mentioned that the titration voltage (-0.05V) fell in the diffusion regions of both the species (metal and the organic acid) and no suppression of the cathodic current of Ru(III) occurred with RSH was progressively added at a voltage (e.g. -0.40V, which lay in the region of 2nd wave of Ru^{III}) where the anodic current was totally absent. It is also noteworthy that Ru(III)-organic acid titrimetric ratio of 1:0.67 (RSH) is equal to the reverse of the ratio of i_d/c of the two species; the average i_d/c for Ru(III) is 1.601 (Table-1) and that of RSH is 2.423 (table-3). The nature of the amperometric curves (almost straight line with only a slight change of slope at the null point which falls right on the residual current line Figs.-2 also indicates the operation of the current compensation phenomenon [11,15,16].

The new methods enable the estimation of Ru(III) solutions as dilute as 5.04 ppm with great accuracy. Even 2.53 ppm solutions could be estimated with RSH reasonably accurately with the maximum error encountered being in the neighborhood of 5%. In this matter, these methods prove to be somewhat superior to the two older methods available in the literature [11,14]. Again, this method is valid for a far greater range of concentrations of Ru(III) solutions in comparison to common spectrophotometric methods of determination [17].

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