

## DETERMINATION OF STABILITY CONSTANTS AND KINETIC PARAMETERS OF A IRREVERSIBLE SYSTEMS

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Antimony (III) in the presence of resacetophenone-Tris (RPT) has undergone irreversible electrode reaction at D.M.E. Kinetic parameters like  $\alpha_n$  and  $K_{i,h}^0$  values and stability constants ( $\beta_1 = 15$ ;  $\beta_2 = 1.75 \times 10^2$ ) for the same irreversible system have been determined simultaneously using Meities and Israel; and Ringbom and Eriksson methods respectively. The forward rate constants revealed that electrode reaction is becoming more and more irreversible as concentration of ligand is increased.

**Key Words:** Stability Constants; Kinetic Parameters; Reversible and Irreversible; Polarography; Forward Rate Constants; Ion Indication

### Introduction

A number of Schiff bases have been derived from *tris*-(hydroxy methyl)methylamine (TRIS)<sup>1-7</sup>. Since not much work has been carried out on resacetophenone-*tris*<sup>8</sup>, in the present investigation the authors, have therefore, used it for the polarographic study of antimony (II). Literature survey revealed that no attempt has been made to determine the kinetic parameters and stability constants simultaneously for the same irreversible system.

### Experimental

Metal ion solution was prepared from analytical grade sample (BDH, AR). 0.1 M KNO<sub>3</sub> was used to keep ionic strength constant. All the studies were carried out in 30% DMF-H<sub>2</sub>O medium. For d.m.e., double distilled mercury was employed. To suppress the maxima triton-X-100 (0.002%) was used. Recrystallized resacetophenone-*tris* (RPT) from alcohol was used as a complexing agent. Double distilled water was used for the preparation of all experimental solutions.

ELICO DC recording polarograph model CL-25 was used to record current-voltage curve. Saturated calomel electrode was employed as reference electrode. ELICO glass capillary with following characteristics in open circuit  $t = 3.8$  sec,  $m = 2.68$  mg/sec at constant height of mercury head was used. The pH of the solution was measured using ELICO pH meter. H-type cell was used to carry out experiments. Pure nitrogen gas was used for the deoxygenation of all experimental solutions prior to recording. The studies were carried out at 30°C.

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## Results and Discussion

### *Kinetic Parameters of Antimony(III)-RPT System*

Antimony (III) gave well-defined single reduction waves in the presence of resacetophenone-*tris* Schiff base in the concentration range of 0.002 to 1.0 M in 30% DMF-H<sub>2</sub>O medium at pH = 10.0. With increasing concentration of ligand diffusion current decreased whereas half-wave potential shifted towards more negative values. Both these facts suggested that antimony was undergoing complexation in the presence of resacetophenone-*tris*. The slope values (Table I) obtained from the log plots of the polarograms for different concentrations of ligand suggested that the reduction was irreversible (Table I).  $E_{3/4} - E_{1/4}$  values also proved that the reduction was irreversible.  $i_d/\sqrt{h}$  (Table II) values were constant at different heights of mercury column, suggested that the electrode reaction was diffusion-controlled. For all the measurements of diffusion current, the current at the end of the drop life was considered instead of average current.

**Table I**  
Effect of ligand concentration of antimony  
Concn. of Sb<sup>3+</sup> = 1.0 mM  
KNO<sub>3</sub> = 0.1 M  
pH = 10.0  
Triton-X-100 = 0.002%

[Ligand] M	$E_{1/2}$ - V vs SEC	$i_d$ ( $\mu A$ )	$E_{3/4} - E_{1/4}$ (mV)	Slope (mV)
0.02	0.892	7.0215	84	84.80
0.04	0.900	6.9648	84	83.62
0.06	0.908	6.8862	84	83.60
0.08	0.916	6.8546	83	83.68
0.10	0.920	6.8205	83	83.82
0.20	0.924	6.8058	83	83.98
0.40	0.928	6.6555	82	82.92
0.60	0.930	6.4115	82	82.68
0.80	0.932	5.5608	80	82.70
1.00	0.934	3.8559	80	82.68

To determine the kinetic parameters like  $\alpha_n$  and  $K_{f,h}^0$  values, Meties and Israel method was adopted in the present investigation. Using the following equation, it was possible to determine the required kinetic parameters.

$$E_{d.e.} = E' = \frac{0.0542}{\alpha_n} [\log(i/i_d - i) - 0.546 \log t].$$

In the above equation both  $E_{d.e.}$  and  $E'$  were with respect to the calomel electrode. The diffusion coefficient for different concentrations of ligand were determined using the Ilkovic equation. From the slopes of the linear plots of

**Table II**  
*Kinetic parameters of antimony schiff base system*  
 Conc. of  $\text{Sb}^{3+}$  = 1.0 mM  
 $\text{KNO}_3$  = 0.1 M  
 $\text{pH}$  = 10.0  
 Triton-X-100 = 0.002%

[Ligand] <i>M</i>	<i>E</i> - <i>V</i> vs SCE	$\alpha_n$	$D^{1/2} \times 10^{-3}$ $\text{cm}^2\text{sec}^{-1}$	$k_{f,h}^0$
0.02	0.882	0.3804	1.626	$1.121 \times 10^{-7}$
0.04	0.892	0.3827	1.615	$1.357 \times 10^{-7}$
0.06	0.904	0.4025	1.592	$2.745 \times 10^{-7}$
0.08	0.912	0.4030	1.586	$3.163 \times 10^{-7}$
0.10	0.915	0.4106	1.581	$4.042 \times 10^{-7}$
0.20	0.918	0.5329	1.574	$1.167 \times 10^{-9}$
0.40	0.921	0.6108	1.570	$8.982 \times 10^{-9}$
0.60	0.928	0.6225	1.485	$1.533 \times 10^{-10}$
0.80	0.930	0.6342	1.317	$2.497 \times 10^{-10}$
1.00	0.932	0.6428	1.123	$3.890 \times 10^{-10}$

**Table III**  
 $\Delta E_{1/2}$  for lead schiff base system in the absence and presence of antimony  
 Conc. of  $\text{Pb}^{2+}$  =  $5 \times 10^{-4}$  M  
 Conc. of  $\text{Sb}^{3+}$  =  $5 \times 10^{-2}$  M  
 Triton-X-100 = 0.002%  
 $\text{KNO}_3$  = 0.1 M  
 $\text{pH}$  = 10.0

[Ligand] <i>M</i>	Antimony absent		Antimony present	
	$E_{1/2}$ of $\text{Pb}^{2+}$ - <i>V</i> vs SCE	$\Delta E_{1/2}$ - <i>V</i> vs SCE	$E_{1/2}$ of $\text{Pb}^{2+}$ - <i>V</i> vs SCE	$\Delta E_{1/2}$ - <i>V</i> vs SCE
0.00	0.398	—	—	—
0.02	0.596	0.198	0.593	0.194
0.03	0.598	0.200	0.596	0.196
0.04	0.600	0.202	0.598	0.198
0.05	0.602	0.204	0.600	0.200
0.06	0.604	0.206	0.602	0.201
0.08	0.608	0.210	0.606	0.203
0.10	0.612	0.214	0.608	0.204
0.20	0.620	0.222	0.618	0.213
0.40	0.628	0.230	0.625	0.226
0.60	0.634	0.236	0.631	0.234
0.80	0.638	0.240	0.637	0.238
1.00	0.641	0.243	0.639	0.241

$E_{d.c.}$  vs  $[\log(i/i_d - i) - 0.546 \log t]$

$\alpha_n$  values were obtained. 'i' and 'i<sub>d</sub>' represent maximum currents during the drop life.

The slope value being equal to  $-0.0542/\alpha_n$ . The intercepts of the above plots gave the values for the parameter  $E'$  at the different concentrations of the ligand. The values of  $E'$ ,  $D^{1/2}$  and  $\alpha_n$  were utilized to evaluate  $K_{f,h}^0$  values. The results of which were given in Table III.  $K_{f,h}^0$  values, suggested that the reaction was becoming more irreversible with gradual increase in the concentrations of the ligand. In other words the reaction was becoming totally irreversible.

#### Determination of Stability Constants for Sb(III)-RPT System

Results obtained in the previous studies for antimony-resacetophenone-*tris* system revealed that the reduction was totally irreversible and diffusion controlled in 0.1 M  $\text{KNO}_3$  as supporting electrolyte. Very few methods were available for the determination of stability constants of metal complexes which undergo irreversible electrode reactions of which Ringbom and Eriksson's ion indicator method was one. Literature survey also revealed that very few references were available for the determination of stability constants of irreversible reactions. Hence, the authors, in the present investigation studied not only the determination of kinetic parameters of irreversible electrode reactions, but also extended the work to determine the stability constants of the same irreversible system.

In order to determine the ligand number and the stability constants of Sb(III)-RPT system by Ringbom and Eriksson's method, lead was chosen as in-

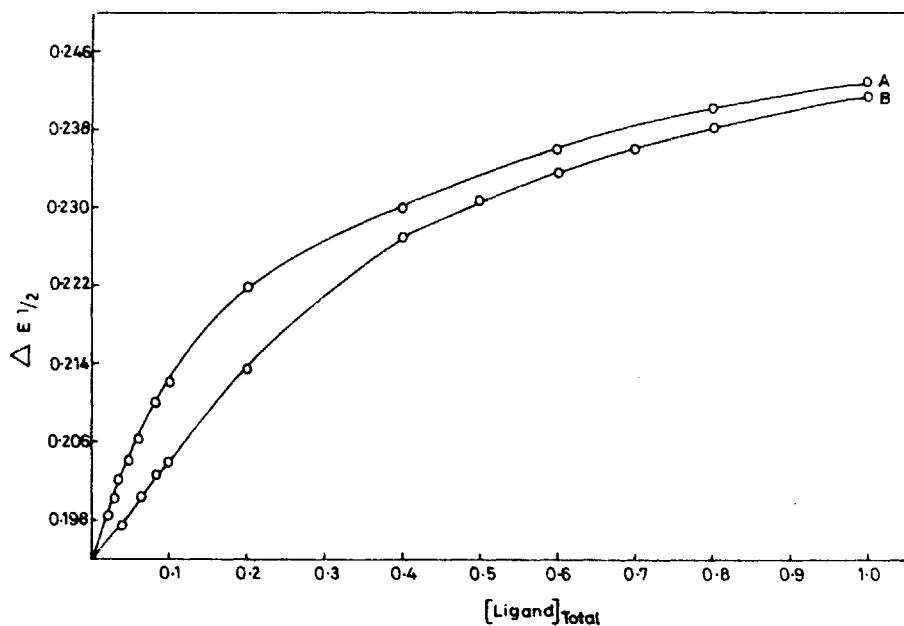


Fig 1 Plots of  $\Delta E_{1/2}$  for the lead-RPT system at  $pH \sim 10.0$  in the absence (A); and presence (B) of  $5 \times 10^{-2}$  M  $\text{Sb}^{3+}$  (Lead ion concentration is  $5 \times 10^{-4}$  M in presence of 0.1 M  $\text{KNO}_3$ )

indicator ion as the electrode reaction of Pb(II)-resacetophenone-*tris* system was reversible<sup>9</sup> and the half-wave potentials of lead were more positive (Table III) than antimony with respect to different concentrations of resacetophenone-*tris*.

To start with a series of polarograms of  $5 \times 10^{-4}$  M of lead ion were recorded at a different concentrations of resacetophenone-*tris* (0.02 to 1.0 M) in 0.1 KNO<sub>3</sub> as a supporting electrolyte at pH = 10.0. The shift in  $E_{1/2}$  at each concentration of the ligand was noted down (Table III) and a graph was drawn between  $\Delta E_{1/2}$  vs total ligand concentration (Fig. 1). The entire set of measurements were then repeated in the presence of fixed concentration of antimony ion ( $5 \times 10^{-2}$  M). The added Sb(III) ion competed with Pb(II) for association with resacetophenone-*tris* thereby reducing the effective amount available for the complexation with the indicator ion lead. As a result, the half-wave potential for lead was now correspond to a smaller value of free ligand concentration.

The observed  $E'_{1/2}$  values therefore occurred at less negative potential in the absence of antimony. In each case  $\Delta E'_{1/2}$  values were noted. A graph of  $\Delta E'_{1/2}$  vs total concentration of the ligand was drawn (Fig. 1). In order to make the change in shift measurable the concentration of antimony used was 100 times greater than that of lead. From the graphs of  $\Delta E_{1/2}$  vs  $[X]$ , and  $\Delta E'_{1/2}$  vs  $[X]$ , free ligand concentration at each total ligand concentration was determined. The curve of  $\Delta E'_{1/2}$  vs [RPT] was lying below that of the first wave i.e.,  $\Delta E_{1/2}$  vs [RPT] and at higher values of resacetophenone-*tris*, it became parallel indicating that the maximum coordination number for Sb(III)-[RPT] system was reached. From the obtained free ligand concentration the  $\bar{n}$  values were calculated (Table IV) using the equation.

$$\bar{n} = \frac{C_X - [X]}{C_V}$$

where

$C_X$  = total ligand concentration

$[X]$  = free ligand concentration

**Table IV**  
*Formation curve data-antimony schiff-base system*

$[\text{RPT}]_{\text{total}}$ M	$[\text{RPT}]_{\text{free}}$ M	$\text{Log}[\text{RPT}]_{\text{free}}$	$\bar{n}$
0.04	0.020	1.6990	0.4
0.06	0.030	1.5229	0.6
0.08	0.040	1.3979	0.8
0.10	0.045	1.3468	1.0
0.20	0.140	0.8539	1.2
0.40	0.320	0.4949	1.6
0.50	0.410	0.3872	1.8
0.60	0.505	0.2967	1.9
0.70	0.600	0.2218	2.0
0.80	0.700	0.1549	2.0
1.00	0.900	0.0458	2.0

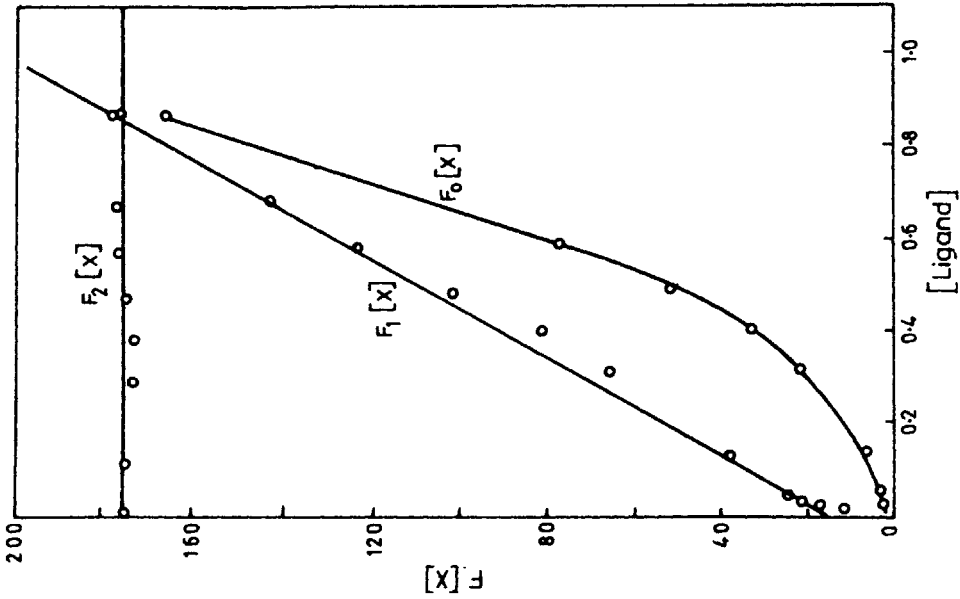


Fig 3 The functions of  $F_0[x]$ ,  $F_1[x]$ ,  $F_2[x]$  plotted as a function of ligand concentration for antimony-RPT system

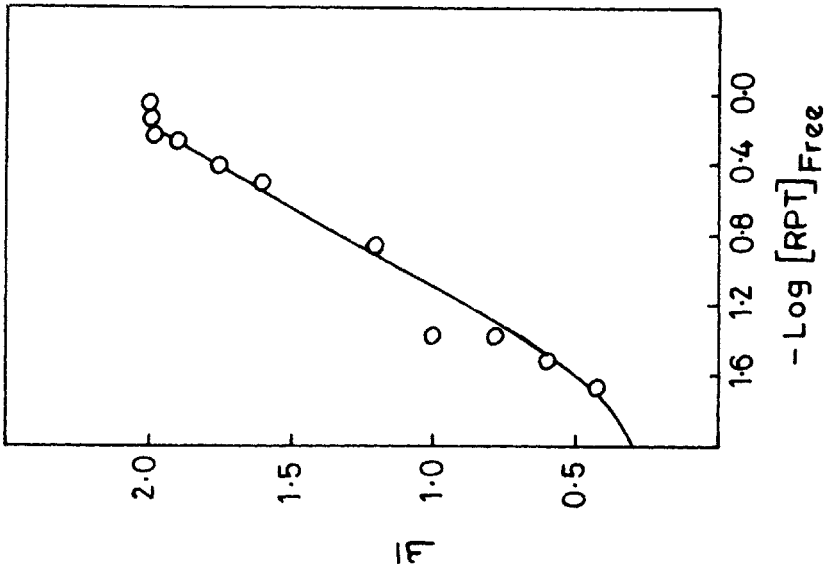


Fig 2 Formation curve of antimony (III) RPT system

and

$C_M$  = concentration of metal ion under investigation.

**Table V**  
Derived functions for antimony schiff-base system

$\frac{[\text{RPT}]_{\text{free}}}{M}$	$F_0[\text{RPT}]$	$F_1[\text{RPT}]$	$F_2[\text{RPT}] \times 10^2$
0.020	1.315	12.60	—
0.030	1.535	17.80	0.9333
0.040	1.880	22.00	1.7500
0.045	2.239	24.78	2.1733
0.140	6.383	38.45	1.6750
0.320	21.960	65.56	1.6800
0.410	34.280	81.17	1.6139
0.505	52.480	101.19	1.7067
0.600	75.860	124.76	1.8293
0.700	137.400	144.48	1.8497
0.900	165.200	182.44	1.8604

$$\beta_1 = 15; \beta_2 = 1.75 \times 10^2$$

The formation curve was constructed between  $\bar{n}$  and  $-\log[ST]_{\text{free}}$  values and was shown in Fig. 2. A constant value of  $\bar{n}$  and limiting plateau on the formation curve indicated that the metal-to-ligand ratio was two. The graphical investigations of formation curve bound by the values of  $-\log[ST]_{\text{free}}$  gave  $F_0[\text{RPT}]$  values. From  $F_0[\text{RPT}]$  values  $F_1[\text{RPT}]$  and  $F_2[\text{RPT}]$  were obtained by usual graphical extrapolation method of DeFord and Hume, (Fig. 3) and corresponding data was presented in Table VI. Though many methods are suggested for determination of stability constants of metal complexes which undergo irreversible electrode reactions at d.m.e., Ringbom and Eriksson method (Ion Indicator method) is considered to be very suitable method. Hence, the present investigation is extended for determination of stability constants of antimony-resacetophenone irreversible system by Ion Indicator method.

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