

## Cyclovoltammetric data for the interaction of thallos chloride with di ethyl amino ethyl cellulose (DEAEC) in HNO<sub>3</sub> using glassy carbon electrode

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### Abstract

The redox behavior data for thallos chloride using 0.1M HNO<sub>3</sub> in absence and presence of polymer di ethyl amino ethyl cellulose were evaluated cyclic voltammetrically. Cyclic voltammetry of thallos chloride (TlCl) was achieved using glassy carbon electrode and in presence of di ethyl amino ethyl cellulose (DEAEC) as natural polymer. The cyclic voltammetry and the kinetic data for the redox reactions of TlCl was studied and their values were discussed. The thermodynamic stability constants and Gibbs free energies of interaction between TlCl and DEAEC were evaluated and their values were discussed.

**Keywords:** cyclic voltammetry, thallos chloride, di ethyl amino ethyl cellulose, kinetic parameters, thermodynamic parameters

### 1. Introduction

Thallos chloride known as thallium (I) chloride, it is created from the reaction of thallium (I) sulfate with hydrochloric acid. It is used as a diagnostic radiopharmaceutical. It used for diagnosis of heart and parathyroid problems. Other side effects as: blurred vision, chest pain or discomfort, chills, confusion, cough difficulty with breathing, difficulty with swallowing and dizziness [1]. Thallos chloride without carrier accumulates in the heart (myocardium) in a similar way to that of potassium. Thallos chloride have been found to visualize areas of interaction or no labeled regions which are confirmed by electrocardiographic and enzyme changes. Also regions of transient myocardial ischemia corresponding to areas. Prefer used by coronary arteries with partial stenoses can be visualized by thallos chloride [2, 3]. Therefor estimation of different redox behavior of TlCl is important for following its amounts.

### 2. Experimental

Thallos chlorid of the type.... was used. Di ethyl amino ethyl cellulose and hydrochloric acid of the type was provided from Al Gomhoria pharmaceutical company. The electrochemical study was carried out by usind DY2000 potentiostat in cell containing 30 ml of 0.1 HCl supporting electrode. The three used electrodes are, pt (platinum wire) count's electrode, silver- silver chloride in saturated KCl used as reference electrode and glassy carbon electrode as working electrode. The cell used is: Ag/AgCl<sub>(s)</sub>, KCl<sub>(sat)</sub> | aqueous 0.1M HCl | GCE. It is very important to clean the working electrode with fine emery paper doped with Al<sub>2</sub>O<sub>3</sub> in manufacture made. Then the working electrode was washed several times with distilled water and dried.

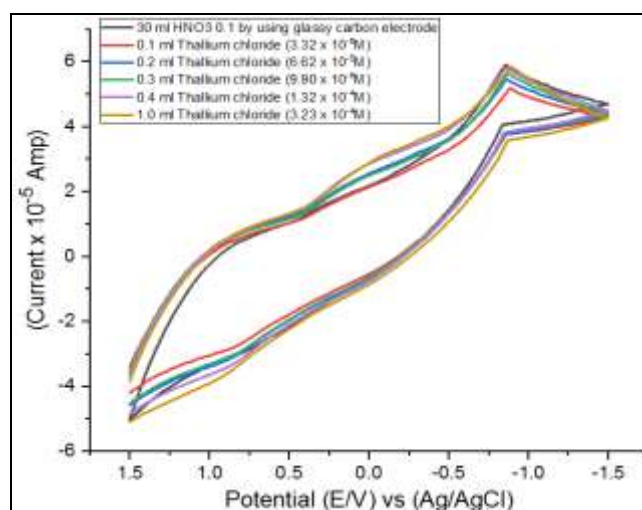
### 3. Results and Discussion

The electrochemical behavior of thallos chloride (TlCl) alone in 0.1 M HCl at 289.15K. Electrochemical behavior of thallos chloride (TlCl) alone in 0.1 M HCl using window

range from 1.5V to ~ 1.5V. Two main peaks were obtained for TlCl, one for the reduction process at ~ -0.1V and the other in the oxidation site at ~0.9V. Quasirversible study was suggested for the redox reaction of TlCl, see Fig. (1). The reduction and oxidation process of Tl alone took place by consuming one electron. The reduction mechanism for TlCl was found to go throw the following equation:



Whereas the oxidation process took place following equations (2) and/or equation (3).



**Fig 1:** Effect of different concentrations of Thallium chloride in 0.1M HNO<sub>3</sub> using glassy carbon electrode at 289.15 K and scan rate 0.1V.S<sup>-1</sup>.

We noticed that both redox waves for TlCl are broad peaks. That is to say, wide range peaks. Proceeding the reduction of TlCl by two mechanisms, i.e. two parallel ways, following equations (1) and (4) from a wide range (0.2- - 0.3V) of reduction as:



Also the oxidation of TlCl happened by two parallel process following equations 2 and 3 resulting in abroad oxidation peak in range (0.7 - 1.0V) Analysis of the cyclovoltammetric TlCl waves: The different equations used for the electrochemical results by cyclic voltammetry are [15-25].

$$I_p = [0.4463 n^{3/2} F^{3/2} D^{1/2} A C / (RT)^{1/2}] v^{1/2} \dots\dots (5)$$

$$D^{1/2} = (\text{slope}, I_p \text{ vs } v^{1/2}) \times (RT)^{1/2} / 0.4463 n^{3/2} F^{3/2} D^{1/2} A C \dots\dots (6)$$

$$\Delta E_p = E_{p2} - E_{p1} = 2.303(RT/nF) \dots\dots (7)$$

$$\Psi = \gamma^2 K_s / \pi(nF/RT) v D_a \dots\dots (8)$$

$$\gamma = \sqrt{D_a / D_c} \dots\dots (9)$$

Where  $\Psi$  is the charge transfer parameter taken as one for

**Table 1:** Effect of different concentrations of Thallium chloride by using GCE at 289.15K and scan rate 0.1V.S<sup>-1</sup>.

[M] x10 <sup>5</sup> mol.L <sup>-1</sup>	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-) Ip,a x10 <sup>6</sup> Amp	Ip,c x10 <sup>6</sup> Amp	Ip,a/I p,c	E <sup>o</sup> Volt	Da x10 <sup>10</sup> cm <sup>2</sup> .s <sup>-1</sup>	Dc x10 <sup>10</sup> cm <sup>2</sup> .s <sup>-1</sup>	α <sub>anac</sub>	K <sub>s</sub> x10 <sup>5</sup>	Γ <sub>c</sub> x10 <sup>9</sup> mol.cm <sup>-2</sup>	(+) Q <sub>c</sub> x10 <sup>6</sup> C	Γ <sub>a</sub> x10 <sup>9</sup> mol.cm <sup>-2</sup>	(-) Q <sub>a</sub> x10 <sup>6</sup> C
3.32	0.803	0.014	0.789	1.39	3.70	0.374	0.408	2.375	16.9	0.522	3.59	1.218	3.69	0.456	1.38
6.62	0.823	0.029	0.794	2.40	5.06	0.474	0.426	1.789	7.97	0.439	2.35	1.667	5.05	0.789	2.39
9.90	0.828	0.035	0.793	3.50	5.12	0.683	0.431	1.699	3.64	0.441	1.58	1.683	5.10	1.149	3.48
13.2	0.831	0.031	0.799	4.15	6.13	0.678	0.431	1.357	2.96	0.436	1.52	2.016	6.11	1.366	4.14
32.3	0.928	-0.033	0.961	5.37	6.58	0.815	0.447	0.377	0.568	0.795	4.53	2.166	6.56	1.766	5.35

#### It was observed from Table (1) the following findings

1. The redox reaction of TlCl is quasireversible one because  $\Delta E_p$  is greater than 0.59 V
2. The cathodic peak are mora developed than the anodic peak with greater limiting current than the oxidation one
3. The cathodic diffusion coefficient  $D_c$  is greater than is the anodic diffusion coefficient  $D_a$  indicating the case of formation of the reduction peak than that of the oxidation
4. The electrode surface coverage for the reduction peak  $\Gamma_c$  is greater than that for the oxidation peak  $\Gamma_a$  indicating more facility reduction to proceed oxidation for TlCl solutions in 0.1M HCL.
5. The electrode quantity of electricity  $Q_c$  for the cathodic peak is greater than  $Q_a$  for the anodic peak indicating that the redox reaction is mora reduction favourable.
6. The  $k_s$ , heterogenous electron rate constant is increase firstly by increase of TlCl concentration from  $3.32 \times 10^{-5}$  to  $6.62 \times 10^{-5}$  due to the high increase in both  $I_{p_c}$  and  $I_{p_a}$ . Also the increase in  $K_s$  by the use of TlCl concentration

better approximation [13],  $\alpha$  is the charge transfer coefficient,  $K_s$  is the standard rate constant for electron transfer,  $v$  is the scan rate,  $D_a$  is the anodic diffusion coefficient,  $D_c$  the cathodic diffusion coefficient,  $F$  faraday constant,  $T$  is the absolute temperature,  $n$  is the number of electrons and  $\alpha = 0.5$  for reversible calculations  $A$  is the area of the working electrode. The  $k_s$  which is the heterogenous electron rate constant can be evaluated by applying equation (10) [31, 36].

$$K_s = 2.18 (D_a n F v / RT)^{1/2} \exp \{ \alpha 2 n F (E_{p_c} - E_{2A}) / RT \} \dots\dots (10)$$

The electron surface coverage was estimated for both reduction and oxidation process by applying equation (11) [30-35].

$$\Gamma = I_p 4RT / n^2 F^2 A v \dots\dots (11)$$

The quantity of the electricity used for the redox reactions was estimated on applying equation (12) [33]

$$Q = n F A \Gamma \dots\dots (12)$$

All the above parameters following equations (5 - 11) for redox behavior of TlCl alone in 0.1 M HCl were calculated and in Table (1) cited.

$3.32 \times 10^{-5} \text{M}$  is because the rush increase in both  $I_{p_a}$  and  $I_{p_c}$ . Decrease of  $K_s$  on using TlCl concentration of  $9.9 \times 10^{-3}$  and  $3.32 \times 10^{-3}$  due to small increase in both  $I_{p_a}$  and  $I_{p_c}$ .

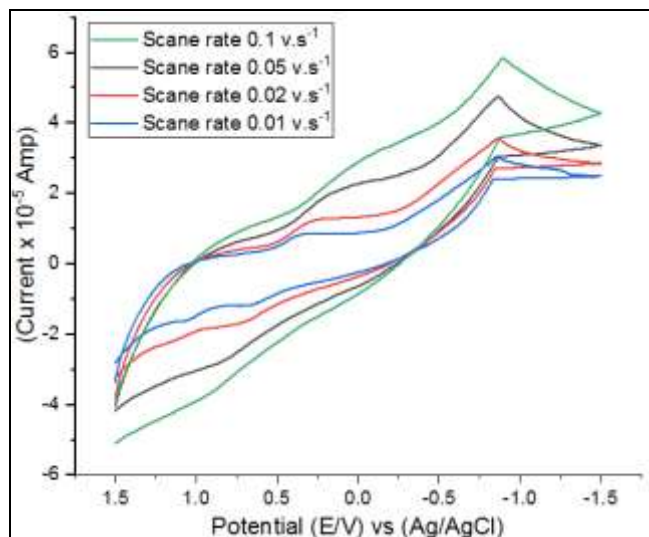
7. All parameters given in Table (1) are approximately increase by the increase of TlCl concentration confirm the diffusion mechanism.

#### Effect of different scan rates, 0.1, 0.05, 0.02, 0.01 V/S were studied for electrochemical behavior of $3.23 \times 10^{-5} \text{M TlCl}$ .

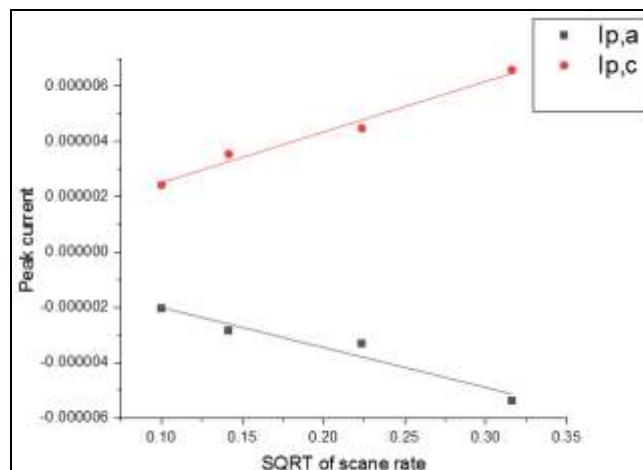
Fig (2) show the different cyclic voltammograms for TlCl at different scan rate giving no new peaks. Fig (2) the relation between peak current and  $v^{1/2}$ , two straight lines for the oxidation and reduction peaks with slope  $\sim 0.5$  indicating the diffusion controlled reaction.

All the data given in Table (2) are increased by the decrease of scan rate other than  $K_s$  values. This indicate the diffusibility of the reactions.

The electrochemical behavior for TlCl in presence of 1% (W/W) di ethyl amino ethyl cellulose.



**Fig 2:** Effect of different scan rates of  $(3.23 \times 10^{-4} \text{ M})$  Thallium chloride by using glassy carbon electrode at 289.15 K.



**Fig 3:** The relation between peak current and SQRT of scan rate for of Thallium chloride alone.

Fig. (2) Represent the electrochemical behavior of the complex formed by the interaction of  $\text{TlCl}$  with (DEAEC) in 0.1 M HCl at 289.15 K.

**Table 2:** Effect of different scan rates of  $(3.23 \times 10^{-4} \text{ M})$  Thallium chloride by using GCE at 289.15K

v V.S <sup>-1</sup>	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-)Ip,a x10 <sup>6</sup> Amp	Ip,c x10 <sup>5</sup> Amp	Ip,a/I p,c	E° Volt	Da x10 <sup>13</sup> cm <sup>2</sup> .s <sup>-1</sup>	Dc x10 <sup>12</sup> cm <sup>2</sup> .s <sup>-1</sup>	ana	ksc x10 <sup>3</sup>	Γ c x10 <sup>9</sup> mol.cm <sup>-2</sup>	(+)Qc x10 <sup>6</sup> C	Γ ax10 <sup>9</sup> mol.cm <sup>-2</sup>	(-) Qa x10 <sup>6</sup> C
0.1	0.928	-0.033	0.961	5.37	6.58	0.815	0.447	3.77	5.678	0.795	45.3	2.166	6.56	1.766	5.35
0.05	0.821	0.1964	0.624	3.30	4.47	0.738	0.509	2.85	5.235	0.808	1.06	2.941	8.91	2.172	6.58
0.02	0.692	0.337	0.355	2.83	3.54	0.799	0.514	5.25	8.208	0.736	0.0536	5.823	17.6	4.659	14.1
0.01	0.627	0.373	0.253	2.03	2.43	0.837	0.500	5.40	7.714	0.819	0.0139	7.984	24.2	6.679	20.2

Same window range from 1.5 ~ -1.5V was used the cyclic voltammograms seen in Fig (2) and data given in Table (2) show the following

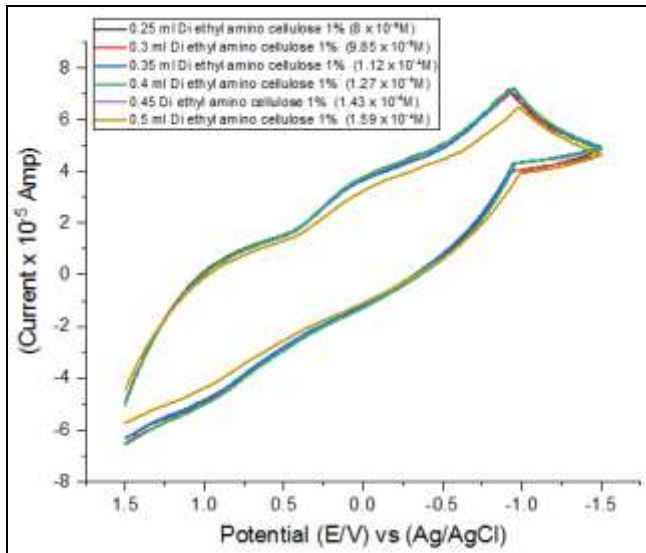
1.  $I_{p,a}$  and  $I_{p,c}$  for the different concentration of di ethyl amino ethyl cellulose are less than that on using  $3.23 \times 10^{-4} \text{ M}$   $\text{TlCl}$  alone indicating complex reaction.
2.  $D_a$  and  $D_c$  values are greater than that of  $3.32 \times 10^{-4} \text{ M}$   $\text{TlCl}$  alone indicating more complexation by more

diffusion.

3.  $\Gamma_a$  and  $\Gamma_c$  are small in presence of di ethyl amino ethyl cellulose than in absence of it indicating also complexation behavior
4. All the heterogenous rate constant values  $k_s$  are small than  $3.23 \times 10^{-4} \text{ M}$   $\text{TlCl}$  alone favouring attraction by complexation.

**Table 3:** Effect of different Di ethyl amino cellulose 1% by using GCE at 289.15K

[M] x10 <sup>4</sup> mol.L <sup>-1</sup>	[L] x10 <sup>4</sup> mol.L <sup>-1</sup>	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-) Ip,a x10 <sup>6</sup> Amp	Ip,c x10 <sup>6</sup> Amp	Ip,a/I p,c	E° Volt	Da x10 <sup>12</sup> cm <sup>2</sup> .s <sup>-1</sup>	Dc x10 <sup>11</sup> cm <sup>2</sup> .s <sup>-1</sup>	ana	ksc x10	Γ c x10 <sup>9</sup> mol.cm <sup>-2</sup>	(+) Qc x10 <sup>5</sup> C	Γ a x10 <sup>10</sup> mol.cm <sup>-2</sup>	(-) Qa x10 <sup>6</sup> C
3.23	0.800	0.941	0.089	0.852	3.36	6.41	0.525	0.515	14.816	5.38	0.067	1.37	2.109	6.39E-06	11.06	3.35
3.23	0.958	0.935	0.138	0.797	3.21	5.23	0.614	0.537	13.518	3.59	0.0263	1.03	1.721	5.21	10.57	3.20
3.23	1.12	0.903	0.081	0.822	2.67	4.28	0.623	0.492	9.335	2.40	0.072	0.656	1.409	4.27	8.782	2.66
3.23	1.27	0.902	0.099	0.802	2.20	3.14	0.700	0.501	6.321	1.29	0.034	0.575	1.032	3.13	7.227	2.19
3.23	1.43	0.946	0.075	0.871	1.65	2.88	0.574	0.511	3.585	1.09	0.024	1.26	0.947	2.87	5.442	1.65
3.23	1.59	0.921	0.077	0.844	1.19	2.53	0.471	0.499	1.854	0.838	0.031	0.736	0.832	2.52	3.914	1.19



**Fig 4:** Effect of different concentrations of Di ethyl amino cellulose 1% on potassium permanganate by using glassy carbon electrode at 289.15 K and scan rate 0.1 V.S<sup>-1</sup>.

**Effect of different scan rates on TICI + di ethyl amino ethyl cellulose**

Effect of different scan rates was studied for interaction of TICI with di ethyl amino ethyl cellulose and cyclic voltammetry data was observed in Table (5) with smaller value than that for TICI alone indicating the complexation reaction.

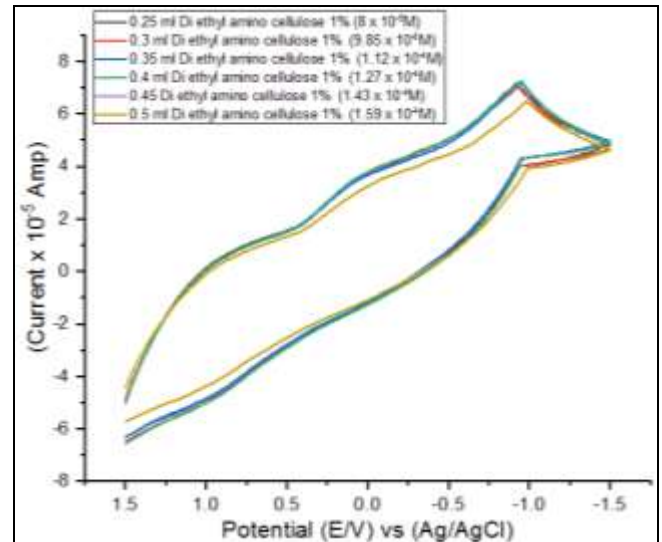
The complexation stability constant ( $\beta$ ) for TICI – DEAEC complexes in 0.1 M HCl is the application of equation (13) [27, 36]

$$(E_p)_c - (E_p)_M = 2.303(RT/nF) * (\log \beta_c + 2.303(RT/nF) \log C_L) \dots\dots (13)$$

Where  $\beta_c$  is the stability constant,  $(E_p)_M$  is the peak potential of TICI in absence of DEAEC,  $(E_p)_c$  is the peak potential for the complex. Other symbols are explained before.

The Gibbs free energies of interaction between TICI and DEAEC were calculated [19, 26] by using equation (14) [30, 39].

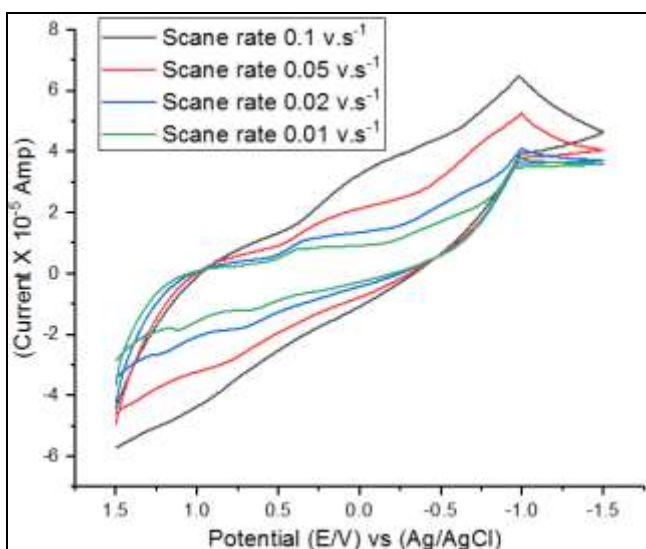
$$\Delta G = -2.303 RT \log \beta_{MX} \dots\dots\dots (14)$$



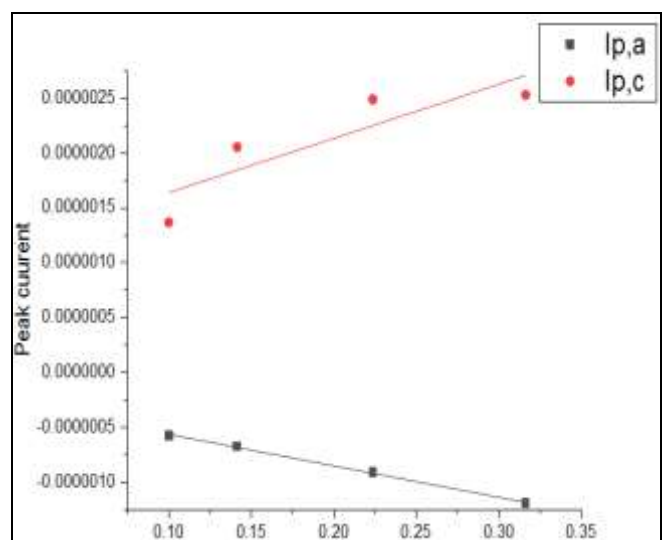
**Fig 4:** Effect of different concentrations of Di ethyl amino cellulose 1% on potassium permanganate by using glassy carbon electrode at 289.15 K and scan rate 0.1 V.S<sup>-1</sup>.

**Table 4:** Effect of different scan rates of in the presence of Di ethyl amino cellulose 1% by using GCE at 289.15 K.

v V.S <sup>-1</sup>	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-)Ip,a x10 <sup>7</sup> Amp	Ip,c x10 <sup>5</sup> Amp	Ip,a/Ip,c	E° Volt	Da x10 <sup>14</sup> cm <sup>2</sup> .s <sup>-1</sup>	Dc x10 <sup>12</sup> cm <sup>2</sup> .s <sup>-1</sup>	αna	ksc x10 <sup>4</sup>	Γ c x10 <sup>9</sup> mol.cm <sup>-2</sup>	(+)Qc x10 <sup>6</sup> C	Γ ax10 <sup>9</sup> mol.cm <sup>-2</sup>	(-) Qa x10 <sup>6</sup> C
0.1	0.921	0.077	0.844	11.9	2.53	0.471	0.499	2.101	0.949	1.493	78.3	0.832	2.52	0.391	1.19
0.05	0.730	0.217	0.514	9.07	2.49	0.364	0.474	2.440	1.838	0.898	2.18	1.637	4.96	0.597	1.81
0.02	0.659	0.346	0.313	6.71	2.05	0.327	0.503	3.341	3.131	1.160	0.273	3.379	10.2	1.104	3.34
0.01	0.598	0.413	0.184	5.74	1.37	0.420	0.506	4.897	2.774	1.999	0.065	4.498	13.6	1.889	5.73



**Fig 5:** Effect of different scan rates of in the presence of Di ethyl amino cellulose 1% by using glassy carbon electrode at 289.15 K.



**Fig 6:** The relation between peak current and SQRT of scan rate in presence of Di ethyl amino cellulose 1%

**Table 5:** Stability constant for (Thallium chloride - Di ethyl amino cellulose) complex.

[M] x10 <sup>4</sup> mol.L <sup>-1</sup>	[L] x 10 <sup>4</sup> mol.L <sup>-1</sup>	(Ep,1/2)M	(Ep,1/2)C	ΔE v	J (L/J)	Log β <sub>j</sub>	ΔG (KJ/mol)
3.20	0.800	0.447	0.515	-0.068	0.25	0.372	0.899
3.19	0.958	0.447	0.537	-0.089	0.3	0.284	1.955
3.19	1.12	0.447	0.492	-0.045	0.35	0.301	-3.289
3.18	1.27	0.447	0.501	-0.054	0.4	0.258	-3.459
3.18	1.43	0.447	0.511	-0.063	0.45	0.0735	-3.458

From the data given in Tables (3-5), we conclude that the interaction between TlCl and DEAEC leads to formation of strong complex. Also the Gibbs free energies of interaction between TlCl and DEAEC support the complexation reaction between the two

### Conclusion

We explained the redox behavior for thallos chloride from cyclic voltammetric data in 0.1 M HCl using glassy carbon electrode at 289.15 K.

Effect of di ethyl amino ethyl cellulose was studied and their effect were interpreted.

The complex formation between thallos chloride and di ethyl amino ethyl cellulose was found to happen and Gibbs free energies were obtained explaining strong complexation interaction.

### Declaration of Interests

The authors declare that they have no conflict with anybody about this work.

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