



## **ELECTROCHEMICAL BEHAVIOUR OF COMPLEXES OF Tl(I) WITH L-PHENYLALANINE IN AQUEOUS-NON-AQUEOUS MEDIA**

**SUMAN MEENA, SMITA AGARWAL and O. D. GUPTA \***

Department of Chemistry, University of Rajasthan, JAIPUR – 302004 (Raj.) INDIA

### **ABSTRACT**

Polarographic study of Tl(I) complexes with L-Phenylalanine has been carried out in non-aqueous (20% ethanol, 40% ethanol) medium under varying temperatures 308 K and 318 K, in presence of KNO<sub>3</sub> as supporting electrolyte. DeFord & Hume's method is used to calculate the stepwise formation constants. The reduction is found to be reversible and diffusion controlled involving one electron in each case. The complexes with metal to ligand ratio as 1 : 1, 1 : 2, 1 : 3 have been reported. The changes in thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  accompanying complexation have been evaluated. The mathematical Mihailov's method has also been applied for the comparison of stability constants values.

**Key words:** Thallium(I), Phenylalanine, Ethanol, Polarographic study.

### **INTRODUCTION**

The study of metal complexes in non-aqueous solvents by a polarographic method has attracted much attention in recent years. Znako and Manusova<sup>1</sup> and Sartori and Giacomello<sup>2</sup> made the early attempts to study polarographic behaviour is observed that non-aqueous solvent affect diffusion current, nature of reduction half-wave potential<sup>3-5</sup> and all other relevant properties.

Sharma and Gupta<sup>6</sup> have reported the electrokinetic study of Ga(III) with DL- $\alpha$ -alanine in aqueous and 25% ethanol in water at D. M. E. Saini et al.<sup>7,8</sup> have studied the complexes of Cd(II) with antibiotic durg at D. M. E. in 20% methanol-water and ethanol-water mixture. Polarographic studies of complexes in methanol and ethanol have been carried out by Migal and co-workers<sup>9-12</sup> and have shown that there is sharp increase in the stability of complexes above 80% alcohol concentration, which they attributed to solvation

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\* Author for correspondence; E-mail: [gupta\\_od@yahoo.co.in](mailto:gupta_od@yahoo.co.in), [a.smita51@yahoo.com](mailto:a.smita51@yahoo.com)

effect. Different workers<sup>13-17</sup> have obtained different results. In view of the conflicting reports this field of work is quite demanding for systematic study on the influence of aqueous-organic solvent mixture on complex formation.

The present paper deals with the complexation reaction of Tl(I) and determination of stability constants of various species formed by Tl(I) with L-Phenylalanine in aqueous mixture of ethanol at 308 K and 318 K. The measurements, have been carried out in 20%, 40% aqueous-ethanol mixtures.

Amino acids are well known for their tendency to form complexes with metals, have great significance in biological and pharmaceutical fields and are directly involved in all the metabolic, enzymatic reactions<sup>18</sup>. Amino acids have good chelating ability with metal ions and play an important role in biology, pharmacy and laboratory reagents<sup>19,20</sup>. L-Phenylalanine is amino acid which is used in this on the other hand thallium and its complexes are often highly toxic<sup>21</sup>. Part of the reason for thallium's high toxicity is that, when present in aqueous solution as the univalent ( $Tl^+$ ) ion. It exhibits some similarities with essential alkali metal cations like  $K^+$  (Potassium ion). So it can thus enter the body via potassium uptake path ways.

## EXPERIMENTAL

A CL-362 polarographic analyser was used to record polarograms, using saturated calomel electrode as reference electrode and dropping mercury electrode was used as microelectrode. All reagent grade chemicals were used. The test solutions were prepared in measuring flasks of pyrex glass using conductivity water. Various solutions were prepared containing 0.1 M conc. of Tl(I), varying concentration of L-Phenylalanine from 0.001 M to 0.007 M and 20%, 40% Ethanol.  $KNO_3$  was used to maintain ionic strength constant at 1.0 M. Nitrogen gas was passed through each solution for 15-20 mins to remove dissolved oxygen. Triton X-100 was used in all solutions to suppress the observed maxima. The gradual increase in current with increase in potential was noted and plotted to obtain the polarograms for the solutions. The d.m.e. had the characteristics,  $m = 4.62$  mg/s,  $t = 2$  sec per drop. The temperature was kept constant by using Haake type water circulation thermostat.

## RESULTS AND DISCUSSION

The reduction of Tl(I) in presence of N-Phenylalanine was found to be reversible in non-aqueous (20%, 40% ethanol) medium. Direct proportionality of the diffusion current to

the square root of effective height of mercury column indicates the reduction is diffusion controlled. The current was found to decrease with the increase of ligand concentration as a result of complex formation. The complex ion formed is of much larger size as compared to aqua metal ion, hence the low values of diffusion currents with the increase of ligand concentration.

The values of overall formation constant  $\log \beta_j$  were calculated by the graphical extrapolation method. The experimentally determined values calculated for Tl(I)-L-Phenylalanine system in 20% ethanol medium at 308 K and 318 K are recorded in Tables 1 and 3, respectively. The overall formation constants were obtained by extrapolation of  $F_j(X)$  to the zero ligand concentration. The formation constant  $\log \beta_1$  and  $\log \beta_2$  of the two species are 3.00 and 6.041 at 308 K and the same value at 318K are found 2.87 and 5.82, respectively.

For the 40% ethanol media the overall formation constants for Tl(I)-L-Phenylalanine system are recorded in Table 2 and 4 at 308 K and 318 K.

**Table 1: Polarographic measurements and  $F_j(X)$  function values for Tl(I)-L-Phenylalanine system in 20% ethanol at 308 K**

Ionic strength ( $\mu$ ) = 1.0 (KNO<sub>3</sub>), Triton X-100 = 0.0002%, [Tl(I)] = 0.1 mM,

$C_x$ (mol/L)	$i_d$ $\mu A$	$E_{1/2}$ (-V vs S.C.E)	$F_0(X)$	$F_1(X) \times 10^3$	$F_2(X) \times 10^6$
0.000	7.69	0.510	-	-	-
0.001	7.39	0.528	1.8413	0.841	-
0.002	7.24	0.557	6.4713	2.735	0.867
0.003	7.17	0.579	14.589	4.529	1.176
0.004	6.99	0.594	26.147	6.286	1.321
0.005	6.62	0.600	35.150	6.830	1.166
0.006	6.489	0.608	48.792	7.965	1.16
0.007	6.39	0.620	78.001	11.00	1.428

$\log \beta_1 = 3.00$ ,  $\log \beta_2 = 6.0413$   
 $C_x$  = L-Phenylalanine concentration (moles litre<sup>-1</sup>)

**Table 2: Polarographic measurements and  $F_j[X]$  function values for Tl(I)-L-Phenylalanine system in 20% ethanol at 318 K**Ionic strength ( $\mu$ ) = 1.0 (KNO<sub>3</sub>), Triton X-100 = 0.0002%, [Tl(I)] = 0.1 mM

$C_X$ (mol/L)	$i_d$ $\mu A$	$E_{1/2}$ (-V vs S.C.E)	$F_0[X]$	$F_1[X] \times 10^3$	$F_2[X] \times 10^5$
0.000	7.73	0.500	-	-	-
0.001	7.43	0.519	2.17	1.170	4.20
0.002	7.29	0.542	5.17	2.085	6.67
0.003	7.21	0.557	9.091	2.69	6.46
0.004	6.99	0.569	14.714	3.428	6.69
0.005	6.78	0.577	20.471	3.86	6.22
0.006	6.59	0.586	29.341	4.723	6.22
0.007	6.55	0.606	60.153	8.450	11.10

 $\log \beta_1 = 2.87$ ,  $\log \beta_2 = 5.82$  $C_x$  = L-Phenylalanine concentration of (moles litre<sup>-1</sup>)**Table 3: Polarographic measurements and  $F_j[X]$  function values for Tl(I)-L-phenylalanine system in 40% ethanol at 308 K**Ionic strength ( $\mu$ ) = 1.0 (KNO<sub>3</sub>), Triton X-100 = 0.0002%, [Tl(I)] = 0.1 mM,

$C_X$ (mol/L)	$i_d$ $\mu A$	$E_{1/2}$ (-V vs S.C.E)	$F_0[X]$	$F_1[X] \times 10^3$	$F_2[X] \times 10^6$
0.000	7.58	0.512	-	-	-
0.001	7.29	0.528	1.9204	0.920	-
0.002	7.14	0.567	8.4758	3.737	1.118
0.003	7.00	0.585	16.9938	5.33	1.286
0.004	6.69	0.596	26.837	6.45	1.287
0.005	6.52	0.605	39.193	7.63	1.226
0.006	6.39	0.614	56.347	9.224	1.287
0.007	6.30	0.629	102.28	14.46	1.851

 $\log \beta_1 = 3.176$ ,  $\log \beta_2 = 6.107$  $C_x$  = L-Phenylalanine concentration (moles litre<sup>-1</sup>)

**Table 4: Polarographic measurements and  $F_j[(X)]$  function values for Tl(I)-L-phenylalanine system in 40% ethanol at 318 K**Ionic strength ( $\mu$ ) = 1.0 (KNO<sub>3</sub>), Triton X-100 = 0.0002%, [Tl(I)] = 0.1 mM,

$C_X$ (mol/L)	$i_d$ $\mu A$	$E_{1/2}$ (-V vs S.C.E)	$F_0[(X)]$	$F_1[(X)] \times 10^3$	$F_2[(X)] \times 10^6$
0.000	7.64	0.482	-	-	-
0.001	7.05	0.500	2.1347	1.34	0.034
0.002	6.95	0.535	7.9448	3.472	1.186
0.003	6.76	0.552	15.1847	4.728	1.209
0.004	6.64	0.564	24.641	5.910	1.202
0.005	6.52	0.574	36.732	7.146	1.209
0.006	6.42	0.583	50.937	8.322	1.203
0.007	5.96	0.597	94.1400	13.305	1.743

$\log \beta_1 = 3.04, \log \beta_2 = 6.07$   
 $C_x =$  L-Phenylalanine concentration (moles litre<sup>-1</sup>)

It is concluded from the above results that when aqueous medium replaced by aqueous-nonaqueous media, the value of stability constants increase with the increase in the concentration of non-aqueous solvent. The effect of non-aqueous solvents on the stability of the complexes depends on several factors such as dielectric constant, viscosity of the media, depolarizer and ion-pair formation etc.

The decrease in diffusion current with increase in the percentage of non-aqueous solvent may will be explained with decreasing value of the diffusion coefficient, in aqueous and nonaqueous solvents mixture. It is obvious that in addition to water molecules some molecules of ethanol occupy a place in the solvation sphere of the depolarizer. The size of these molecules being greater than the size of water molecules, decrease the value of diffusion coefficient which in turn is responsible for the decrease in diffusion current as the amount of nonaqueous solvent is increased. The higher viscosity of the resulting medium, which hinders in the movement of the depolarizer, is also in part, responsible for the decrease in diffusion current ( $i_d$ ).

The overall change in thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  of complex

formation for Tl(I)-Phenylalanine system in 20% ethanol and 40% ethanol solvent mixtures at 308 K are recorded in Table 5, respectively.

**Table 5: Stability constants values for Tl(I)-L-Phenylalanine system in aqueous-ethanol (20%, 40%) mixtures**

Temp.	Stability constants	Methods	20% ethanol	40% ethanol
308 K	$\log\beta_1$	DeFord & Hume's	3.00	3.17
		Mihailov's	3.05	3.30
	$\log\beta_2$	DeFord & Hume's	6.04	6.10
		Mihailov's	5.95	6.12
318 K	$\log\beta_1$	DeFord & Hume's	2.87	3.04
		Mihailov's	2.67	3.08
	$\log\beta_2$	DeFord & Hume's	5.82	6.07
		Mihailov's	5.86	6.10

The more negative value of  $\Delta G^\circ$  for 1 : 2 complex shows that the driving tendency of the complexation reaction is from left to right and the reaction tends to proceed spontaneously. The negative values of  $\Delta H^\circ$  suggested that the formation of these complexes is an exothermic process.

The values of stability constants for Tl(I)-L-Phenylalanine system in 20%, 40% ethanol-aqueous solvent mixture have also been further verified by mathematical method given by Mihailov and the data are given in Table 6.

**Table 6: Thermodynamic parameters of Tl(I)-L-phenylalanine system in aqueous-ethanol (20%, 40%) mixture**

Medium	Temp.	Complex species	$\Delta G^\circ(-)$ kcal/mole	$\Delta H^\circ(-)$ kcal/mole	$\Delta S^\circ(-)$ kcal/mole deg <sup>-1</sup>
Ethanol 20%	308 K	$\text{MX}_1$	4.2559	11.4697	0.0234
		$\text{MX}_2$	8.5700	19.4985	0.0354
Ethanol 40%	308 K	$\text{MX}_1$	4.5056	11.8844	0.0239
		$\text{MX}_2$	8.6649	9.3438	0.0022

M = Tl(I), X = L-Phenylalanine

### Effect of temperature on all studied systems

The system under consideration was investigated at temp 308 K and 318 K. The variation of temperature has no effect on the nature of reduction, while the value of stability constants decreased with increased in temperature due to easy reduction and increased degree of reversibility.

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