



POLAROGRAPHIC DETERMINATION OF STABILITY CONSTANT VALUES OF THALLIUM (I) COMPLEXES WITH L-THREONINE IN AQUEOUS NONAQUEOUS MEDIA

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ABSTRACT

Polarographic studies of stability constants of various species formed by Tl(I)-L-Threonine have been carried out in aqueous-nonaqueous mixture of 20% DMF and 20% ethanol under varying temperatures at 308 K and 318 K and potassium nitrate was used as supporting electrolyte. The reduction was found to be reversible and diffusion controlled involving one electron transfer and ligand have shown the formation of 1 : 1, 1 : 2 complexes. DeFord and Hume's method as modified by Inving has been applied for the determination of composition and stepwise formation constants of complex species and the mathematical Mihailov's method has been also applied for the comparison of stability constant values. The complexes with metal to ligand ratio as 1 : 1, 1 : 2 have been reported. The changes in thermodynamic parameters ΔH° , ΔG° and ΔS° have been evaluated.

Key words: Thallium(I), L-Threonine, Polarographic study, Reversible, Stability constants.

INTRODUCTION

The study of complexation of metal with various ligands polarographically in aqueous media have been carried out from a long time. The study of metal complexes in non-aqueous solvents by polarographic method has attracted much attention in recent years. Many workers¹⁻⁶ have studied various metal-ligand complexes polarographically using various non-aqueous solvents.

Different workers⁷⁻⁹ 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. Despite this, little is known about the chemistry of amino acids and metal complexes in non-aqueous media and mixed solvents¹⁰⁻¹².

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The L-amino acids and their compounds are used in biology, industry, pharmacy and laboratory reagents¹³⁻¹⁵. They also control transamination, decarboxylation and metabolism processes in human body.

Electrochemistry in non-aqueous solution has played an important role in exploring new chemical possibilities as well as providing the methods to evaluate static solvent effect on various chemical process.

The early studies done by Sartori and Giacomello¹⁶ and Zanko and Manusova¹⁷ using polarography in aqueous-organic solvent mixture, it has become possible to carry out various measurements for both inorganic and organic substance in non-aqueous media. It has been observed that non-aqueous solvents affect diffusion current, nature of reduction, half-wave potential¹⁸⁻²⁰ and all other relevant properties. Tl(I) complexes with aza compounds have been studied by many coworkers^{21,22} in aqueous and non-aqueous media.

Kuppusamy et al.²³ evaluated the electrochemical behaviour of Co(II) in acetonitrile-water mixture at D. M. E. Kumar and coworkers²⁴ have evaluated stability constants of Cd(II) and Pb(II) with macrocyclic polyether in ethanol-water mixture.

Golube and Kalibchuk²⁵ studied the influence of solvents on the thiocyanato complexes of number of metal ions. Stanely and Mahanan²⁶ studied in non-aqueous medium and also investigated some mixed-ligand complexes. Lohiya and coworker²⁷ studied the electrochemical behaviour at D. M. E. of copper-2-amino-lepedine complexes in aqueous mixture of 1,4-dioxan, DMF, acetonitrile and formamide mixtures. Electrochemical studies²⁸ of Cd(II)-Itaconic acid system in aqueous-nonaqueous media has been carried out at D. M. E. by using KCl as supporting electrolyte at 298 K and 308 K temperatures. Polarographic studies²⁹ of 2,2'-oxydiacetic acid with In (III) in aqueous and aqueous-nonaqueous media have been carried out at constant ionic strength by using KNO₃ as supporting electrolyte at 300 K and 310 K temperature.

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-Threonine in aqueous mixture of 20% ethanol and 20% DMF at 308 K and 318 K. Amino acids have good chelating ability with metal ions and play an important role in biology, pharmacy and laboratory reagents³¹. Thallium and its complexes are often highly toxic³². It exhibits some similarities with essential alkali metal action like K⁺ so it can thus enter the body via potassium uptake pathways.

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 micro electrode. All reagent grade chemicals were used. Various solutions were prepared containing 0.1 M concentration of Tl(I), varying concentration of L-Threonine from 0.001 M to 0.007 M in 20% DMF, 20% ethanol-aqueous mixture.

The supporting electrolyte KNO_3 was used and the requisite amount was added to maintain ionic strength constant ($\mu = 1.0 \text{ M}$), 0.002% Triton X-100 was used in all solutions to suppress the observed maxima. Before polarographic measurements, purified N_2 gas was passed for 10-15 mins to remove dissolved oxygen. The temperature was kept constant (308 K, 318 K) using Haake-type ultra thermostat the capillary has the following characteristic $m = 4.6 \text{ mg/s}$, $t = 2 \text{ sec.}$ and height of mercury column $h_{\text{eff}} = 43 \text{ }\mu\text{m}$.

RESULTS AND DISCUSSION

The reduction of Tl(I) complex with ligand L-Threonine give well defined wave and reduction was found to be reversible and diffusion controlled in 20% aqueous-nonaqueous media at different temperatures (308 K, 318 K). The reduction process involves one electron transfer. This is concluded by observing the constancy ratio of i_d and $h_{\text{eff}}^{1/2}$ for each system and the slopes of log plots of $\log i/i_d - i$ vs $E_{d.e.}$ at both the temperatures.

In all aqueous and aqueous-non aqueous solvents at both the temperature as the increasing amount of ligand (0.001 to 0.007) is added to solution containing Tl(I), requisite amount of KNO_3 and Triton X-100, it is observed that there is cathodic shift and decrease in diffusion current. This indicates the complexation between metal and ligand. The complex ion formed is of much larger size as compared to aqua metal ion, hence the low values of i_d with the increase of ligand concentration.

The values of overall formation constants $\log \beta_j$ were determined by DeFord and Hume's method at 308 K and 318 K. β values was obtained by the graphical method developed by Leden.

The experimentally determined values calculated for Tl(I)-L-Threonine system in 20% DMF media at 308 K and 318 K are recorded in Tables 1 and 2, respectively. The overall formation constants were determined by extrapolation of $F_j(X)$ functions to the zero ligand concentration.

Table 1: Polarographic measurements and $F_j(X)$ function values for Tl(I)-L-threonine system in 20% DMF at 308K[Tl(I)] = 0.1 mM, Ionic strength (μ) = 1.0 (KNO₃)

C_x (mol/L)	i_d μA	$E_{1/2}$ (-V vs S.C.E)	$F_0(X)$	$F_1(X) \times 10^4$	$F_2(X) \times 10^7$
0.000	4.50	0.4635	–	–	–
0.001	4.39	0.4874	0.0239	26.062	2.506
0.002	4.38	0.5060	0.0425	103.702	2.567
0.003	4.32	10.5243	0.0608	158.599	1.751
0.004	4.28	0.5475	0.0840	217.088	1.350
0.005	4.21	0.5595	0.0960	386.742	1.543
0.006	4.16	0.5751	0.1116	809.096	2.245
0.007	4.09	0.5850	0.1215	1224.616	2.597

 $\log \beta_1 = 4.681$, $\log \beta_2 = 7.398$ C_x = Concentration of L-Threonine (moles litre⁻¹)**Table 2: Polarographic measurements and $F_j(X)$ function values for Tl(I)-L-threonine system in 20% DMF at 318K**[Tl(I)] = 0.1 mM, Ionic strength (μ) = 1.0 (KNO₃)

C_x (mol/L)	i_d μA	$E_{1/2}$ (-V vs S.C.E)	$F_0(X)$	$F_1(X) \times 10^4$	$F_2(X) \times 10^7$
0.000	4.47	0.4620	–	–	–
0.001	4.35	0.4887	29.161	2.816	2.816
0.002	4.28	0.5078	65.556	3.228	1.614
0.003	4.25	0.5238	115.221	3.807	1.269
0.004	4.22	0.5380	200.592	4.990	1.247
0.005	4.17	0.5492	315.50	6.290	1.258
0.006	4.11	0.5738	924.698	15.395	2.566
0.007	4.03	0.5881	1485.936	21.213	3.030

 $\log \beta_1 = 4.380$, $\log \beta_2 = 7.079$ C_x = Concentration of L-Threonine (moles litre⁻¹)

Table 3: Polarographic measurements and $F_j(X)$ function values for Tl(I)-L-threonine system in 20% Ethanol at 308 K[Tl(I)] = 0.1 mM, Ionic strength (μ) = 1.0 (KNO₃)

C_x (mol/L)	i_d μA	$E_{1/2}$ (-V vs S.C.E)	$F_0(X)$	$F_1(X) \times 10^4$	$F_2(X) \times 10^7$
0.000	4.48	0.4650	–	–	–
0.001	4.44	0.4900	28.182	2.718	2.718
0.002	4.40	0.5110	62.662	3.083	1.541
0.003	4.35	0.5375	220.980	7.333	2.744
0.004	4.31	0.5585	322.157	8.029	2.007
0.005	4.26	0.5620	435.512	8.690	1.738
0.006	4.21	0.5795	864.968	14.400	2.780
0.007	4.14	0.5880	1241.652	17.724	2.732

 $\log \beta_1 = 4.748, \log \beta_2 = 7.431$ C_x = Concentration of L-Threonine (moles litre⁻¹)**Table 4: Polarographic measurements and $F_j(X)$ function values for Tl(I)-L-threonine system in 20% Ethanol at 318K**[Tl(I)] = 0.1 mM, Ionic strength (μ) = 1.0 (KNO₃)

C_x (mol/L)	i_d μA	$E_{1/2}$ (-V vs S.C.E)	$F_0(X)$	$F_1(X) \times 10^4$	$F_2(X) \times 10^7$
0.000	4.45	0.4640	–	–	–
0.001	4.31	0.4920	0.0280	30.910	2.990
0.002	4.25	0.5110	0.0470	65.448	1.611
0.003	4.20	0.5299	0.0659	152.088	1.679
0.004	4.17	0.5440	0.0800	237.684	1.479
0.005	4.13	0.5580	0.0940	412.097	1.644
0.006	4.06	0.5800	0.1160	986.279	2.737
0.007	3.99	0.5915	0.1275	1588.547	3.240

 $\log \beta_1 = 4.301, \log \beta_2 = 7.204$ C_x = Concentration of L-Threonine (moles litre⁻¹)

The formation constants $\log \beta_1$ and $\log \beta_2$ of the two species are 4.681 and 7.398 at 308 K and at 318 K are found 4.380 and 7.079, respectively.

For the 20% ethanol media the overall formation constants were also calculated and recorded in Tables 3 and 4 at 308 K and 318 K, respectively. The formation constants $\log \beta_1$ and $\log \beta_2$ of these complex species are 4.748 and 7.431 at 308 K and the values at 318 K are 4.301 and 7.204, respectively.

For the verification, mathematical Mihailov's method was also applied to evaluate the stability constants from $F_0[(X)]$ function values and the values are recorded in Table 5. From these tables on comparison the overall formation constants determined by both methods are found to be in good agreement.

Thermodynamic parameters have been also calculated (ΔH° , ΔG° and ΔS°). The negative value of ΔG° shows that the reaction tends to proceed spontaneously. The negative value of ΔH° indicate the exothermic nature of the reaction and this favours the increasing stability at lower temperature.

Table 5: DeFord & Hume's and Mihailov's stability constants of Tl(I)-L Threonine system

Solvent	Temperature	$\log \beta_j$	DeFord & Hume's method	Mihailov's method
20% DMF	308 K	$\log \beta_1$	4.681	3.717
		$\log \beta_2$	7.398	7.272
	318 K	$\log \beta_1$	4.380	3.931
		$\log \beta_2$	7.079	7.222
20% Ethanol	308 K	$\log \beta_1$	4.748	4.532
		$\log \beta_2$	7.431	7.072
	318 K	$\log \beta_1$	4.301	4.214
		$\log \beta_2$	7.204	7.225

CONCLUSION

It is concluded that stability constants are higher in aqueous non-aqueous mixture than in aqueous medium. The values of stability constants increases with the increase in the percentage of organic solvent in mixture because of decrease of dielectric constant. Which is responsible for decreasing solution of metal ion and ligand easily occupy coordination sites.

(availability of ligand increase) and stability of complexes also depends on several factors such as dielectric constant, viscosity of media, depolarizer and ion-pair formation etc.

The variation of temperature has no effect on the nature of reduction while the values of stability constants decreased with increased in temp due to easy reduction and increased degree of reversibility.

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