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REDUCTION OF Tl(I)–L-THREONINE COMPLEXES IN NON-AQUEOUS MEDIA AT DROPPING MERCURY ELECTRODE

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ABSTRACT

Polarographic studies of thallium(I) with L-threonine in non-aqueous medium (40% DMSO, 40% DMF, 40% ethanol) have been carried out under varying temperatures (308 K, 318 K) and potassium nitrate was used as supporting electrolyte. The reduction was found to be reversible and diffusion controlled and ligand have shown the formation of 1 : 1, 1 : 2 complexes. Values of stability constnats were calculated by using modified DeFord and Hume's method and the mathematical Mihailov's method has been also applied for comparison the stability constant values.

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

INTRODUCTION

Amino acids are the chemical units or "Building block" of the body that make up proteins, which improve the growth and maintenance of all cells are dependent upon them. L-amino acids and their compounds are used in biology, industry, pharmacy and laboratory reagents[1-3]. They also control transamination, decarboxylation and metabolism processes in human body.

Voltammetric technique was used to study the binary and ternary complexes of Cd (II) with L-amino acids and the investigation has been used to determine the thermodynamic parameters such as (ΔH, ΔG and ΔS, respectively)[4].

Interaction of Cd (II) with L-amino acids has been studied by simple d.c. polarography[5]. Deschangs et al.[6] have reported the isolation of complexes of Cu (II) with threonine and threonine from human serum and have also prepared complexes of Cu (II)

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with amino acids which have been studied polarographically[7-13]. Stanely and Mahanan[14] studied in non-aqueous medium and also investigated some mixed-ligand complexes. The coordinated system Cu (II)-neutral L-isoleucine and Cu (II)-L-isoleucinate ion were studied polarographically in aqueous medium at ionic strength, $\mu = 1$ M ($NaClO_4$) and 25 ± 0.1°C and the stability constants of the complexes have been determined[15]. Thallium (I) complexes with aza compounds have been studied by many workers[16,17] in aqueous and non-aqueous media. Lohiya et al.[18] 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 mixture. Polarographic studies[19] of 2,2′-oxydiacetic acid with In (III) in aqueous and aqueous-nonaqueous media have been carried out at constant ionic strength ($\mu = 1$) by using KNO_3 at 300 K and 310 K temperatures. On the basis of these studied thallium (I) amino acid complexes are a part of the accessible physiological role of the elements for most tissues. Present paper deals with the study of Tl (I) with L-Threonine in nonaqueous media.

EXPERIMENTAL

AR grade chemicals were used. Polarograms were recorded by using CL-362 plarographic analyser. All the half-wave potentials refer to saturated calomel electrode (reference-electrode). The solutions of 0.1 mm Tl (I) and various concentration of L-threonine and requisite amount of supporting electrolyte potassium nitrate (1 M) were prepared. All the polarogram were recorded after deaeration with purified nitrogen gas for 15-20 minutes.

The capillary has the following characteristics m = 4.67 mg/sec. and t = 2 sec, constant temperatures (308 K, 318 K) were maintained using a Haake type thermostat.

RESULTS AND DISCUSSION

The reduction of Tl (I) in presence of L-Threonine was found to be reversible in non-aqueous medium (40%, DMSO, 40% DMF, 40% ethanol) and diffusion controlled (indicated by direct proportionality of diffusion current to square root of effective height of mercury column).

The values of diffusion current decreased with the increases of ligand concentration because larger size of complex ion than aqua metal ion.

The values of overall formation constants log β_j were calculated by the graphical DeFord and Hume's method. The log β_j were obtained by extrapolation of $F_j[(X)]$ functions values to the zero ligand concentration. The formation constants log β_1 and log β_2 of complex species are 4.716 and 7.462 at 308 K. The formation constant values at 318 K are found 4.398 and 7.079, respectively. The experimentally determined values calculated for Tl (I)-L-Threonine system in 40% DMSO medium at 308K and 318K are recorded in Tables 1 and 2, respectively.

Table 1: Polarographic measurements and $F_j[(X)]$ function values for the Tl(I)-L-threonine system in 40% DMSO at 308 K

[Tl (I) = 0.1 mM], μ = 1.0M (KNO_3)

C_x (moles/Liter)	i_d (μA)	$\Delta E_{1/2}$ -V vs SCE	$F_0[(X)]$	$F_1[(X)] \times 10^4$	$F_2[(X)] \times 10^7$
0.00	4.45	0.4625	-	-	-
0.001	4.33	0.4889	29.834	2.983	2.983
0.002	4.29	0.5140	120.284	5.964	2.982
0.003	4.25	0.5307	192.117	6.370	2.123
0.004	4.21	0.5478	272.405	6.785	1.696
0.005	4.14	0.5618	464.775	9.275	1.85
0.006	4.10	0.5662	603.949	10.049	2.921
0.007	4.04	0.5881	1432.188	20.445	1.675

C_x = L-Threonine concentration, moles/ liter, log β_1 = 4.716, log β_2 = 7.462

Table 2: Polarographic measurements and $F_j[(X)]$ function values for the Tl(I)-L-threonine system in 40% DMSO at 318K

[Tl (I) = 0.1 mM], μ = 1.0M (KNO_3)

C_x (moles/Liter)	i_d (μA)	$\Delta E_{1/2}$ -V vs SCE	$F_0[(X)]$	$F_1[(X)] \times 10^4$	$F_2[(X)] \times 10^7$
0.00	4.50	0.4621	-	-	-
0.001	4.36	0.4883	28.880	2.788	2.788
0.002	4.34	0.5011	60.315	2.966	1.483

Cont…

C_x (moles/Liter)	i_d (μA)	$\Delta E_{1/2}$ -V vs SCE	$F_0[(X)]$	$F_1[(X)] \times 10^4$	$F_2[(X)] \times 10^7$
0.003	4.31	0.5190	94.84	3.113	1.237
0.004	4.27	0.5309	200.280	4.982	1.245
0.005	4.22	0.5489	306.196	6.104	1.221
0.006	4.19	0.5590	451.796	7.513	1.253
0.007	4.15	0.5873	1355.189	19.345	2.764

C_x = L-Threonine concentration, moles/ liter, log β_1 = 4.398, log β_2 = 7.079

In 40% DMF solvent the overall formation constants for Tl(I)-L-threonine system were also calculated by DeFord and Hume's method and values are recorded in Table 3 and 4 at 308 K and 318 K, respectively. The formation constants log β_1, log β_2 of these complex species are 4.892 and 7.477 at 308 K and the formation constants values at 318 K are 4.857 and 7.301, respectively.

Table 3: Polarographic measurements and $F_j[(X)]$ function values for the Tl(I)-L-threonine system in 40% DMF at 308 K

[Tl (I) = 0.1 mM], μ = 1.0M (KNO_3)

C_x (moles/Liter)	i_d (μ A)	$\Delta E_{1/2}$ -V vs SCE	$F_0[(X)]$	$F_1[(X)] \times 10^4$	$F_2[(X)] \times 10^7$
0.00	4.46	0.4600	-	-	-
0.001	4.30	0.4923	31.267	3.027	3.026
0.002	4.26	0.5183	86.159	4.258	2.129
0.003	4.21	0.5520	331.789	11.026	3.675
0.004	4.16	0.5610	489.756	12.219	3.055
0.005	4.10	0.5670	592.925	12.038	2.476
0.006	4.08	0.5745	796.159	13.253	2.209
0.007	4.02	0.5899	1475.706	21.067	3.009

C_x = L-Threonine concentration, moles/ liter, log β_1 = 4.892, log β_2 = 7.477

Table 4: Polarographic measurements and F_j[(X)] function values for the Tl(I)-L-threonine system in 40% DMF at 318 K

[Tl (I) = 0.1 mM], μ = 1.0M (KNO_3)

C_x (moles/Liter)	i_d (μA)	$\Delta E_{1/2}$ -V vs SCE	F_0[(X)]	F_1[(X)] × 10^4	F_2[(X)] × 10^7
0.00	4.48	0.4630	-	-	-
0.001	4.35	0.4890	28.536	2.754	2.753
0.002	4.30	0.5140	75.231	3.711	1.855
0.003	4.26	0.5470	266.66	8.856	2.952
0.004	4.20	0.5550	373.250	9.306	2.326
0.005	0.5620	0.5620	500.034	9.981	2.996
0.006	0.5725	0.5725	765.597	12.743	2.124
0.007	0.5815	0.5815	1109.175	15.831	2.262

C_x = L-Threonine concentration, moles/ liter, log β_1 = 4.857, log β_2 = 7.301

The log β_j values for Tl (I)-L-threonine system in 40% ethanol was also calculated by graphical method of DeFord and Hume and the values have been recorded in Table 5 and 6 at 308 K and 318 K, respectively. The formation constants log β_1 and log β_2 of the complex species are 4.778 and 7.462 at 308 K and the formation constants values at 318 K are 4.380 and 7.255, respectively.

Table 5: Polarographic measurements and F_j[(X)] function values for the Tl (I)-L-threonine system in 40% ethanol at 308 K

[Tl (I) = 0.1 mM], μ = 1.0M (KNO_3)

C_x (moles/Liter)	i_d (μA)	$\Delta E_{1/2}$ -V vs SCE	F_0[(X)]	F_1[(X)] × 10^3	F_2[(X)] × 10^7
0.00	4.46	0.4680	-	-	-
0.001	4.40	0.4965	30.556	2.956	2.955
0.002	4.35	0.5170	67.081	3.304	1.652
0.003	4.30	0.5535	2.70.654	8.988	2.996

Cont…

C_x (moles/Liter)	**i_d (μA)**	**$\Delta E_{1/2}$ -V vs SCE**	**$F_0[(X)]$**	**$F_1[(X)] \times 10^3$**	**$F_2[(X)] \times 10^7$**
0.004	4.25	0.5625	394.096	9.827	2.457
0.005	4.21	0.5700	534.564	10.671	2.134
0.006	4.15	0.5760	699.116	11.635	1.939
0.007	4.09	0.5945	1464.794	20.911	2.987

C_x = L-Threonine concentration, moles/ liter, log β_1 = 4.778, log β_2 = 7.462

Table 6: Polarographic measurements and $F_j[(X)]$ function values for the Tl (I)-L-threonine system in 40% ethanol at 318 K

[Tl (I) = 0.1 mM], μ = 1.0M (KNO_3)

C_x (moles/Liter)	**i_d (μA)**	**$\Delta E_{1/2}$ -V vs SCE**	**$F_0[(X)]$**	**$F_1[(X)] \times 10^3$**	**$F_2[(X)] \times 10^7$**
0.00	4.40	0.4670	-	-	-
0.001	4.30	0.4950	30.276	2.928	2.927
0.002	4.26	0.5185	76.580	3.779	1.889
0.003	4.20	0.5330	134.202	4.440	1.480
0.004	4.14	0.5475	239.872	5.972	1.493
0.005	4.11	0.5640	456.097	9.102	1.820
0.006	4.07	0.5742	684.539	11.392	1.899
0.007	4.01	0.5960	1612.278	23.018	3.288

C_x = L-Threonine concentration, moles/ liter, log β_1 = 4.380, log β_2 = 7.255

It is concluded from the above results that for a definite composition of the non-aqueous solvent mixture, the stability of complexes decreases with respect to the dielectric constants of the solvents. The dielectric constant values of DMSO, DMF and ethanol are found to be 48.9, 39.7 and 24.3, respectively. The less value of dielectric donstant of DMF in comparison to DMSO suggests that the less solvation of metal ion in DMF which explains the greater stability of the complexes.

The values of stability constants for Tl (I)-L-Threonine system in 40% DMSO, 40%

DMF and 40% ethanol solvent mixtures have also been further verified by mathematical method given by Mihailov and data are recorded in Table 7.

Table 7: DeFord and Hume's and mihailov's stability constants of Tl(I)-L-threonine systems

Solvent	Temp. (K)	$\log\beta_j$	DeFord and Hume's	Mihailov's
40% DMSO	308 K	$\log \beta_1$	4.716	4.073
		$\log \beta_2$	7.462	7.269
	318 K	$\log \beta_1$	4.398	4.315
		$\log \beta_2$	7.079	6.981
40% DMF	308 K	$\log \beta_1$	4.892	4.626
		$\log \beta_2$	7.479	7.178
	318 K	$\log \beta_1$	4.857	4.480
		$\log \beta_2$	7.301	7.138
40% Ethanol	308 K	$\log \beta_1$	4.778	4.658
		$\log \beta_2$	7.462	7.049
	318 K	$\log \beta_1$	4.380	3.932
		$\log \beta_2$	7.255	7.256

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