

Determination of stability constants of thallium(I) complexes with amino acids by DeFord & Hume's method in aqueous medium

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ABSTRACT

The stability constants of complexes formed by Thallium (I) with Serine and Leucine have been investigated in aqueous medium, the complex with metal Serine as 1:1, 1:2 and complexes of the Tl(I) with Leucine as 1:1, 1:2 have been reported. The values of formation constant of Serine are $\log \beta_1 = 2.1760$, $\log \beta_2 = 3.85325$ at 308K and $\log \beta_1 = 1.9030$, $\log \beta_2 = 3.6739$ at 318K and complexes of Tl(I) with Lecucine have $\log \beta_1 = 4.0290$, $\log \beta_2 = 5.2922$ at 308K and $\log \beta_1 = 3.4772$, $\log \beta_2 = 4.4151$ at 318K, respectively were calculated by DeFord and Hume's method.

Keywords: Thallium(I), serine, leucine, D.M.E., polarographic study.

INTRODUCTION

Many workers¹⁻² have studied biologically active metal complexes of amino acids which are important in analytical, biochemical and pharmaceutical fields³⁻⁵ and attracts wide attention in different fields of research. A large number of such complexes have been studied polarographically. Electrochemical methods are most suitable to investigate the redox properties of new drugs; which give insight into it. Electroanalytical techniques are also used in clinical chemistry and laboratory medicine⁶. Electrode kinetics of Zn(II) and Ni(II) with 1-amino acid have been studied by P.S. Verma *et al.*⁷⁻⁸ The importance of such compounds has been recognised in biochemical and pharmaceutical fields and attracting wide attention in different fields of research. Polarographic behaviour of divalent metal ion with acetate⁹, isovalerate¹⁰, 1,3-diaminopropane¹¹ and oxalate¹² has been studied and determined stability constants in aqueous medium. Stanely, E. Mahanan¹³ studied in non-aqueous medium, and also investigated some mixed-ligand complexes. Sarkar and Cruck

have reported the isolation of complexes of Cu(II) with threonine from normal human serum and have prepared complexes of Cu(II) with amino acids. Mixed-ligand complexes of Cu(II), Zn(II), Ni(II) and Co(II) with wide range of ligands have been studied polarographically in aqueous media¹⁴⁻²⁰.

Polarographic studies of Histidine with some p-block elements like Ga(III), In(III), Tl(I) have been carried out separately at constant ionic strength ($m = 1.0M$) by using KCl at 298K and 308K temperatures²¹.

On the basis of these studied thallium(I) amino acids complexes are a part of the accessible physiological role of the elements for most tissues. In view of the little work done, specially polarographically, on the amino acids complexes of Tl(I), the present paper deals with the study of these complexes at two different temperatures and determination of stability constants of the resulting complexes in aqueous medium by graphical method of DeFord and Hume.²² The thermodynamic parameters have been also evaluated.

EXPERIMENTAL

A CL-362 polarographic analyser is used to record polarograms, using a saturated calomel electrode as the reference electrode which has a relatively large surface area to inhibit its ready polarisation.

It is essential that the DME has microdimensions so that it is readily polarised. All the chemical used were of A.R. grade. Serine and Leucine were used as complexing agents. Potassium nitrate was used as a supporting electrolyte to maintain the ionic strength constant at 1.0M.

Triton X-100 was used to suppress the maxima observed. The concentration of maxima suppressor does not need to exceed 0.01% and indeed higher concentration are undesirable since they can lead to distortion, lowering and shifting of the position of polarographic curve.

The temperature was maintained constant at 308K and 318K. The capillary has the following characteristics, $m = 4.62$ mg/s, $t = 2$ sec and h_{eff}

$= 100$ cm. The deaeration was done using N₂ for 15-20 minutes, which was purified by passing through vanadium pentoxide and water solution.

RESULTS AND DISCUSSION

Current-voltage curves were obtained. The concentration of amino acids was varied from 0.001M to 0.007M. The values of the half-wave potentials for metal ions and their complexes shifted to more negative values on increasing the concentration of ligand. Because on increasing the concentration of the ligand, diffusion current decreases. Tl(I)-Serine and Tl(I)-Leucine system, the log plots $\log i/d-i$ vs E_{de} indicate that reduction is reversible and diffusion controlled. A plot of $E_{1/2}$ vs $\log[(X)]$ resulted a smooth curve indicating the formation of successive complexes. The method of DeFord and Hume's²² was applied to determine the values of stability constants of successive complexes. The stability constants determined by two methods are recorded in Table 1. Thermodynamics functions have been evaluated and recorded in Table 2. The polarographic measurements have been recorded in Table 3 to 6.

Table 1 : Stability constants for complexes of Tl(I) with Amino acids determined by DeFord Hume's method at 308K and 318K, respectively.

System	Methods	Temperature	Stability constant	
			log β_1	log β_2
Tl(I)-Leucine	DeFord and	308K	4.0290	5.2922
	Hume's	318K	3.4772	4.4151
Tl(I)-Serine	DeFord and	308K	2.1760	3.85325
	Hume's	318K	1.9030	3.6739

Table 2 : Thermodynamic functions (ΔG° , ΔH° , ΔS°) are recorded below

System	Complex Species	ΔG° (-)	ΔH° (-)	ΔS° (-)
		KCal/mol	KCal/mol	cal/K/mol
Tl(I)-Leucine	MX1	3.0561	97.123	0.3054
	MX2	7.4422	39.310	0.1034
Tl(I)-Serine	MX1	12.83	12.235	0.0019
	MX2	22.601	7.1083	0.0503

M = Tl(I), X = Serine / Leucine

Table 3: Polarographic measurements and $F_j[(X)]$ function values for the TI(I)-Serine system at 308K[TI(I)] = 0.1mM, μ = 1.0M (KNO₃), Temp. 308K

C_x (Moles/Litre)	$E_{1/2}$ (-V vs S.C.E)	$\log I_m/I_c$	$F_0[(X)]$	$F_1[(X)] \times 10^2$	$F_2[(X)] \times 10^3$
0.000	-	-	-	-	-
0.001	0.0181	0.00250	3.0432	2.0432	5.4051
0.002	0.0330	0.00502	5.5488	2.2744	5.8250
0.003	0.0391	0.00755	6.5594	3.5531	6.8136
0.004	0.0482	0.01266	8.0765	3.9974	6.2201
0.005	0.0539	0.01523	8.9190	4.5838	6.8194
0.006	0.0584	0.01783	9.9616	5.4602	6.5852
0.007	0.0785	0.02044	11.5802	5.9496	6.8147

 C_x = Serine concentration, moles litre⁻¹**Table 4: Polarographic measurements and $F_j[(X)]$ function values for the TI(I)-Serine system at 318K**[TI(I)] = 0.1mM, μ = 1.0M (KNO₃), Temp. 318K

C_x (Moles/Litre)	$E_{1/2}$ (-V vs S.C.E)	$\log I_m/I_c$	$F_0[(X)]$	$F_1[(X)] \times 10^2$	$F_2[(X)] \times 10^3$
0.000	-	-	-	-	-
0.001	0.0182	0.00201	2.26991	1.2699	3.7002
0.002	0.0339	0.00505	4.16265	1.5813	3.4509
0.003	0.0392	0.00965	4.92325	2.3077	4.7205
0.004	0.0482	0.01223	6.05973	3.2649	4.7569
0.005	0.0539	0.01482	6.6922	4.1384	4.7281
0.006	0.0584	0.01743	7.32483	5.5410	4.7296
0.007	0.0782	0.02058	9.84778	6.2396	4.7281

 C_x = Leucine concentration, moles litre⁻¹**Table 5: Polarographic measurements and $F_j[(X)]$ function values for the TI(I)-Leucine system at 308K**[TI(I)] = 0.1 mM, μ = 1.0M (KNO₃), Temp. 308K

C_x (Moles/Litre)	$E_{1/2}$ (-V vs S.C.E)	$\log I_m/I_c$	$F_0[(X)]$	$F_1[(X)] \times 10^2$	$F_2[(X)] \times 10^4$
0.000	-	-	-	-	-
0.001	0.5061	0.0025	2.3545	1.3549	3.3382
0.002	0.5582	0.0051	10.8848	4.9421	1.9604
0.003	0.5982	0.0076	17.3564	5.4520	1.4769
0.004	0.6460	0.0001	25.2392	6.0594	1.2594
0.005	0.6892	0.0127	32.2109	6.2421	1.0440
0.006	0.6922	0.0153	32.8016	6.3001	1.3150
0.007	0.6984	0.0179	33.6863	6.4652	1.3541

 C_x = Leucine concentration, moles litre⁻¹

Table 6: Polarographic measurements and $F_j[(X)]$ function values for the TI(I)-Leucine system at 318K[TI(I)] = 0.1mM, μ = 1.0M (KNO₃), Temp. 318K

C_x (Moles/Litre)	$E_{1/2}$ (-V vs S.C.E)	$\log I_m/I_c$	$F_0[(X)]$	$F_1[(X)] \times 10^2$	$F_2[(X)] \times 10^4$
0.000	-	-	-	-	-
0.001	0.5060	0.0005	1.6205	0.6205	2.3795
0.002	0.5574	0.0010	7.4728	3.2364	3.1820
0.003	0.5980	0.0015	11.9160	3.6386	2.6526
0.004	0.6460	0.0020	17.3553	4.0838	2.7478
0.005	0.6891	0.0070	22.51196	4.2239	2.6478
0.006	0.6920	0.0101	22.5266	4.5877	2.6461
0.007	0.6981	0.0122	23.1345	6.0620	2.6542

 C_x = Leucine concentration, moles litre⁻¹

This show that the variation of temperature has no effect on the nature of reduction while the value of stability constants decreases with increase in temperature because metal ligand bond is weaker at higher temperature and causing easy reduction and increased degree of reversibility.

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