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Electrochemical Studies of Tl(I) Complexes with Adipic Acid and Nicotinic Acid in Aqueous Media

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ABSTRACT

The polarographic determination of stability constants of metal complexes of Thallium(I) with Adipic acid and Nicotinic acids under varying temperatures 308K and 318K in aqueous media have shown the formation of 1:1 and 1:2 complexes. The values of overall stability constants of complexes have been calculated by DeFord and Hume's method which is further verified by Mihailov's method. The reduction process was found to be reversible and diffusion controlled. The change in thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ accompanying complexation have been also evaluated.

K**ey words:** Thallium(I), Adipic acid, Nicotinic acid, polarography, Mihailov's method, DeFord-Hume's method, Reversible.

INTRODUCTION

The studies of complexation of metal with various ligands polarographically in aqueous media have been carried out from a long time[1-3]. The number of electrochemical studies of metal ligand complexes are found to be very useful in various field such as analytical, biochemical and parmaceutical[4-6]. Kupppusanry Selveraj[7], Jaganathan Malike and a behaviour of Co(II) in aceto-nitrile-water mixture at DME. Vijay Kumar and coworkers[8] have evaluated stability constant of Cd(II) and Pb(II) with macrocyclic in ethanol-water mixture. Golube[9-11] studied the influence of solvents on the thiocyanato complexes of number of metal ions. Rajendra Kumar Lohiya and coworkers[12] evaluated the electrochemical studies at DME of copper-2-amino-lepedine complexes in aqueous 1,4-dioxan, DMF, acetonitrile and formamide mixture.

Electrochemical methods are most suitable to investigate the redox properties of new drugs, which give insight into it. Electroanalytical technique are also used in clinical chemistry and laboratory medicine[13].

Polarographic behaviour of divalent metal ion with acetate[14], isovalerate[15], 1,3-diaminopropane[16] and oxalate[17-18] has been studied and determined stability constants in aqueous medium.

The present study deals with polarogrpahic study of complexes of Tl(I) with Adipic acid and Nicotinic acid in aqueous medium at 308K and 318K temperatures. The overall formation constant of complexes have also been calculated using mathematical method of Mihailov.

EXPERIMENTAL

A CL-362 polarographic analyser was used to record polarograms using saturated calomel electrode as the reference electrode and dropping mercury electrode was used as microelectrode. All the chemicals which were used are of reagent grade purity. The stock solution of Thallium(I) was prepared from thallium chloride. Adipic acid and Nicotinic acid were used as complexing agents and all solution were prepared in double distilled water.

The supporting electrolyte used was KNO_3 and requisite amount was added to maintain ionic strength constant (μ = 1.0M). A solution of 0.002% triton X-100 was used as maxima suppressor. The temperature was kept constant using Haake-type ultra thermostat. Before polarographic measurements, purified N_2 gas was passed for 10 to 15 minutes, after presaturation with conductivity to be used in the study.

The capillary has the following characteristics, m = 4.62 mg/s, t = 2 sec and h_{eff} = 100 cm.

RESULTS AND DISCUSSION

Current-voltage curves were obtained. The concentration of Adipic acid and Nicotinic acid was varied from 0.001M to 0.007M. Reduction of Tl(I) complex with ligand give well defined wave. The diffusion current was found to decrease with the increase of ligand concentration as a result of the complex formation and the value of half-wave potential for metal ions and their complexes shifted to more negative value on increasing the concentration of ligand.

The complex ion formed is of much larger size as compared to the aqueous metal ion hence there is the low value of i_d with the increase of ligand concentration. Direct proportionaly of diffusion current to the square root of effective height of mercury column indicates the reduction to be diffusion controlled and reversible.

A plot of $E_{1/2}$ versus current resulted a curve indicating the formation of successive complexes. The method of DeFord and Hume's was applied to determine the value of stability constants of successive complexes. The polarographic measurements have been recorded in Table 2-5 and Mihailov's mathematical approach was applied to evaluate stability constants from $F_0(X)$ functions values and the following relation was used.

$$\beta_n = \frac{A.a^n}{n!}$$

where n is the number of complex formed which can be known from DeFord and Hume's method.

The stability constants obtained by two methods have been recorded in Table-1, which are in good agreement.

Table 1.

System	Temperature	Methods	Stability Constant	
			$\log\beta_1$	$\log\beta_2$
Tl(I)-Adipic acid	308K	DeFord and Hume	4.11	6.78
		Mihailov	4.04	6.59
	318K	DeFord and Hume	3.20	5.78
		Mihailov	2.4	5.82
Tl(I)-Nicotinic acid	308K	DeFord and Hume	4.31	7.00
		Mihailov	3.81	6.89
	318K	DeFord and Hume	3.30	5.70
		Mihailov	2.79	5.69

Complexes of Tl(I) with adipic acid are less stable than that of Nicotinic acid because in adipic acid both donar atom is oxygen whereas in nicotinic acid one oxygen and one nitrogen and on nitrogen availability of electron is more so form more stable complexes.

Thermodynamic parameters have been also calculated for which the complexation studies were carried out at two different temperatures.

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

Metal	Complex species	ΔG° (–) (Kcal mol^{-1})	ΔH° (–) (Kcal mol^{-1})	ΔS° (–) (Kcal mol^{-1})
Tl(I)- Adipic acid	MX_1	4.687	40.785	113.52
	MX_2	8.463	134.457	396.21
Tl(I)-Nicotinic acid	MX_1	4.833	45.267	127.15
	MX_2	8.345	58.265	156.97

M = Tl(I), X = Adipic acid/Nicotinic acid

Table 2: Polarographic measurements and $F_j[(X)]$ functions values for the Tl(I)-Adipic acid system at 308K.

Tl(I) = 0.1mM, μ = 1.0 (KNO_3) Temp. = 308K

C_x (mol L^{-1})	$E_{1/2}$(-V vs SCE)	$\Delta E_{1/2}$	$F_0[(X)]$	$F_1[(X)] \times 10^3$	$F_2[(X)] \times 10^7$
0.001	0.4562	0.0262	17.372	16.372	16.368
0.002	0.4671	0.0371	45.06	22.023	11.009
0.003	0.4777	0.0477	71.071	23.357	7.784
0.004	0.4869	0.059	104.153	25.789	6.446
0.005	0.4962	0.0662	150.072	29.814	5.962
0.006	0.5071	0.0771	233.153	38.692	6.448
0.007	0.143	0.0843	340.957	48.565	6.937

C_x = Adipic acid concentration, moles/ liter,log β_1 = 4.11, log β_2 = 6.778

Table 3: Polarographic measurements and $F_j[(X)]$ functions values for the Tl(I)-Adipic acid system at 318K

Tl(I) = 0.1mM, μ = 1.0 (KNO_3) Temp. = 318K

C_x (mol L^{-1})	$E_{1/2}$(-V vs SCE)	$\Delta E_{1/2}$	$F_0[(X)]$	$F_1[(X)] \times 10^3$	$F_2[(X)] \times 10^7$
0.001	0.4215	0.0212	2.455	1.455	14.55
0.002	0.4335	0.0352	5.612	2.306	11.514
0.003	0.4486	0.0483	9.114	2.704	9.005
0.004	0.4518	0.0515	13.097	3.024	7.553
0.005	0.4597	0.0594	18.076	3.415	6.824
0.006	0.4603	0.0600	25.417	4.002	6.666
0.007	0.4724	0.0691	34.203	4.743	6.772

C_x = Adipic acid concentration, moles/ liter,log β_1 = 3.20, log β_2 = 5.778

Table 4: Polarographic measurements and $F_j[(X)]$ functions values for the Tl(I)-Adipic acid system at 308K

Tl(I) = 0.1mM, μ = 1.0 (KNO_3) Temp. = 308K

C_x (mol L^{-1})	$E_{1/2}$(-V vs SCE)	$\Delta E_{1/2}$	$F_0[(X)]$	$F_1[(X)] \times 10^3$	$F_2[(X)] \times 10^7$
0.001	0.4415	0.4415	17.45	16.45	1.64
0.002	0.4550	0.4550	40.87	20.43	1.02
0.003	0.4783	0.4783	100.24	33.41	1.01
0.004	0.4900	0.4900	160.99	40.25	1.00
0.005	0.5103	0.5103	225.48	45.09	8.01
0.006	0.5555	0.5555	306.30	50.55	8.22
0.007	0.5774	0.5774	401.05	57.15	8.16

C_x = Adipic acid concentration, moles/ liter,log β_1 = 4.31, log β_2 = 7.00

Table 5: Polarographic measurements and Fj[(X)] functions values for the Tl(I)-Nicotinic acid system

Tl(I) = 0.1mM, μ = 1.0 (KNO_3) Temp. = 318K

C_x (mol L^{-1})	$E_{1/2}$(-V vs SCE)	$\Delta E_{1/2}$	$F_0[(X)]$	$F_1[(X)] \times 10^3$	$F_2[(X)] \times 10^7$
0.001	4201	0.198	2.177	1.177	11.74
0.002	0.4353	0.0350	4.0202	1.601	7.99
0.003	0.4532	0.0529	8.785	2.595	8.641
0.004	0.4618	0.0615	11.410	2.652	6.623
0.005	0.4684	0.0681	15.232	2.846	5.686
0.006	0.4749	0.0746	20.123	3.187	5.306
0.007	0.4805	0.0802	27.474	3.782	5.398

C_x = Adipic acid concentration, moles/ liter,log β_1 = 3.90, log β_2 = 5.01

This shows that the variation of temperature has no effect on the nature of reduction while the value of stability constants decrease with the increase in temperature because metal ligand bond is weaker at higher temperature and causing easy reduction and increased degree of reversibility i.e. lower temperature favours the formation of stable complexes.

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