

Polarographic Studies of Indium(III) and Thallium(I) Complexes with DL- α -Alanine

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The polarographic behaviour of indium(III) and thallium(I) with DL- α -alanine have been studied in aqueous as well as in 25 % ethanol-water (v/v) media using a dropping mercury electrode. Indium(III) reduces reversibly in aqueous media and quasi-reversibly in 25 % ethanol-water (v/v) media involving three electrons in all solutions, whereas Tl(I) reduces reversibly in both aqueous as well as in 25 % ethanol-water (v/v) media involving one electron transfer process. The reduction is found to be diffusion controlled in both cases. The $E_{1/2}$ have been determined by Gellings method. DL- α -Alanine formed 1:1 and 1:2 metal:ligand complexes with In(III) at pH = 4-4.25 and with Tl(I) at pH = 6-6.5. The stability constants of In(III)-DL- α -alanine and Tl(I)-DL- α -alanine have been determined using Deford-Hume method at temperature 30 and 40 °C. The values of ΔG , ΔH and ΔS at 30 °C have also been reported.

Key Words: Polarography, In(III), Tl(I) Complexes, DL- α -alanine.

INTRODUCTION

Although the reduction of In(III) and Tl(I) at dropping mercury electrode has been investigated in various complexing and non-complexing media by many workers¹⁻¹² to be reversible and by other as quasi-reversible. Polarography can be advantageously applied to the study of complex metal ions when the reductions of both metal ion and metal ion complex proceed reversibly at the dropping mercury electrode. Saxena and co-workers¹³⁻¹⁵ have studied several metal complexes of amino-acids which have been found useful application in biological and pharmaceutical fields¹⁶. Present communication reports the polarographic behaviour of indium(III) and thallium(I) in aqueous as well as in 25 % ethanol-water (v/v) media.

EXPERIMENTAL

All the chemicals used were of analytical grade and the stock solutions are prepared in double distilled water. Ionic strength was maintained constant using KCl. The concentration of metal ions, KCl and Triton-X-100 in test solution were 1.0 mM, 0.1 M and 0.002 %, respectively. The pH of the test solutions adjusted using dil. HCl/NaOH solution. An Elico digital polarograph (CL-357) was used for obtaining the current voltage curves. Purified nitrogen was used for removing the dissolving oxygen. The potential were measured against a saturated calomel electrode (SCE).

The capillary had following characteristics: $m = 4.66$ mg/s, $t = 3.0$ s, $m^{2/3}t^{1/6} = 3.350$ at $h_{\text{Hg}} = 100$ cm.

RESULTS AND DISCUSSION

Indium(III) and thallium(I) in presence of DL- α -alanine in aqueous media produce a single well defined reversible wave, whereas in 25 % ethanol-water (v/v) media In(III) and Tl(I) produce a single well defined quasi-reversible and reversible wave in 0.1 M KCl as supporting electrolyte and 0.002 % Triton-X-100 as maximum suppressor at pH = 4-4.25 and 6-6.5. The plots of i_d vs. $h_{\text{eff}}^{1/2}$ were found to be linear and passing through the origin, thereby indicating the diffusion controlled nature of the reduction in both cases.

Successive addition of DL- α -alanine made the $E_{1/2}$ of In(III) and Tl(I) to shift towards more negative side and also diffusion current to decrease. Tables 1 and 2 clearly indicate complexation between In(III) and Tl(I) with DL- α -alanine.

TABLE-1
POLAROGRAPHIC MEASUREMENTS AND F_j [X] VALUES FOR
INDIUM-DL- α -ALANINE SYSTEM IN AQUEOUS MEDIA AT 30 °C

Conc. of DL- α -alanine	$-E_{1/2}$ (V)	$\Delta E_{1/2}$	i_d (μA)	F_0	F_1	F_2
0.00	0.5500	–	3.70	–	–	–
0.01	0.5510	0.0010	3.55	1.166	16.65	965.00
0.02	0.5530	0.0030	3.42	1.526	26.33	966.53
0.03	0.5552	0.0052	3.25	2.067	35.57	952.33
0.04	0.5579	0.0790	2.25	2.820	45.50	962.65
0.05	0.5620	0.0100	3.10	3.759	55.18	963.68

POLAROGRAPHIC MEASUREMENTS AND F_j [X] VALUES FOR
INDIUM-DL- α -ALANINE SYSTEM IN 25 % ETHANOL-WATER MEDIA AT 30 °C

Conc. of DL- α -alanine	$-E_{1/2}^r$ (V)	$\Delta E_{1/2}^r$	i_d (μA)	F_0	F_1	$F_2 \times 10^3$
0.00	0.5530	–	3.50	–	–	–
0.01	0.5550	0.002	3.45	1.275	27.59	1.759
0.02	0.5580	0.005	3.25	1.910	45.61	1.780
0.03	0.5610	0.008	3.05	2.870	62.48	1.747
0.04	0.5640	0.011	2.95	4.190	79.74	1.743
0.05	0.5670	0.014	2.95	5.920	98.40	1.763

Since In(III) reduced quasireversibly, the $E_{1/2}^r$ values of In(III) at various ligand concentrations are calculated using Gelling method¹⁷. The $E_{1/2}^r$ values are used to calculate $F_0(X)$ using the expression:

$$F_0(X) = \text{anti log} \left(\frac{0.4343nF \Delta E_{1/2}}{RT} + \log \frac{I_M}{I_C} \right) \quad (1)$$

TABLE-2
POLAROGRAPHIC MEASUREMENTS AND $F_j [X]$ VALUES FOR
THALLIUM- DL- α -ALANINE SYSTEM IN AQUEOUS MEDIA AT 30 °C

Conc. of DL- α -alanine	$-E_{1/2}$ (V)	$\Delta E_{1/2}$	id (μ A)	F_0	F_1	F_2
0.000	0.4650	—	3.50	—	—	—
0.008	0.4674	0.0024	3.48	1.1023	12.79	73.75
0.016	0.4685	0.0035	3.29	1.2140	13.37	73.54
0.032	0.4722	0.0072	3.15	1.4618	14.42	69.38
0.040	0.4747	0.0097	3.15	1.6083	15.20	75.00
0.048	0.4770	0.0120	3.15	1.7564	15.76	74.16
0.056	0.4790	0.0140	3.10	1.9271	16.56	77.85

Conc. of DL- α -alanine	$-E_{1/2}^r$ (V)	$\Delta E_{1/2}^r$	id (μ A)	F_0	F_1	$F_2 \times 10^3$
0.000	0.4700	—	3.05	—	—	—
0.008	0.4725	0.0025	3.02	1.1106	13.83	103.75
0.016	0.4750	0.0050	2.99	1.2336	14.60	100.00
0.032	0.4772	0.0072	2.64	1.5197	16.24	101.25
0.040	0.4799	0.0099	2.64	1.6853	17.13	103.25
0.048	0.4820	0.0120	2.59	1.8648	18.01	104.37
0.056	0.4865	0.0165	2.80	2.0488	18.73	102.32

In the above expression $\Delta E_{1/2}$ was replaced by $\Delta E_{1/2}^r$. The other derived functions were obtained as usual. The plot of $E_{1/2}$ vs. $\log C_x$ in both cases are smooth curves (not linear), showing, therefore the formation of two or more complex species in equilibrium.

The classical method due to Lingane¹⁸, therefore, cannot be used for the determination of formation constants. Defored and Hume¹⁹ treatment as modified by Irving²⁰ has been applied. The formation constants of the complexes formed are obtained by plotting $F_{0j} [X]$ functions against [ligand] followed by graphical extrapolation.

$$F_0(X) = \text{anti log} \left(\frac{0.4343nF(E_{1/2})_S - (E_{1/2})_C}{RT} + \log \frac{I_M}{I_C} \right) \quad (2)$$

$$= 1 + \beta_1[X] + \beta_2[X]^2 + \dots + \beta_N[X]^N \quad (3)$$

$$F_1[X] = F_0[X] - 1 = \beta_1 + \beta_2[X] + \beta_3[X]^2 + \dots + \beta_N[X]^{N-1} \quad (4)$$

In the case of In(III) $(E_{1/2})_S$ and $(E_{1/2})_C$ is replaced by $(E_{1/2}^r)_S$ and $(E_{1/2}^r)_C$. where $(E_{1/2}^r)_S$ and $(E_{1/2}^r)_C$ are the half wave potentials for the uncomplexed and complexed metal ions, respectively. I_S and I_C are the experimentally determined diffusion current constants of these species (β_0), formation constant of the zero

complex, is defined as unity $[X]$, is the concentration of ligand. β_1 is the formation constant of 1:1 complex. The intercept of the plot of $F_1(X)$ vs. (X) extrapolated to $(X) = 0$, is equal to $\beta_1[X]$. The plot of $F_2[X]$ vs. $[X]$ is a straight line which indicates that only two complexes represented as $\text{In}(\text{DL-}\alpha\text{-alanine})_n$ and $\text{Tl}(\text{DL-}\alpha\text{-alanine})_n$ where $n = 1, 2$. The values of stability constants for In(III) and Tl(I) complexes with DL- α -alanine in aqueous as well as in 25 % ethanol-water (v/v) media at 30 and 40 °C are given in Table-3.

TABLE-3
STEPWISE METAL STABILITY CONSTANTS AND THERMODYNAMIC
FUNCTIONS OF In(III) AND Tl(I) COMPLEXES OF DL- α -ALANINE
AT DIFFERENT TEMPERATURES ($\mu = 0.1 \text{ M KCl}$)

Metal	Temp. (°C)	Stability constants	Thermodynamic functions			
			ΔH (Kcal/mol)	ΔG (Kcal/mol)	ΔS (cal/degree/mol)	
Aqueous media						
In(III)	30	β_1	7.0	-6.850	-1.17	-18.74
		β_2	965.0	-3.470	-4.13	+2.17
	40	β_1	5.0			
		β_2	830.0			
Tl(I)	30	β_1	12.2	-2.010	-1.50	-1.68
		β_2	74.0	-10.960	-0.37	-34.93
	40	β_1	11.0			
		β_2	44.0			
25 % ethanol-water media						
In(III)	30	β_1	10.0	-2.280	-1.38	-2.97
		β_2	1750.0	-1.820	-4.49	+8.81
	40	β_1	9.0			
		β_2	1620.0			
Tl(I)	30	β_1	13.0	-0.914	-1.54	+2.06
		β_2	103.0	-4.060	-2.79	-4.19
	40	β_1	12.4			
		β_2	82.0			

The first stepwise formation constant is greater than the second. This is in agreement with the general trend of the stepwise formation constant values; K_N being greater than K_{N+1} owing to the steric and statistical considerations.

Thermodynamic functions: The overall changes in thermodynamic functions, free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complexation reaction have been determined at 30 °C (Table-3) with the help of following equations:

$$\Delta G = -RT \ln \beta \quad (\beta = \text{overall stability constant})$$

$$\Delta H \text{ is determined with help of an isobar } (d \ln \beta)/dt = \Delta H/RT^2$$

ΔS is then evaluated from the relation,

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (T = \text{absolute temperature})$$

The negative values of ΔG shows that complexation reaction tends to proceed spontaneously. The negative enthalpy changes indicate the exothermic nature of the reaction. The positive entropy values indicate that complexation is favoured by enthalpy and entropy factors.

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