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POLAROGRAPHIC STUDY OF MIXED LIGAND COMPLEXES OF Pb (II) AND Tl (I) WITH THIOGLYCEROL AND SOME AMINO ACIDS IN AQUEOUS-DMSO MEDIUM

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ABSTRACT

The mixed ligand complexes of Pb (II) and Tl (I) with thioglycerol (TG) and some amino acids (Glutamic Acid/Aspargine/Glycine/L-methionine) in 20% dimethyl sulphoxide (DMSO) have been investigated at the dropping mercury electrode (DME) at constant ionic strength KNO_3 (μ = 1.0 M) and 303 ± 2K temperature. Triton X-100, (0.002%) was used as maximum suppressor. The mixed ligand complexes of Pb (II) and Tl (I) were found to be reversible and diffusion controlled, involving two electrons [Pb (II)] and one electron [Tl (I)]. It was found that only a single mixed ligand entity MA_iX_j is formed. The stability constants have been evaluated by Souchay and Faucherre's method.

Key words: Thioglycerol, Glycine, Stability constant, Pb (II), Tl (I).

INTRODUCTION

Polarographic behavior of number of organic sulphur compounds has been the subject of considerable investigation. A survey of literature reveals that mercapto acids and other sulphur containing compounds with active-SH group have gained importance in the fields of pharmaceutical, biological and analytical chemistry[1,2] and in the sphere of coordination chemistry[3]. Biological active metal complexes with amino acids are also important in diverse disciplines and have been studied by many coworkers[4-7]. As a part of our investigation of mixed ligand complexes of mercaptans and carboxylic ligands with various metal ions[8], the present mixed ligand system with Pb (II) and Tl (I) have been studied polarographically using TG and amino acids as mixed ligands.

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EXPERIMENTAL

Thioglycerol (95% Evan's chemetics, Inc N.Y.) and sodium salts of amino acids were used as complexing agents. All other reagents used were of AR grade. Stock solutions were prepared in double distilled water. Freshly prepared solutions were always used to avoid effect of ageing and hydrolysis. Triton X-100 (0.002%) was used as maximum suppressor and KNO_3 (μ = 1.0 M) as supporting electrolyte. An automatic polaroscan systronic (India) 1634 with a saturated calomel electrode as a reference electrode and platinum electrode as an auxiliary electrode was used for determining current-voltage curve. The capillary characteristics in KNO_3 (μ = 1.0 M) at $E_{d.e.}$= -0.60 volts vs SCE, $m^{2/3}t^{1/6}$ = 2.9241 $mg^{2/3}$ $sec^{-1/2}$ (h = 55 cm) at 303 ± 2 K. All measurements were done with the cell immersed in a thermostatic bath, controlled at the desired temperature. N_2 was used for de-aeration.

Formation of mixed ligand complexes was studied at 303 ± 2K by scanning polarograms of $Pb(NO_3)_2$ or $TlNO_3$ at constant ionic strength (μ = 1.0 M) KNO_3 and 0.002% triton X-100 as maximum suppressor for two different sets of different ligand composition in 20% ($^v/_v$) DMSO. Metal ligand compositions of two different sets were:

I set-0.3 mM $Pb(NO_3)_2$ or $TlNO_3$, 0.002% Triton X-100 and KNO_3 (μ = 1.0 M) with constant concentrations of amino acids (C_x = 40 mM) and varying concentration of TG (C_A = 10 mM to 80 mM)

II set-0.3 mM of Pb $(NO_3)_2$ or $TlNO_3$, 0.002% Triton X-100 and KNO_3 (μ = 1.0 M) with constant concentration of TG (C_A = 40 mM) and varying concentration of amino acids (C_x = 10 mM to 80 mM)

RESULTS AND DISCUSSION

Linear plots of i_d vs $h_{eff}^{1/2}$ passing through the origin established the diffusion controlled nature in each case. All the plots of log $\frac{i}{i_d - i}$ vs $-E_{d.e}$ yielded straight line with mean values of the slope of 30 ± 2 mV for Pb (II) and 60 + 2 mV for Tl (I) system showing the reversibility of the reduction. $E_{1/2}$ values were found to shift towards more negative values with increasing concentrations of mixed ligands, showing the complex formation. (Tables 1 and 2).

Table 1: Mixed ligand system with Pb (II) at (303 ± 2K) $\Delta E_{1/2}$ (Pb (II) metal ion) = 0.475 volts, id Pb (II) metal ion) = 3.72 μA in 20% ($^V/_V$) DMSO

Concentration of mixed ligands x 10^{-2} M		TG + Glycine system		TG + Glutamic acid system		TG + Aspargine system		TG + L-Methionine system	
C_A	C_X	Is/Ic	$\Delta E_{1/2}$ volts	Is/Ic	$\Delta E_{1/2}$ volts	Is/Ic	$\Delta E_{1/2}$ volts	Is/Ic	$\Delta E_{1/2}$ volts
1.0	4.0	1.690	0.2138	1.005	0.2271	0.930	0.1751	1.244	0.1878
2.0	4.0	1.409	0.2264	1.047	0.2375	0.961	0.1855	1.353	0.2008
4.0	4.0	1.016	0.2381	1.022	0.2512	1.388	0.2001	1.094	0.2121
6.0	4.0	1.033	0.2455	0.781	0.2559	1.192	0.2074	0.951	0.2185
8.0	4.0	1.057	0.2515	0.791	0.2618	0.961	0.2115	1.014	0.2240
4.0	1.0	1.338	0.2008	1.180	0.2122	0.978	0.1698	1.000	0.1731
4.0	2.0	1.054	0.2196	0.971	0.2306	1.137	0.1846	1.180	0.1931
4.0	6.0	1.107	0.2514	1.005	0.2622	1.062	0.2098	1.261	0.2241
4.0	8.0	0.994	0.2587	0.989	0.2697	1.127	0.2173	1.324	0.2314

Table 2: Mixed ligand system with Tl (I) at (303 ± 2K) $\Delta E_{1/2}$ (Tl(I) metal ion) = 0.500 volts, id (Tl (I) metal ion) = 4.4 μA in 20% ($^V/_V$) DMSO

Concentration of mixed ligands x 10^{-2} M		TG + Glycine system		TG + Glutamic acid system		TG + Aspargine system		TG + L-Methionine system	
C_A	C_X	Is/Ic	$\Delta E_{1/2}$ volts	Is/Ic	$\Delta E_{1/2}$ volts	Is/Ic	$\Delta E_{1/2}$ volts	Is/Ic	$\Delta E_{1/2}$ volts
1.0	4.0	1.571	0.2366	1.205	0.2428	2.178	0.2287	1.666	0.2340
2.0	4.0	1.205	0.2596	1.257	0.2647	1.641	0.2455	1.272	0.2550
4.0	4.0	1.128	0.2846	1.419	0.2906	1.666	0.2645	1.629	0.2755
6.0	4.0	1.313	0.2999	1.219	0.3011	1.205	0.2718	1.246	0.2956
8.0	4.0	0.942	0.3078	1.081	0.3103	1.067	0.2781	1.313	0.3053
4.0	1.0	0.920	0.2388	0.901	0.2395	1.982	0.2245	1.438	0.2393

Cont…

Concentration of mixed ligands x 10^{-2} M		**TG + Glycine system**		**TG + Glutamic acid system**		**TG + Aspargine system**		**TG + L-Methionine system**	
C_A	**C_X**	**$\frac{Is}{Ic}$**	**$\Delta E_{1/2}$ volts**	**$\frac{Is}{Ic}$**	**$\Delta E_{1/2}$ volts**	**$\frac{Is}{Ic}$**	**$\Delta E_{1/2}$ volts**	**$\frac{Is}{Ic}$**	**$\Delta E_{1/2}$ volts**
4.0	2.0	1.050	0.2610	0.911	0.2605	1.629	0.2463	1.396	0.2598
4.0	6.0	0.956	0.2978	1.067	0.3016	1.215	0.2749	1.257	0.2918
4.0	8.0	1.268	0.3065	1.082	0.3133	1.094	0.2817	1.246	0.3002

Souchay and Faucherre[9] derived an equation, where metal ion forms complex with two ligand species simultaneously in solution. If the complexing reaction of the following type is considered:

$$M + iA + jX \;\; MA_iX_j \qquad \ldots(1)$$

and with the restriction that a single mixed ligand entity MA_iX_j is formed, the shift in the $E_{1/2}$ of the polarographic wave of the metal ion as a function of the concentration of the added reagents A and X is given by -

$$\Delta E_{1/2} = \frac{2.303RT}{nF} \log\left[\frac{D_{free}}{D_{comp}}\right]^{1/2} - \frac{2.303RT}{nF} \log K_{MA_iX_j}$$

$$-i\frac{2.303RT}{nF} \log C_A - j\frac{2.303RT}{nF} \log C_X \qquad \ldots(2)$$

The ratio (D_{free}/D_{comp}) was obtained from the value of limiting current, From plots of $\Delta E_{1/2}$ vs – log C_A with C_X kept constant and $\Delta E_{1/2}$ vs – log C_X with C_A kept constant, values for "i" and "j" can be obtained by intersect method, because on differentiation -

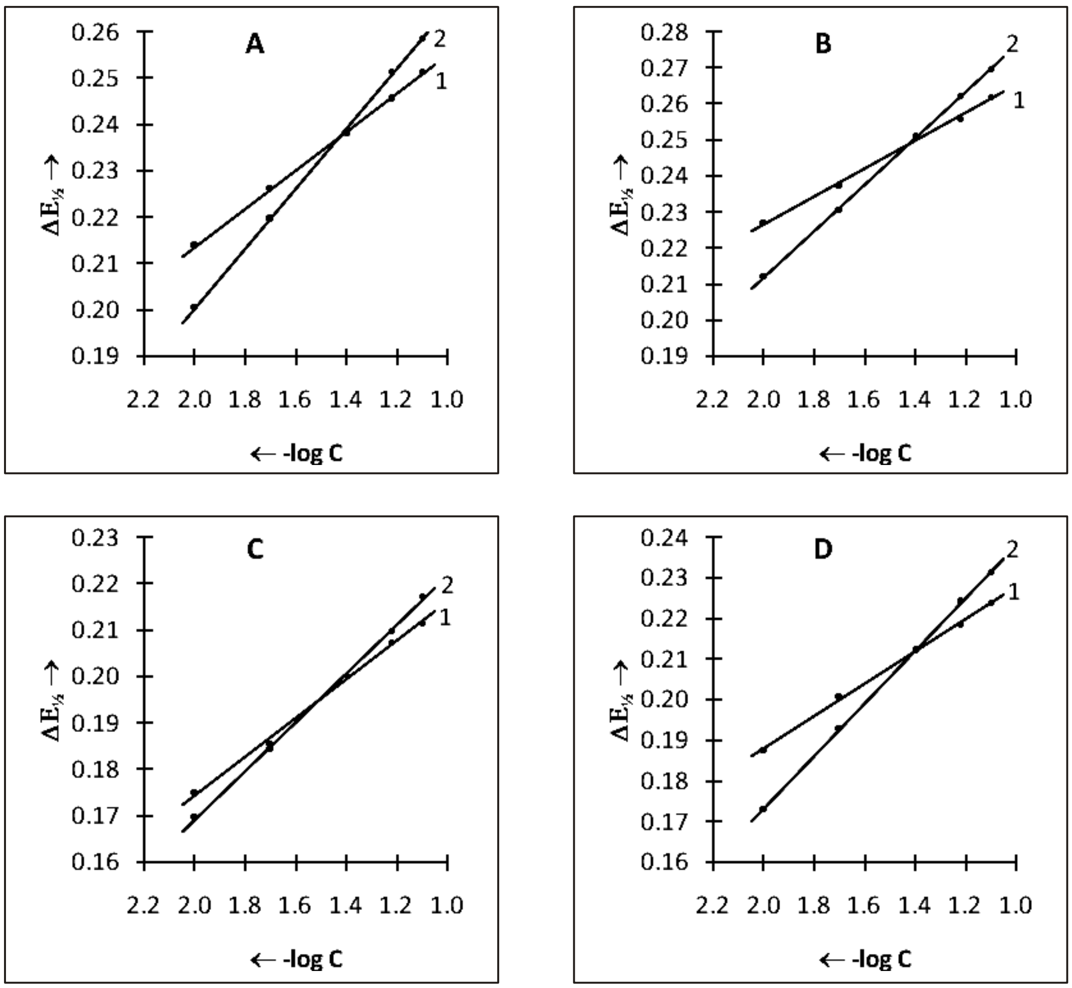
$$\left[\frac{\partial(\Delta E_{1/2})}{\partial(\log C_A)}\right]_{C_X} = -i\,\frac{2.303RT}{nF} \qquad \ldots(3)$$

$$\left[\frac{\partial(\Delta E_{1/2})}{\partial(\log C_X)}\right]_{C_A} = -j\,\frac{2.303RT}{nF} \qquad \ldots(4)$$

Plots of(i) $\Delta E_{1/2}$ vs – log C_A (C_X kept constant) and

(ii) $\Delta E_{1/2}$ vs – log C_X (C_A kept constant) yielded

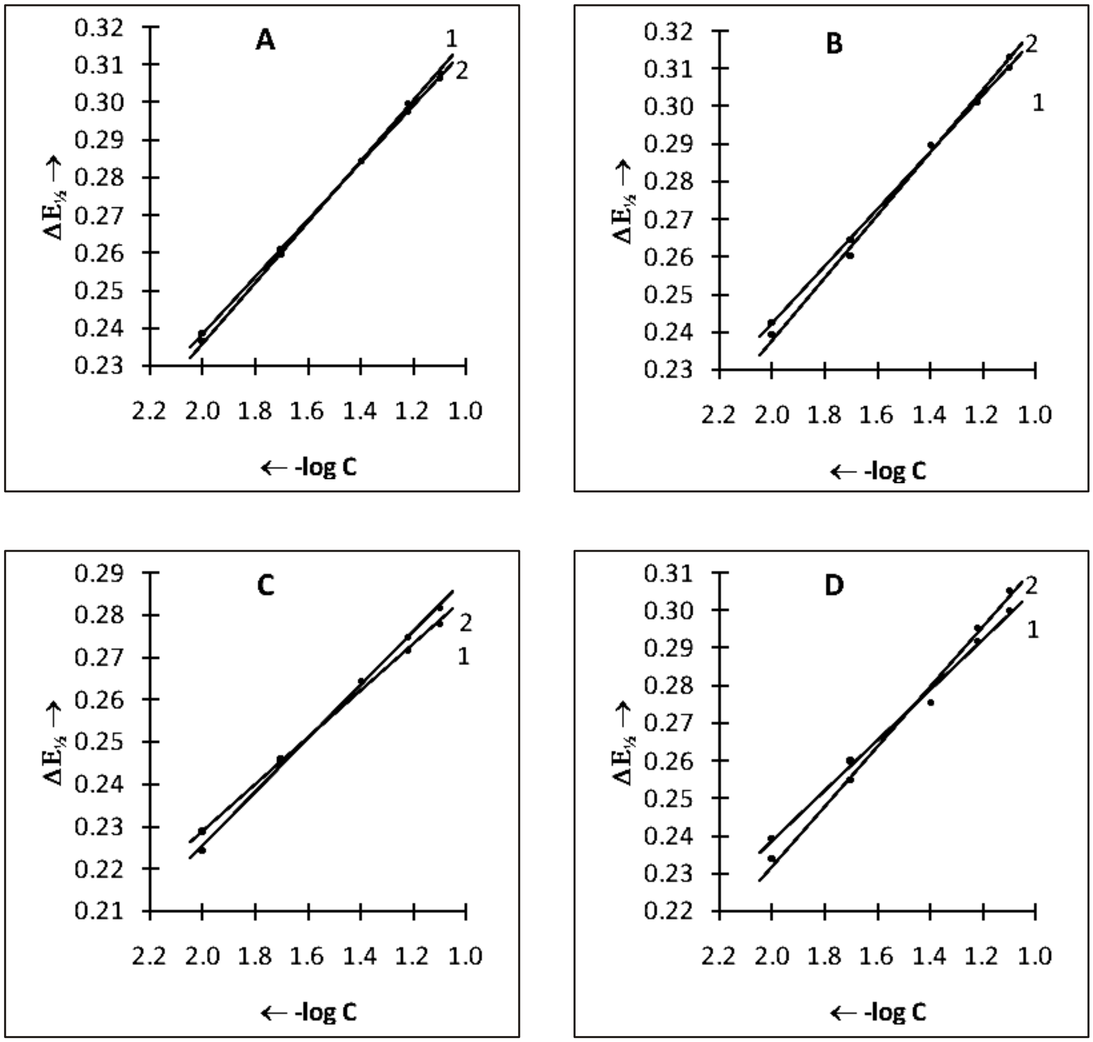
Straight lines (Figs. 1, 2, Curve 1 represents varying concentrations of C_A (TG) and constant concentration of C_X (Glycine/ Glutamic Acid/ Aspargine/ L-Methionine) and Curve 2 represents varying concentrations of C_X (Glycine/ Glutamic Acid/Aspargine/L-Methionine) and constant concentration of C_A (TG)) and thus establishing the formation of single mixed ligand entity. The coordination numbers "i" and "j" of the ligands A and X are determined from the plots of Figs. 1 and 2 and the value of "i" and "j" are given in Table 3.



Curve 1 represents varying concentrations of C_A and constant concentration of C_X

Curve 2 represents varying concentrations of C_X and constant concentration of C_A

Fig. 1: Plots of $\Delta E_{1/2}$ as a function of –log C in 20% ($^V/_V$) DMSO for complexes of Pb (II) with (A) TG + glycine (B) TG + glutamic acid (C) TG + aspargine (D) TG + L-methionine systems



Curve 1 represents varying concentrations of C_A and constant concentration of C_X

Curve 2 represents varying concentrations of C_X and constant concentration of C_A

Fig. 2: Plots of $\Delta E_{1/2}$ as a function of –log C in 20% ($^V/_V$) DMSO for complexes of Tl (I) with (A) TG + glycine (B) TG + Glutamic acid (C) TG + Aspargine (D) TG + L-methionine systems

Substituting the whole value of "i" and "j", the stability constants log $K_{MA_iX_j}$ of the ligand complexes are determined using equation (2) and are given in Table 3.

Table 3

	TG + Glycine system with		TG + Glutamic acid system with		TG + Aspargine system with		TG + L-Methionine system with	
	Pb (II)	**Tl (I)**	**Pb (II)**	**Tl (I)**	**Pb (II)**	**Tl (I)**	**Pb (II)**	**Tl (I)**
Coordination number "i" of ligand A	1.38	1.33	1.31	1.26	1.35	0.92	1.35	1.33
Coordination number "j" of ligand X	2.14	1.26	2.18	1.37	1.76	1.07	2.18	1.15
Mean log $K_{MA_iX_j}$	12.20	7.58	12.62	7.63	10.85	7.25	11.34	7.51

CONCLUSION

The present investigation clearly reveals the formation of only single mixed ligand species ($PbAX_2$) of Pb (II) and (TlAX) of Tl (I) with TG and amino acids in 20% ($^v/_v$) DMSO medium.

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