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Polarographic study of mixed ligand complexes of Pb (II) and Tl (I) with thio disuccinic acidand some amino acids in aqueous medium

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Abstract

The mixed ligand complexes of Pb (II) and T1 (I) with TDSA in aqueous with some amino acids (Glutamic Acid, Aspargine, Glycine and L-methionine) have been investigated at the dropping mercury electrode (DME) at constant ionic strength KNO_3 (m=1.0m) and 303 ± 2K temperature. Triton x-100 (0.002%) was used as maximum suppressor. The reduction of Pb (II) and T1 (I) were found to be reversible and diffusion controlled, involving two electrons [Pb(II)] and one electron [T1(I)] respectively. 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: Amino Acids, Thio di succinic acid, Pb (II), T1(I), mixed ligand complexes.

Introduction

Polarographic behaviour of number of organic sulphur compounds have 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[4-5]. As a part of our investigation of mixed ligand complexes of mercaptans and carboxylic ligands with various metal ions[7], the present mixed ligand system with Pb (II) and T1 (I) have been studied polarographically using TDSA and amino acids as mixed ligands.

Experimental

Thio di succinic acid (95% Evan's chemetics, Inc N.Y.) and amino acids were used as complexing agents. All other reagents used were of AR grade. Stock solutions were prepared in doubly distilled water. Freshly prepared solutions were always used to avoid the offer of ageing and hydrolysis. Triton x-100 (0.002%) was used as maximum suppressor and KNO_3 (μ=1.0M) as supporting electrolyte. An automatic polaroscan systronic (India) 1634 with a saturated calomel electrode as a reference electrode and platinum electrode as a auxiliary electrode was used for determining current voltage curve. The capillary characteristics in KNO_3 (μ=1.0M) at $E_{d.e.}$=-0.60 volts vs sce, $m^{2/3}t^{1/6}$ = 2.3697 $mg^{2/3}$ $sec^{-1/2}$ (h=55cm) at 298 ± 2K. All measurements were done with the cell immersed in a thermostatic bath, controlled at the desired temperature. N_2 was used for deaeration.

Formation of mixed ligand complexes were studied at 303±2K by scanning polarograms of Pb $(NO_3)_2$ or $TlNO_3$ and 0.002% Triton x-100 as maximum suppressor for two different sets of different ligand composition in (v/v) aqueous. Metal ligand compositions of two different sets were:

Ist set-

0.33mM Pb $(NO_3)_2$ or Tl NO_3, 0.002% Triton x-100 and KNO_3 (m=1.0M) with constant concentrations of amino acids (C_x = 40mM) and varying concentration of TDSA (C_A = 10mM to 60mM)

IInd set-

0.33mM of Pb $(NO_3)_2$ or $TiNO_3$, .002% Triton x-100 and KNO_3 (m=1.0M) with constant concentration of TDSA (C_A = 40mM) and varying concentration of amino acids (C_X = 10mM to 60mM)

Result 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 vs -$E_{d.e}$ yielded straight line with mean values of the slope of 30 ± 2mv for Pb^{2+} and 60+2mv for Ti+ system showing the reversibility of the reduction. values were found to shift towards more negative values with increasing concentrations of mixed ligands, showing the complex formation. (Table 1 & 2).

Souchay and Faucherre (8) derived an equation, where metal ion form complex with two ligand species simultaneously in solution. If the complexing reaction of the following type is considered:

$$M+iA+jX \rightleftarrows MA_iX_j \qquad (1)$$

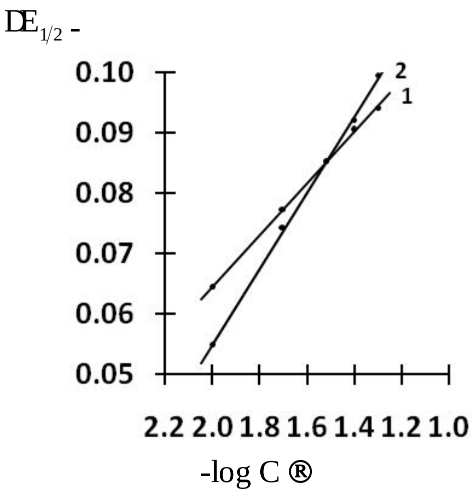
and with the restriction that a single mixed ligand entity MA_iX_j is formed, the shift in the $E_{1/2}$ of the polarographic wave of the metal ion as a function of the concentration of the added reagents A and X is given by

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

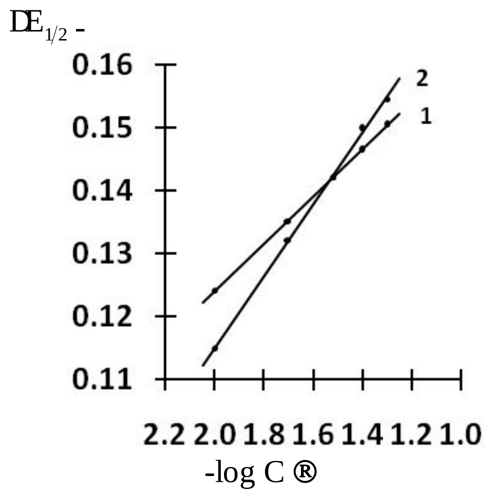
$$- i\frac{2.303RT}{nF}\log C_A - j\frac{2.303RT}{nF}\log C_X \qquad (2)$$

PLOTS OF $DE_{1/2}$ AS A FUNCTION OF - log C IN 20% (V/V) ACETONITRILE FOR COMPLEXES OF Pb (II)- WITH TDSA AND AMINO ACIDS (a) TDSA + GLYCINE (b) TDSA + ASPARAGINE (c) TDSA + L-METHIONINE (d) TDSA + GLUTAMIC ACID SYSTEMS (FIG. - I - 1)

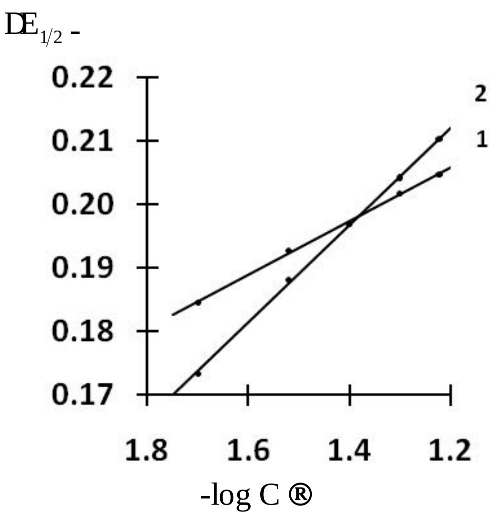
(a)
TDSA + GLY.



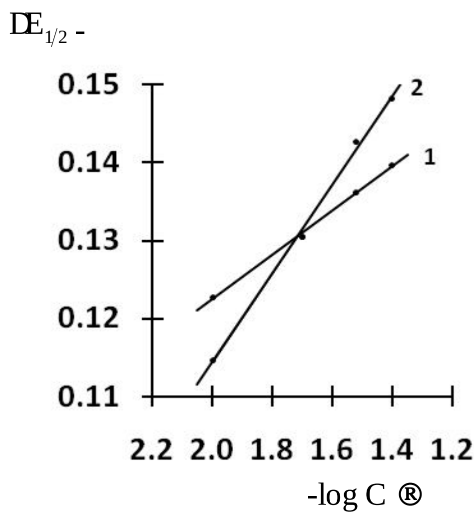
(b)
TDSA + ASP.



(c)
TDSA + METH.



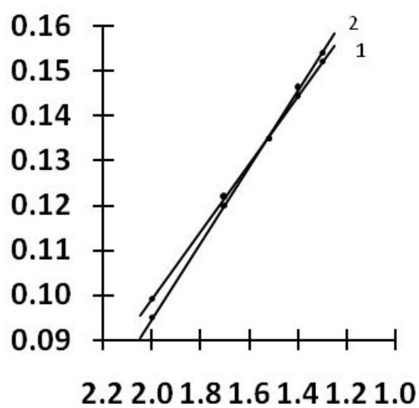
(d)
TDSA + GLU. A.



PLOTS OF $\Delta E_{1/2}$ AS A FUNCTION OF - log C IN 20% (V/V) ACETONITRILE FOR COMPLEXES OF Tl (II) WITH TDSA AND AMINO ACIDS (a) TDSA + GLYCINE (b) TDSA + ASPARAGINE (c) TDSA + L-METHIONINE (d) TDSA + GLUTAMIC ACID SYSTEMS (FIG. - I - 2)

(a)
TDSA + GLY.

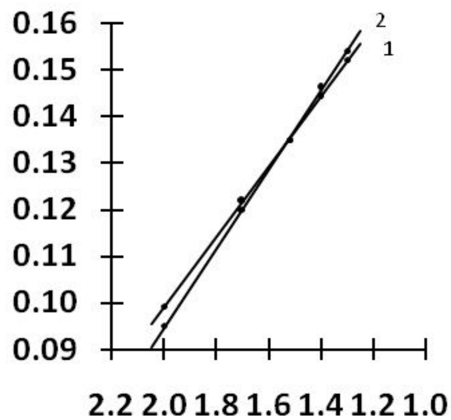
$\Delta E_{1/2}$ -



-log C ®

(b)
TDSA + ASP.

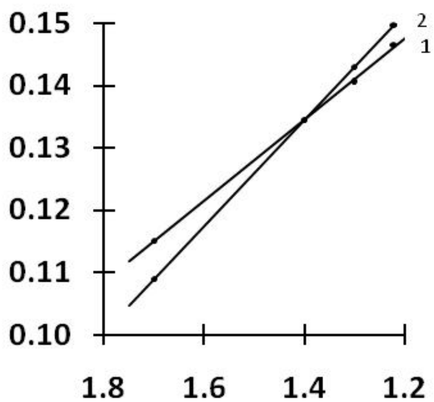
$\Delta E_{1/2}$ -



-log C ®

(c)
TDSA + METH.

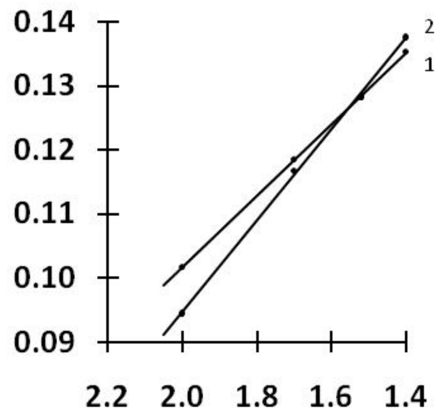
$\Delta E_{1/2}$ -



-log C ®

(d)
TDSA + GLU. A.

$\Delta E_{1/2}$ -



-log C ®

MIXED LIGAND SYSTEM WITH Tl(I) AT 25ºC (3032K),

$\Delta E_{1/2}$ Tl(I) = 0.505 Volts, i_d= 6.0 A in 20% (v/v) Acetonitrile

(Table - 1) / (Fig - 1)

	Conc. Of Mixed Ligand in $\times 10^{-2} M$		TDSA + Glycine System		Conc. Of Mixed Ligand in $\times 10^{-2} M$		TDSA + Asparagine System	
	C_A	C_X	I_S / I_C	$\Delta E_{1/2}$	C_A	C_X	I_S / I_C	$\Delta E_{1/2}$
1	0.01	0.03	1.01	0.094	0.01	0.03	0.90	0.108
2	0.02	0.03	0.98	0.119	0.02	0.03	1.13	0.126
3	0.03	0.03	1.09	0.134	0.03	0.03	0.92	0.136
4	0.04	0.03	1.00	0.146	0.04	0.03	1.05	0.144
5	0.05	0.03	1.13	0.154	0.05	0.03	0.93	0.153
6	0.03	0.01	1.07	0.099	0.03	0.01	0.96	0.102
7	0.03	0.02	1.01	0.121	0.03	0.02	0.95	0.124
8	0.03	0.03	0.96	0.144	0.03	0.03	1.01	0.146
9	0.03	0.04	0.95	0.152	0.03	0.04	0.98	0.154

	Conc. Of Mixed Ligand in $\times 10^{-2} M$		TDSA + Methionine System		Conc. Of Mixed Ligand in $\times 10^{-2} M$		TDSA + Glutamic Acid System	
	C_A	C_X	I_S / I_C	$\Delta E_{1/2}$	C_A	C_X	I_S / I_C	$\Delta E_{1/2}$
1	0.02	0.04	0.92	0.115	0.01	0.03	1.07	0.094
2	0.04	0.04	1.05	0.134	0.02	0.03	1.2	0.116
3	0.05	0.04	1.57	0.14	0.03	0.03	1.33	0.128
4	0.06	0.04	1.81	0.146	0.04	0.03	1.05	0.137
5	0.04	0.02	1.39	0.109	0.03	0.01	1.22	0.101
6	0.04	0.05	1.2	0.143	0.03	0.02	1.17	0.118
7	0.04	0.06	1.09	0.149	0.03	0.04	1.13	0.135

MIXED LIGAND SYSTEM WITH Pb(II) AT 25^{o}C (3032K),

$DE_{1/2}$ Pb(II) = 0.466 Volts, id= 3.7 A in 20% (v/v) Acetonitrile

(Table - 2) / (Fig - 2)

	Conc. Of Mixed Ligand in ´ $10^{-2} M$		TDSA + Glycine System		Conc. Of Mixed Ligand in ´ $10^{-2} M$		TDSA + Asparagine System	
	C_A	C_X	I_S / I_C	$DE_{1/2}$	C_A	C_X	I_S / I_C	$DE_{1/2}$
1	0.01	0.03	3.05	0.064	0.01	0.03	1.04	0.124
2	0.02	0.03	2.84	0.077	0.02	0.03	1.14	0.135
3	0.03	0.03	1.94	0.085	0.03	0.03	1.20	0.142
4	0.04	0.03	1.68	0.09	0.04	0.03	1.37	0.146
5	0.05	0.03	1.86	0.094	0.05	0.03	1.60	0.15
6	0.03	0.01	0.94	0.055	0.03	0.01	0.96	0.115
7	0.03	0.02	1.15	0.074	0.03	0.02	0.79	0.132
8	0.03	0.04	1.85	0.092	0.03	0.04	1.30	0.149
9	0.03	0.05	1.89	0.099	0.03	0.05	1.39	0.154

	Conc. Of Mixed Ligand in ´ $10^{-2} M$		TDSA + Methionine System		Conc. Of Mixed Ligand in ´ $10^{-2} M$		TDSA + Glutamic Acid System	
	C_A	C_X	I_S / I_C	$DE_{1/2}$	C_A	C_X	I_S / I_C	$DE_{1/2}$
1	0.02	0.04	0.49	0.184	0.01	0.02	1.24	0.122
2	0.03	0.04	0.92	0.192	0.02	0.02	1.04	0.13
3	0.04	0.04	1.12	0.196	0.03	0.02	1.58	0.136
4	0.05	0.04	0.69	0.201	0.04	0.02	0.97	0.139
5	0.06	0.04	0.46	0.204	0.02	0.01	1.06	0.114
6	0.04	0.02	1.15	0.173	0.02	0.03	1.02	0.142
7	0.04	0.03	0.69	0.188	0.02	0.04	0.79	0.148
8	0.04	0.05	1.05	0.204				
9	0.04	0.06	0.97	0.21				

Table 3.

	TDSA + Glycine System		TDSA + Asparagine System		TDSA + Methionine System		TDSA + Glutamic Acid System	
	Tl (I)	Pb (II)	Tl (I)	Pb (II)	Tl (I)	Pb (II)	Tl (I)	Pb (II)
Coordination No. 'i' of ligand C_A	1.45	1.45	1.08	1.25	1.11	1.41	1.21	0.96
Coordination No. 'j' of ligand C_X	1.28	2.14	1.30	1.93	1.41	2.61	0.95	1.92
Mean $\log K_{MA_iX_j}$	5.30	7.42	5.36	9.32	5.07	10.86	5.20	9.54

The ratio (D_{free}/D_{comp}) was obtained from the value of limiting current from plots of $DE_{1/2}$ vs - log C_A with C_X 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.

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

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

Plot of (i) $DE_{1/2}$ vs - log C_A (C_X kept constant) (ii) $DE_{1/2}$ vs log C_X (C_A kept constant) yielded Straight lines (fig. I, II) and thus established 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 fig- (I), (II) and the value of (i) & (j) are given in Table (1) & (2).

Substituting "i" and "j", the stability constants log of the ligand complexes are determined using equation (2) and are given in table (1) & (2).

Conclusion

The present investigation clearly reveals the formation of only single mixed ligand species (Pb AX_2) of Pb^{2+} and (T1AX) of $T1^{+1+}$ with TDSA and amino acids in aqueous.

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