



# POLAROGRAPHIC STUDY OF MIXED LIGAND (CARBOXYMETHYLMERCAPTOSUCCINATE-ALANINATE OR ASPARTATE OR GLUTAMINATE OR VALINATE WITH CADMIUM (II) LEAD (II) AND THALLIUM (I) IN AQUEOUS ETHANOL MEDIA.

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## ABSTRACT

Mixed ligand systems (carboxymethylmercaptosuccinate – alaninate, carboxymethyl-mercaptosuccinate-aspartate, carboxymethylmercaptosuccinate-glutamate, carboxymethylmercaptosuccinate-valinate, with Cd(II), Pb(II) and Tl(I) in aqueous-non aqueous (3:2 v/v aqueous ethanol) media at constant ionic strength ( $\text{KNO}_3$ ,  $\mu = 1.0 \text{ M}$ ), pH ( $6.2 \pm 0.02$ ) and temperature ( $303 \pm 2\text{K}$ ) have been studied polarographically. Thymol (0.01%) was used as wave maxima suppressor. It was shown that only one mixed ligand entity ( $\text{M}_{\text{A}_i\text{X}_j}$ ) is formed in all cases of carboxymethylmercaptosuccinate alaninate/ aspartate/ glutamate/ valinate systems where 'i' and j are one for all Cd(II) Pb(II), and Tl(I) metal complexes formed. A and X are carboxymethylmercaptosuccinate and alaninate/ aspartate/ glutamate/ valinate/ respectively. Compositions and stability constants of single mixed ligand species formed have been evaluated employing Souchay and Faucherre's method.

**Key words:** Polarography, mixed complex, stability constant.

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## INTRODUCTION

The successful application of the chelating properties of carboxymethylmercaptosuccinic acid referred to herein as R-S-R' where  $\text{R}=\text{CH}_2\text{COOH}$  and  $\text{R}'=\text{CH-COOH}$  has been demonstrated by Evan and his group.<sup>1</sup> The sulphur in the R-S-R' and the two adjacent carboxyl groups are ideally arranged with the metal ion.<sup>2-4</sup> The use of the polarographic technique for the study of analysis,<sup>5,6</sup> complexation,<sup>7-17</sup> and behavioral<sup>18-20</sup> of study of organic compound is well known.<sup>18-20</sup> In view of its importance in diverse disciplines and interesting results obtained by earlier workers, it was considered worthwhile to investigate polarographic study of mixed ligand (carboxymethylmercaptosuccinate- alaninate or aspartate or glutamate or valinate with cadmium (II) lead (II) and thallium (I) in aqueous ethanol media for which no reference could be traced out in the literature.

## EXPERIMENTAL

The sodium salts of carboxymethylmercaptosuccinate (95%, Evan's Chemetics, Inc. New York), L-alanine, L-aspartic acid, L-glutamine and L-valine (E, Merck India Ltd.) were used as complexing agents. All other reagents used were also of AnalaR grade. Freshly prepared solution of carboxymethylmercaptosuccinate in 50% ethanol was used and other stock solutions were prepared in doubly distilled air free conductivity water. Thymol (0.01%) was used as wave maximum suppressor and potassium nitrate solution ( $\mu = 1.0\text{M}$ ) as the supporting electrolyte. An automatic recording polarograph Systronics (India) model 1632, with a saturated calomel electrode as a reference electrode and platinum electrode as auxillary electrode was used for determining current voltage curves. The capillary characteristics in potassium nitrate solution ( $\mu = 1.0 \text{ M}$ ) at  $E_d = -0.07\text{V}$  with respect to a saturated calomel

electrode (SCE) were calculated  $m^{2/3} t^{1/6} = 2.4913 \text{ mg}^{2/3} \text{ s}^{-1/2}$  ( $h = 45\text{cm}$ ). All measurements were made with the cell immersed in a thermostatic bath. Dissolved air was removed by bubbling purified nitrogen through the cell and necessary corrections for the potential drop and charging current were made as usual.

### RESULTS AND DISCUSSION

The formation of each mixed ligand complex was studied at  $303 \pm 2\text{K}$  and  $6.8 \pm 0.02$  pH by recording polarograms of  $\text{Cd}(\text{NO}_3)_2$  or  $\text{Pb}(\text{NO}_3)_2$  or  $\text{TlNO}_3$  at constant ionic strength  $\text{KNO}_3$  ( $\mu=1.0 \text{ M}$ ) for two different sets of different ligand composition in 3:2 v/v aqueous-ethanol and 0.01 % thymol. Metal ligand compositions of two different sets were.

#### SET-1

1.0 mM  $\text{Cd}(\text{NO}_3)_2$  or  $\text{Pb}(\text{NO}_3)_2$  and a constant alaninate or aspartate or glutamate or valinate concentration ( $C_X$ ) of  $2.0 \times 10^{-2} \text{ M}$  with a carboxymethylmercaptosuccinate concentration ( $C_A$ ) varying between  $0.6 \times 10^{-2}$  to  $4.0 \times 10^{-2} \text{ M}$ . 0.5 mM  $\text{TlNO}_3$  and a constant alaninate or aspartate or glutamate or valinate concentration ( $C_X$ ) of  $2.0 \times 10^{-2} \text{ M}$  with a carboxymethylmercaptosuccinate concentration ( $C_A$ ) varying between  $0.6 \times 10^{-2}$  and  $4.0 \times 10^{-2} \text{ M}$ .

#### SET-2

1.0 mM  $\text{Cd}(\text{NO}_3)_2$  or  $\text{Pb}(\text{NO}_3)_2$  and a constant carboxymethyl-mercaptosuccinate concentration ( $C_A$ ) of  $2.0 \times 10^{-2} \text{ M}$  with alaninate, aspartate, glutamate, valinate concentration ( $C_X$ ) varying between  $0.6 \times 10^{-2} \text{ M}$  to  $4.0 \times 10^{-2} \text{ M}$ . 0.5 mM  $\text{Tl}(\text{NO}_3)_2$  and a constant carboxymethylmercaptosuccinate concentration ( $C_A$ ) of  $2.0 \times 10^{-2} \text{ M}$  with alaninate, glutamate, aspartate, valinate concentration ( $C_X$ ) varying between  $0.6 \times 10^{-2} \text{ M}$  to  $4.0 \times 10^{-2} \text{ M}$ .

The plots of  $\log i/(i_d-i)$  vs  $E_{d,e}$  for all polarograms yielded straight lines with slopes that agreed with the theoretical value corresponding to  $n=2$  for  $\text{Cd}(\text{II})$  and  $\text{Pb}(\text{II})$  and  $n=1$  for  $\text{Tl}(\text{I})$  systems respectively. The values of the slopes for different systems are given in the Table B-IV showing the reversibility of the reduction.

Rectilinear plots of  $id$  vs  $h_{\text{eff}}^{1/2}$  showing constancy of  $id/\sqrt{h_{\text{eff}}}$ . The  $E_{1/2}$  values evaluated from the log plots of each of the above mentioned current voltage curves and corresponding diffusion current values have been recorded (Table B-1, 2, 3). All the measurements were carried out in well buffered solutions of pH 6.8, which remains almost stable ( $6.8 \pm 0.02$ ) within all concentration ranges of complexing agents used. All the buffer solutions used, were prepared by Clark and Lubs method<sup>22</sup>. All the  $E_{1/2}$  values of the metal ion in presence of mixed ligands or single ligand are more negative than that of the free metal ion. Since the ion must be first liberated from the complex, this requires certain amount of energy. From the shift in the half wave potential of the complexed metal ion and the concentration of the complex forming agents, both the stability constant and its composition can be calculated.

Souchay and Faucherre<sup>23</sup> derived an equation where a metal ion complexes with two ligand species simultaneously in solution. If the complexing reaction of the following type is considered:



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

$$\Delta E'_{1/2} = \frac{2.303RT}{nF} \log \left[ \frac{D_{\text{free}}}{D_{\text{comp}}} \right]^{1/2} - \frac{2.303RT}{nF} \log K_{MA_iX_j} - i \frac{2.303RT}{nF} \log C_A - j \frac{2.303RT}{nF} \log C_X \quad (2)$$

The ratio  $D_{\text{free}}/D_{\text{comp}}$  may be obtained from the values of the 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 of  $i$  and  $j$  can be obtained by intersect method because on differentiation.

For each of the mixed ligand systems carboxymethylmercaptosuccinate-alaninate/aspartate/glutamate/valinate, 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) yielded straight lines [Fig. 1,2] and thus establish the formation of a single mixed ligand entity.

The values of coordination numbers 'i' and 'j' of A and X were determined from the graph shown-

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

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

in (Fig. 1,2) for each system and are given in (Table-4), where A and X are the carboxymethylmercaptosuccinate and alaninate/ aspartate/ glutamate/ valinate respectively. Integral values of 'i' and 'j' are used in the calculation of stability constants using equation (2) as described in method and are consolidated in Table 4.

### CONCLUSION

The present investigations suggest the formation of only one kind of mixed ligand species ( $MA_iX_j$ ) for each mixed ligand system. The type of mixed ligand species formed are  $[MAX]^{-3}$  with Cd(II) and Pb(II), and  $[MAX]^{-4}$  with Tl(I) metal in carboxymethylmercaptosuccinate - valinate and carboxymethylmercaptosuccinate -alaninate mixed ligand systems  $[MAX]^{-4}$  with Cd(II) and Pb(II)  $[MAX]^{-5}$  with Tl(I) metal in carboxymethylmercaptosuccinate-glutamate and carboxymethylmercaptosuccinate-aspartate mixed ligand systems.

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Table-1: Mixed ligand system with Cadmium (II) [All replicate measurements were made] at (303±2K).  $E_{1/2}$  ( $Cd^{+2}$  metal ion) = 0.591 volts,  $i_d$  ( $Cd^{+2}$  metal ion) = 4.30  $\mu_A$

Concentration of mixed ligands x 10 <sup>-2</sup> M		C.M.M.S. Valinate System		C.M.M.S. Alaninate System		C.M.M.S. Glutamate System		C.M.M.S. Aspartate System	
$C_A$	$C_X$	Log Im/Ic	$\Delta$	Log Im/Ic	$\Delta$	Log Im/Ic	$\Delta$	Log Im/Ic	$\Delta$
		$E_{1/2}$ (V)		$E_{1/2}$ (V)		$E_{1/2}$ (V)		$E_{1/2}$ (V)	
0.6	2.0	1.043	0.050	1.037	0.045	1.075	0.037	1.094	0.029
1.0	2.0	1.061	0.056	1.085	0.051	1.085	0.043	1.102	0.035
2.0	2.0	1.096	0.065	1.096	0.065	1.105	0.052	1.146	0.044
3.0	2.0	1.108	0.070	1.227	0.062	1.113	0.057	1.152	0.048
4.0	2.0	1.128	0.074	1.396	0.065	1.149	0.060	1.165	0.052
2.0	0.6	1.038	0.044	1.072	0.040	1.036	0.033	1.038	0.024
2.0	1.0	1.070	0.052	1.081	0.047	1.038	0.040	1.075	0.032
2.0	3.0	1.105	0.072	1.105	0.067	1.075	0.060	1.128	0.051
2.0	4.0	1.106	0.077	1.128	0.072	1.128	0.063	1.214	0.055

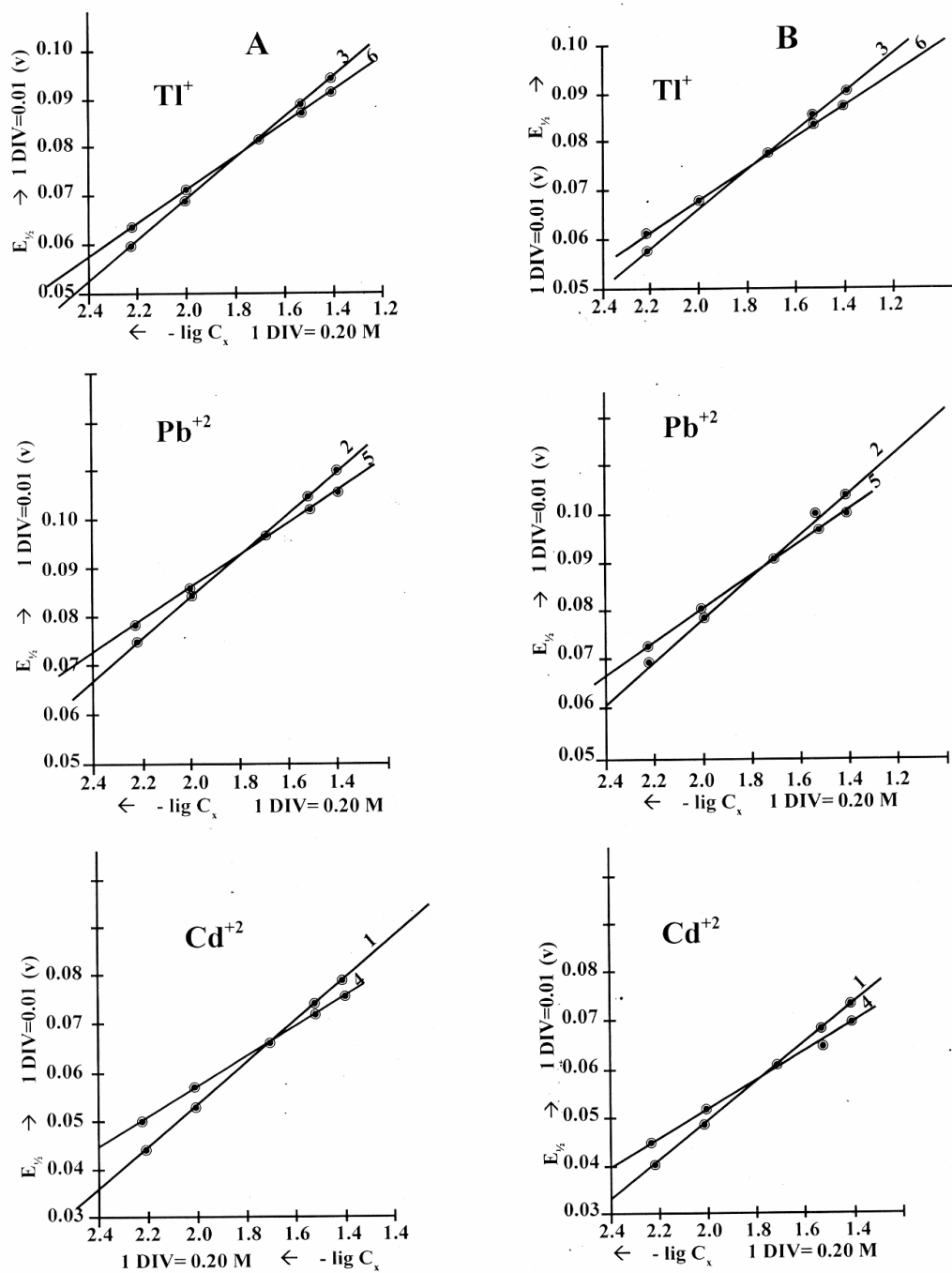


Fig.-1: Plots of  $\Delta E_{1/2}$  as a function of  $-\log C$  for CMMS + Valinate (A-curve 1-6) and CMMS + alaninate (B- curve 1-6) mixed ligand system.

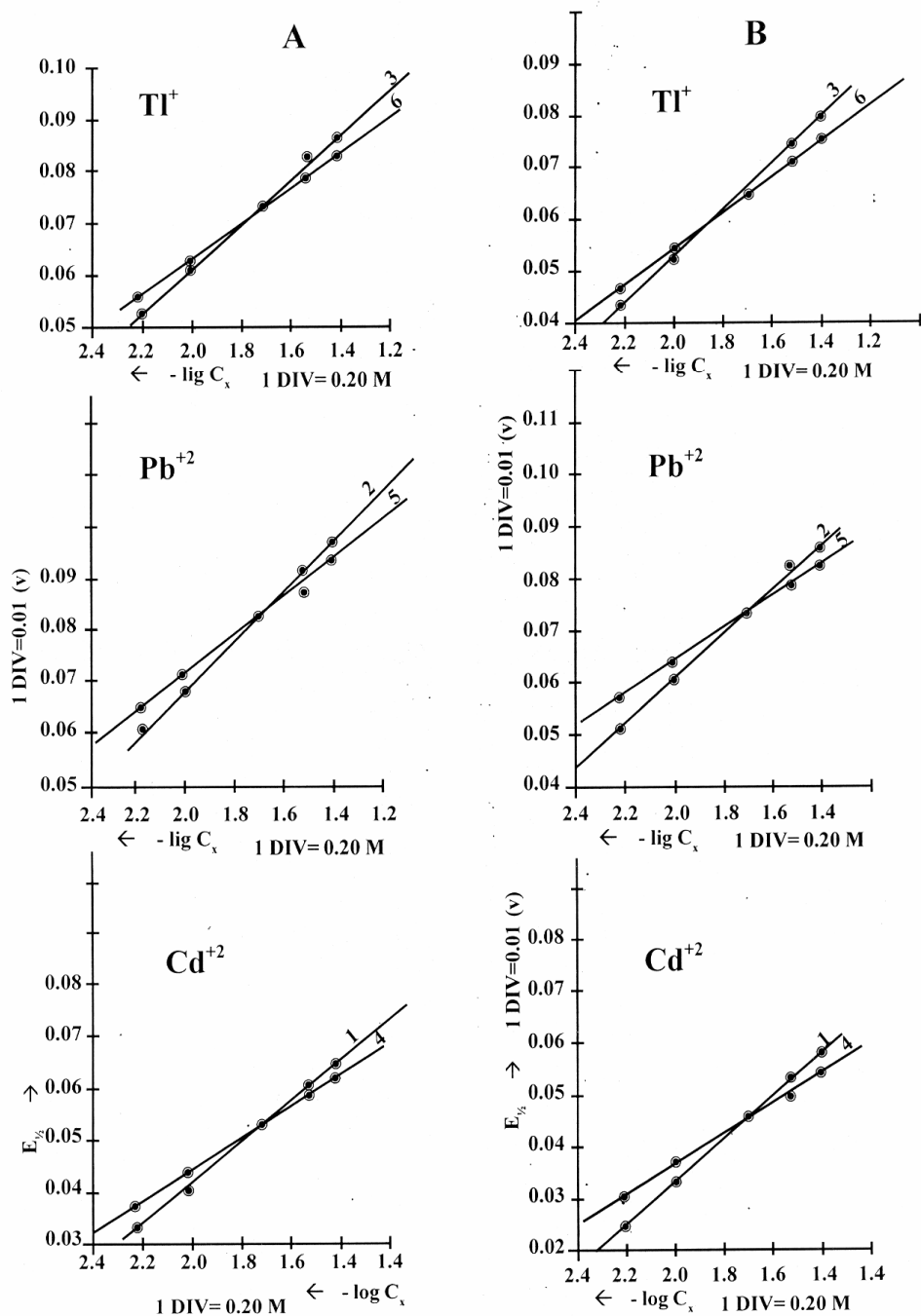


Fig.-2: Plots of  $\Delta E_{1/2}$  as a function of  $-\log C$  for CMMS + glutamate (A-curve 1-6) and CMMS + aspartate (B-curve 1-6) mixed ligand system.

Table-2: Mixed ligand system with Lead Pb (II) [All replicate measurements were made] at (303±2K).  $E_{1/2}$  (Pb<sup>+2</sup> metal ion) = 0.409 volts,  $i_d$  (Pb<sup>+2</sup> metal ion) = 3.60  $\mu_A$

Concentration of mixed ligands x 10 <sup>-2</sup> M		C.M.M.S. Valinate System		C.M.M.S. Alaninate System		C.M.M.S. Glutamate System		C.M.M.S. Aspartate System	
C <sub>A</sub>	C <sub>X</sub>	Log Im/Ic	$\Delta$	Log Im/Ic	$\Delta$	Log Im/Ic	$\Delta$	Log Im/Ic	$\Delta$
		$E_{1/2}$ (V)		$E_{1/2}$ (V)		$E_{1/2}$ (V)		$E_{1/2}$ (V)	
0.6	2.0	0.018	0.078	0.022	0.072	0.031	0.065	0.036	0.056
1.0	2.0	0.022	0.085	0.036	0.079	0.051	0.071	0.057	0.063
2.0	2.0	0.036	0.095	0.046	0.089	0.062	0.081	0.078	0.072
3.0	2.0	0.067	0.100	0.062	0.095	0.073	0.085	0.090	0.077
4.0	2.0	0.075	0.103	0.067	0.097	0.084	0.091	0.096	0.081
2.0	0.6	0.057	0.074	0.046	0.068	0.058	0.060	0.062	0.051
2.0	1.0	0.062	0.083	0.051	0.077	0.066	0.067	0.067	0.059
2.0	3.0	0.084	0.102	0.090	0.097	0.101	0.088	0.120	0.077
2.0	4.0	0.101	0.106	0.125	0.100	0.148	0.092	0.207	0.080

Table-3: Mixed ligand system with Thallium TI (I) [All replicate measurements were made] at (303±2K).  $E_{1/2}$  (TI<sup>+2</sup> metal ion) = 0.457 volts,  $i_d$  (TI<sup>+2</sup> metal ion) = 3.14  $\mu_A$

Concentration of mixed ligands x 10 <sup>-2</sup> M		C.M.M.S. Valinate System		C.M.M.S. Alaninate System		C.M.M.S. Glutamate System		C.M.M.S. Aspartate System	
C <sub>A</sub>	C <sub>X</sub>	Log Im/Ic	$\Delta$	Log Im/Ic	$\Delta$	Log Im/Ic	$\Delta$	Log Im/Ic	$\Delta$
		$E_{1/2}$ (V)		$E_{1/2}$ (V)		$E_{1/2}$ (V)		$E_{1/2}$ (V)	
0.6	2.0	0.980	0.064	1.019	0.061	1.095	0.056	1.045	0.041
1.0	2.0	1.075	0.071	1.045	0.068	1.132	0.063	1.060	0.054
2.0	2.0	1.102	0.080	1.073	0.077	1.182	0.072	1.090	0.064
3.0	2.0	1.117	0.086	1.090	0.082	1.193	0.078	1.133	0.070
4.0	2.0	1.150	0.090	1.105	0.086	1.219	0.081	1.150	0.074
2.0	0.6	1.009	0.060	1.009	0.058	1.060	0.052	1.019	0.044
2.0	1.0	1.029	0.068	1.032	0.066	1.165	0.061	1.073	0.052
2.0	3.0	1.060	0.088	0.117	0.084	1.167	0.082	1.117	0.073
2.0	4.0	1.117	0.093	0.133	0.089	1.203	0.084	1.150	0.078

Table-4

S.No.	Carboxymethyl Mercapto Succinate Valinate System with;			Carboxymethyl Mercapto Succinate Alaninate System with;			Carboxymethyl Mercapto Succinate Glutamate System with;			Carboxymethyl Mercapto Succinate Aspartate System with;		
	Cd(II)	Pb(II)	Tl(I)	Cd(II)	Pb(II)	Tl(I)	Cd(II)	Pb(II)	Tl(I)	Cd(II)	Pb(II)	Tl(I)
1. Co-ordination number "i" of ligand A	1.006	1.02	1.109	1.031	1.08	1.06	0.981	1.11	1.08	0.978	1.10	1.19
2. Co-ordination number "j" of ligand X	1.39	1.31	1.396	1.355	1.40	1.31	1.27	1.42	1.38	1.35	1.37	1.43

3. Mean log $KM_{i,j}^{A,X}$	9.091	10.058	9.610	8.917	9.920	9.500	8.655	9.655	9.363	8.390	9.367	9.078
4. Standard deviation	±0.492	±0.520	±0.470	±0.504	±0.468	±0.477	±0.492	±0.476	±0.473	±0.501	±0.4770	±0.459
5. Slopes of log plots	0.031	0.032	0.062	0.031	0.032	0.061	0.032	0.031	0.061	0.031	0.031	0.062

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