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COMPLEXATION BEHAVIOUR OF Cd (II), Pb (II) AND Tl (I) WITH n-BUTYL-3-MERCAPTOPROPIONATE IN PRESENCE OF FEW AMINO-ACIDS IN AQUEOUS – NON AQUEOUS MEDIA

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ABSTRACT

Complexation behaviour of Cd (II), Pb (II) and Tl (I) with n-butyl-3-mercaptopropionate in presence of few amino acids in aqueous and non-aqueous media have been studied polarographically at constant ionic strength, pH and temperature in order to ascertain their utility in different biological and pharmaceutical field. Complexation behaviour and stability constant of the species formed have also been evaluated. Effect of nature of solvent, nature of supporting electrolyte, temperature, nature of maximum suppressor, surfactant concentration were also studied for different complex species with each metal in keeping other experimental conditions similar.

Key words: Complexation, Stability constant, Polarography, Ionic strength, Surfactant concentration.

INTRODUCTION

Within few decades the complexes have been fully appreciated as a prominent chemical principle and extensive physicochemical studies have led to an understanding of their behavior[1-12]. Mercaptopropionic acids, mercaptopropionates and their derivatives are versatile compounds which are used as chain transfer and cross linking agents in polymerisations and as reactive intermediates in the production of PVC stabilisers. These compounds may also be useful as acidic ion exchange catalyst, coupling agents in UV curable formulations.

Complexes and complexing agents have long been utilized for the removal of heavy metals from biological systems. Therefore as a part of our investigations the complexation

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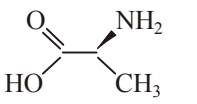
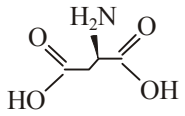
behaviour of Cd (II), Pb (II) and Tl (I) with n-butyl-3-mercaptopropionate in presence of different amino acids in aqueous ethanol media has been studied polarographically.

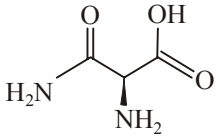
Amino acids which are selected for the present studies are as under;



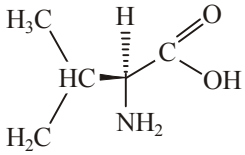
(i) L-Alanine



(ii) L-Aspartic acid



(iii) L-Glutamine



(iii) L-Valine

and the structure of n-butyl-3-mercaptopropionate is as under;

$$HS–CH_2–CH_2–COO(C_4H_9)$$

EXPERIMENTAL

To find out complexation behaviour of Cd (II), Pb (II) and Tl (I) the sodium salts of n-butyl-3-mercaptopropionate (95%, Evan Chemetics, Inc. New York), L-alanine, L-aspartic acid, L-glutamine and L-valine (E-Merck India Ltd.) were used. All other reagents used were also of Analar grade. Freshly prepared solution of n-butyl-3-mercaptopropionate in 50% ethanol was used and other stock solutions were prepared in doubly distilled air free conductivity water. Triton X-100 was used as wave maximum suppressor and potassium nitrate solution (μ = 1.0 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 an auxillary electrode was used for determining current voltage curves. The capillary characteristics in potassium nitrate solution (μ = 1.0 M) at Ed.e = - 0.7V with respect to a saturated calomel electrode (SCE) were calculated as m 2/3 t1/6 = 2.5352 $mg^{2/3}$ $s^{-1/2}$ (h = 45 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[13].

The formation of each complex species was studied at 303 ± 2K and 6.8 ± 0.02 pH by recording polarograms of 1.0 mM Cd $(NO_3)_2$ or 1.0 mM Pb $(NO_3)_2$ or 0.5 mM Tl NO_3 at

constant ionic strength KNO_3 (μ = 1.0 M) for two different sets of different ligand composition (Table 1-4) in 3 : 1 v/v aqueous ethanol and 0.001% Triton X-100.

Table 1: Observation regarding complexatin behaviour of Cadmium (II)

[All replicate measurement were made] at (303 ± 2K)

$E_{½}$ (Cd^{+2} metal ion) = 0.588 volts, i_d (Cd^{+2} metal ion) = 5.87 μ_A

Concentration of n. B. M. P. & A.A. x 10^{-2}M		**n. B. M. P. Valinate system**		**n. B. M. P. Alaninate system**		**n. B. M. P. Glutaminate system**		**n. B. M. P. Aspartate system**	
C_A	**C_X**	**Log I_m/I_c**	**Δ $E_{½}$ (V)**	**Log I_m/I_c**	**Δ $E_{½}$ (V)**	**Log I_m/I_c**	**Δ $E_{½}$ (V)**	**Log I_m/I_c**	**Δ $E_{½}$ (V)**
1.0	4.0	1.02	0.320	1.43	0.299	1.58	0.282	1.82	0.272
2.0	4.0	1.06	0.347	1.82	0.325	2.00	0.309	2.39	2.97
4.0	4.0	1.18	0.373	1.98	0.351	2.23	0.335	2.63	0.327
6.0	4.0	1.40	0.397	2.94	0.364	3.47	0.350	4.62	0.337
8.0	4.0	1.60	0.397	3.48	0.373	4.24	0.360	5.34	0.347
4.0	1.0	1.12	0.353	1.58	0.336	1.93	0.316	1.87	0.308
4.0	2.0	1.17	0.363	1.89	0.344	2.09	0.326	2.38	0.316
4.0	6.0	1.25	0.379	2.21	0.356	2.31	0.331	2.56	0.334
4.0	8.0	1.30	0.382	2.39	0.359	2.42	0.346	2.73	0.338

Table 2: Observation regarding complexatin behaviour of Lead (II)

[All replicate measurement were made] at (303 ± 2K)

$E_{½}$ (Pb^{+2} metal ion) = 0.407 volts, i_d (Pb^{+2} metal ion) = 5.69 μ_A

Concentration of n. B. M. P. & A.A. x 10^{-2}M		**n. B. M. P. Valinate system**		**n. B. M. P. Alaninate system**		**n. B. M. P. Glutaminate system**		**n. B. M. P. Aspartate system**	
C_A	**C_X**	**Log I_m/I_c**	**Δ $E_{½}$ (V)**	**Log I_m/I_c**	**Δ $E_{½}$ (V)**	**Log I_m/I_c**	**Δ $E_{½}$ (V)**	**Log I_m/I_c**	**Δ $E_{½}$ (V)**
1.0	4.0	1.02	0.320	1.05	0.308	1.09	0.300	1.13	0.280

Cont…

Concentration of n. B. M. P. & A.A. x 10^{-2}M		n. B. M. P. Valinate system		n. B. M. P. Alaninate system		n. B. M. P. Glutaminate system		n. B. M. P. Aspartate system	
C_A	C_X	Log I_m/I_c	$\Delta E_{½}$ (V)	Log I_m/I_c	$\Delta E_{½}$ (V)	Log I_m/I_c	$\Delta E_{½}$ (V)	Log I_m/I_c	$\Delta E_{½}$ (V)
2.0	4.0	1.06	0.347	1.09	0.340	1.14	0.328	1.82	0.309
4.0	4.0	1.18	0.373	1.14	0.366	1.21	0.357	1.32	0.336
6.0	4.0	1.40	0.397	1.37	0.380	1.42	0.373	1.45	0.353
8.0	4.0	1.60	0.397	1.48	0.391	1.58	0.385	1.49	0.363
4.0	1.0	1.12	0.353	1.11	0.345	1.11	0.334	1.10	0.317
4.0	2.0	1.17	0.363	1.19	0.355	1.17	0.345	1.20	0.318
4.0	6.0	1.25	0.379	1.26	0.372	1.23	0.365	1.46	0.341
4.0	8.0	1.30	0.382	1.36	0.376	1.38	0.367	1.50	0.343

Table 3: Observation regarding complexatin behaviour of Thalliuam Tl (I)

[All replicate measurement were made] at (303 ± 2K)

$E_{½}$ (Tl^+ metal ion) = 0.482 volts, i_d (Tl^+ metal ion) = 4.98 μ_A

Concentration of n. B. M. P. & A.A. x 10^{-2}M		n. B. M. P. Valinate system		n. B. M. P. Alaninate system		n. B. M. P. Glutaminate system		n. B. M. P. Aspartate system	
C_A	C_X	Log I_m/I_c	$\Delta E_{½}$ (V)	Log I_m/I_c	$\Delta E_{½}$ (V)	Log I_m/I_c	$\Delta E_{½}$ (V)	Log I_m/I_c	$\Delta E_{½}$ (V)
1.0	4.0	1.15	0.198	1.21	0.179	1.22	0.171	1.23	0.157
2.0	4.0	1.20	0.219	1.24	0.202	1.26	1.191	1.28	0.178
4.0	4.0	1.40	0.241	1.54	0.221	1.56	0.210	1.61	0.199
6.0	4.0	1.59	0.253	1.96	0.233	1.77	0.221	1.82	0.211
8.0	4.0	1.77	0.262	2.23	0.241	1.93	0.229	1.99	0.219
4.0	1.0	1.27	0.204	1.38	0.187	1.39	0.175	1.42	0.166
4.0	2.0	1.39	0.222	1.52	0.204	1.54	0.193	1.58	0.182
4.0	6.0	1.50	0.250	1.65	0.231	1.63	0.220	1.68	0.209
4.0	8.0	1.68	0.251	1.84	0.237	1.82	0.226	1.88	0.215

Table 4

S. No.	n-Butyl-3-mercaptopropionate valinate system with;			n-Butyl-3-mercaptopropionate valinate system with;			n-Butyl-3-mercaptopropionate valinate system with;			n-Butyl-3-mercaptopropionate valinate 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. No. of (Cal.) n.B.M.P. in co-ordination (Int.) sphere "i"	3.11 3.0	3.14 3.0	1.16 1.0	3.14 3.0	3.03 3.0	1.86 1.0	3.33 3.0	3.22 3.0	1.30 1.0	3.03 3.0	3.26 3.0	1.234 1.0
2. No. of (Cal.) A.A. in co-ordination (Int.) sphere "j"	1.19 1.0	1.12 1.0	0.871 1.0	1.086 1.0	1.19 1.0	0.992 1.0	1.27 1.0	1.04 1.0	1.04 1.0	1.04 1.0	1.04 1.0	1.01 1.0
3. Mean log KMA_iX_j	17.947	18.301	13.876	17.746	18.064	13.270	17.511	17.756	12.891	17.023	17.046	12.522
4. Standard deviation	± 0.287	± 0.050	± 0.310	± 0.130	± 0.064	± 0.287	± 0.719	± 0.131	± 0.315	± 0.115	± 0.134	± 0.279
5. Slopes of log plots	0.030	0.031	0.060	0.031	0.029	0.059	0.032	0.031	0.059	0.031	0.032	0.059

Cal. – Calculate; Int. - Integrated

RESULTS AND DISCUSSION

The observations and results are summarized in (Tables 1-4). The values I_m/I_c and $\Delta E_{½}$ for each metal in different complexation environment are given in (Table 1-4). The plots of log $i/(i_d-i)$ vs E_{de} for all polarograms yielded straight lines with slopes that agreed with the theoretical value corresponding to n = 2 for Cd (II) and Pb (II) and n = 1 for Tl (I) system respectively. The values of the slopes for different system are given in (Table 4) showing the reversibility of the reduction. Rectilinear plots of i_d vs $h^{½}_{eff}$ showing constancy of $i_d/\sqrt{}$heff. The $E_{½}$ values evaluated from the log plots of each of the above mentioned current voltage curves and corresponding diffusion current values have been recorded (Tables 1-3). All the measurements were carried out in well buffered solutions of pH 6.8, which remains almost stable (6.8 ± 0.02) within all concentration ranges of complexing agents used in the present studies. All the buffer solutions used were prepared by Clark and Lub's method[14]. All the $E_{½}$ 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[15] 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 :

$$M + iA + j\,X \rightarrow MAiXj \qquad \ldots(1)$$

With the restriction that a single mixed-ligand entity MA_iX_j is formed, then the shift in the $E_{½}$ of the polarographic wave of the metal ion as a function of the concentration of added reagents A(n-butyl-3-mercaptopropionate) and X(Amino acids) is given by –

$$\Delta E'_{1/2} = \frac{2.303RT}{nF} \log \left[\frac{D_{free}}{D_{comp}}\right]^{½} - \frac{2.303RT}{nF} \log KMA_iX_j -$$

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

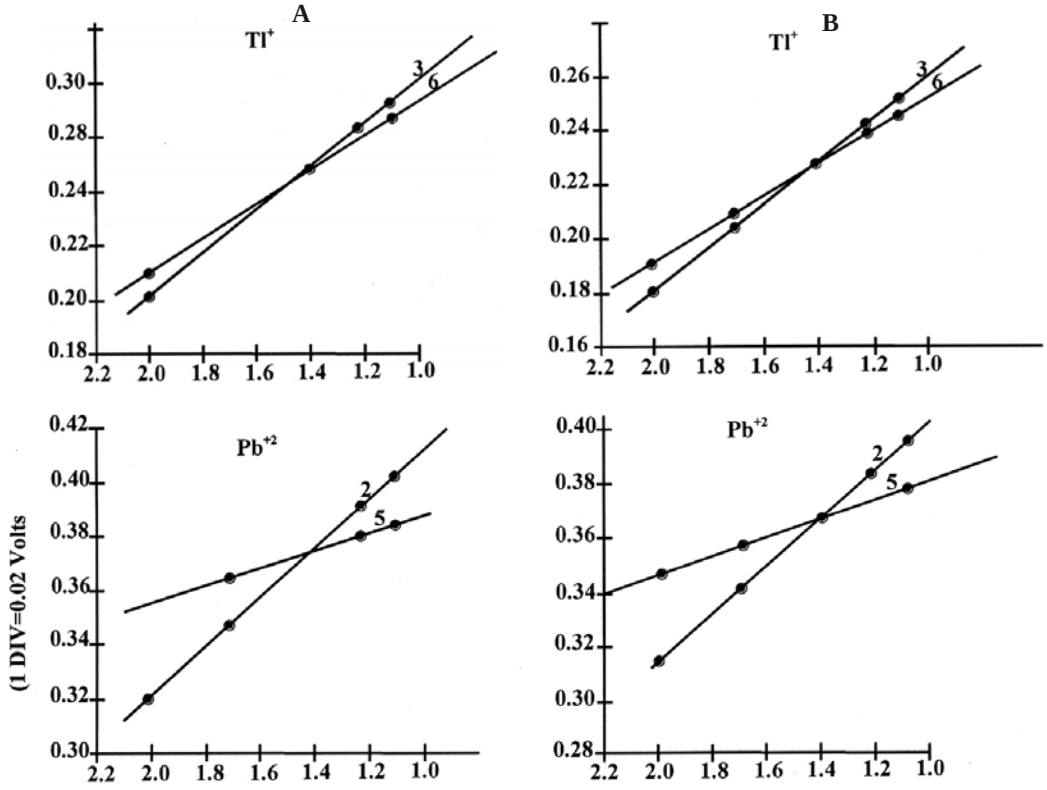
The ratio D_{free}/D_{comp} may be obtained from the values of the limiting current. From plots of $\Delta E½$ vs – log C_A with C_X kept constant and $\Delta E½$ vs – log C_X with C_A kept constant values of "i" and "j" can be obtained by intersect method because on differentiation ;

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

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

For each of the mixed ligand systems n-butyl-3-mercaptopropionate alaninate/ aspartate/glutaminate/valinate, plots of Δ E½ vs log CA (with Cx kept constant) and Δ E½ 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 number's 'i' and 'j' of A and X were determined from the graph shown in (Figs. 1, 2) for each system and are given in (Table 4), where A and X are the n-butyl-3-mercaptopropionate and alaninate/aspartate/glutaminate/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.



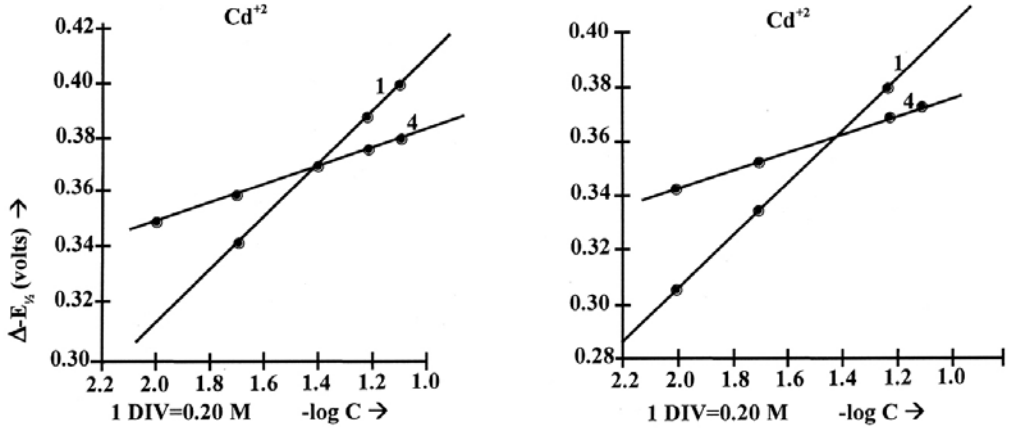
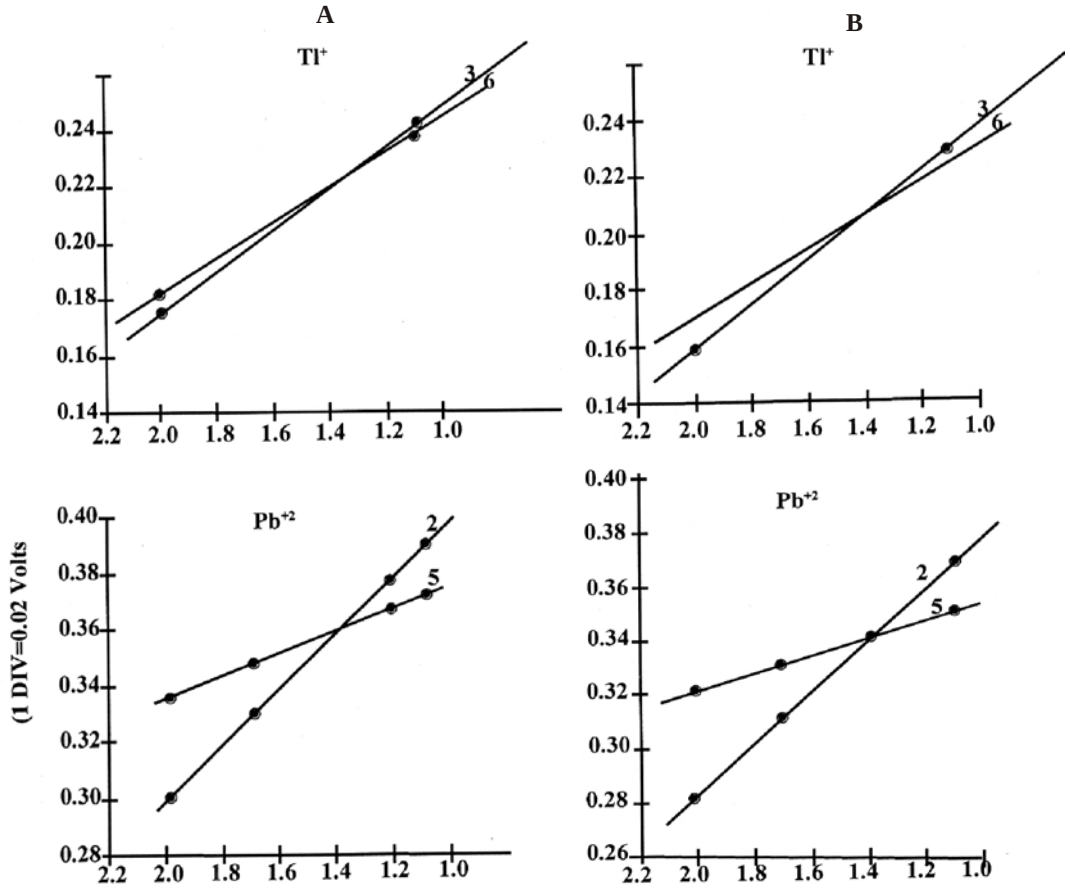


Fig. 1: Plots of ΔE½ as a function of -log C for n.B.M.P. + Valinate (A- curve 1-6) and n.B.M.P.+ alaninate (B-curve 1-6) mixed ligand system



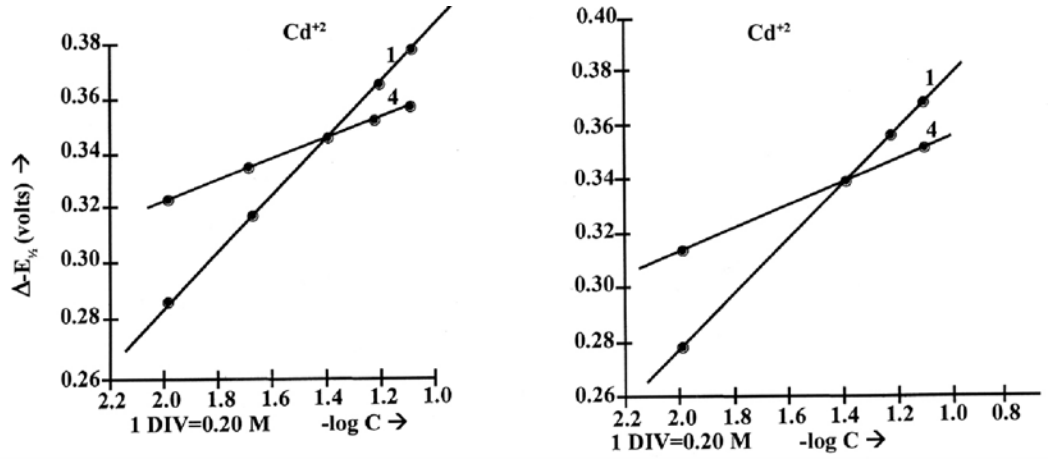


Fig. 2: Plots of ΔE½ as a function of -log C for n.B.M.P. + glutaminate (A- curve 1-6) and n.B.M.P.+ Aspartate (B-curve 1-6) mixed ligand system

Result obtained for different solvent [3 : 1 v/v aqueous ethanol, aqueous acetone, aqueous methanol aqueous acetonitrile, aqueous 1, 4-dioxane and aqueous DMSO shows that the ease of formation of complex species depends on the overall physical properties of the solution. Best slope values are in agreement with theoretical value for one or two electron reduction are obtained with 3 : 1 v/v aqueous ethanol. Markable change in limiting current and half wave potential value was observed with the change in nature of supporting electrolyte. However the best complexation was obtained with 1.0 M KNO_3 and better with 1.0 M $LiNO_3$. Triton X-100 at the concentration of 0.001% was observed as most suitable maximum suppressor over the 0.01% Gelatin and 0.01% Thymol. Better complexatin was observed at 303 K than 298 K for all the complex species studied.

CONCLUSION

The present investigations suggest the formation of only one kind of complex species (MA_iX_j) for each metal ligand system. The type of complex species observed to form are $[MA_3X]^{-6}$ with Cd (II), Pb (II) and $[MAX]^{-3}$ with Tl (I) metal in n-butyl-3-mercaptopropionate-valinate and n-butyl-3-mercaptopropionate alaninate ligand environment.

$[MA_3X]^{-7}$ with Cd (II) and Pb (II) $[MAX]^{-4}$ with Tl(I) metal in n-butyl-3-mercapto-propionate glutaminate and n-butyl-3-mercaptopropionate-aspartate ligand environment.

It is observed from the value of $E_{½}$ with the change of secondary ligand amino acids that the electron donating substituent in ligands shifts $E_{½}$ towards more negative values. It

indicates as electron donating tendency increases the rate of reduction decreases. The order of shifts of $E_{½}$ towards more negative side with four different amino acids in present case is Aspartate < Glutaminate < Alaninate < Valinate which is also the order of log values of stability constants.

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