Asian Journal of Chemistry Vol. 10, No. 4 (1998), 723–729

Polarographic Study of Mixed Ligand Complexes in Aqueous Medium: Lead(II)-Thiourea-Glutamate System

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The mixed ligand complexes of thiourea (tu) and glutamate (glu) ions with Pb(II) have been studied polarographically in aqueous medium at 25 ± 0.5°C and $\mu = 1.0$ M ($NaClO_4$). Four mixed ligand complexes, *viz.*, $[Pb(tu)(glu)]^+$, $[Pb(tu)_2(glu)]^+$, $[Pb(tu)(glu)_2]$ and $[Pb(tu)_2(glu)_2]$ with their respective stability constants $\log \beta_{11} = 4.79$, $\log \beta_{21} = 5.78$, $\log \beta_{12} = 8.76$ and $\log \beta_{22} = 9.01$ respectively were detected. The values of mixed ligand complexes are compared with the stability constants of the simple mono- and bis-complexes of the binary systems. The statistical factors in the complexation constants were evaluated by following the procedure suggested by Walters. The simultaneous π-bonding between the metal ion and ligand was inferred from the deviation observed in the relationship of $\log K_N$ and $(N - 1)$ where N represents the coordination number as suggested by Van Panthaleion Van Eck.

INTRODUCTION

Complexes of thiourea and glutamic acid with some metal ions have been studied by various workers[1–4]. Complexes of Cd(II) with organic and inorganic ligands have been reported by polarographic technique from our laboratory[5–7]. Mixed ligand complexes of Cd(II) and Pb(II) with thiourea and glycine/β-alanine at the isoionic point of the amino acids has already been reported[8, 9]. Cd(II) complexes with thiourea and glutamate have also been investigated in a previous report[10]. The study is further extended to determine the composition and stability constants of simple and mixed ligand complexes of Pb(II) with thiourea and glutamate in aqueous medium by polarographic method at 25 ± 0.5°C.

Schaap and McMasters[11] applied an extension of DeFord and Hume method[12] for the calculation of consecutive stability constants to the more general system, where more than one kind of ligand was added to the central metal ion to form polynuclear species.

According to Schaap and McMasters[11] mixed complexes should be preferred over simple complexes whenever the concentrations of the ligands involved are such that the products of the formation constants for the simple complexes and the concentrations of the ligand, raised to the appropriate power, are approximately equal, *i.e.*,

$$K_{MX_i}[X]^i = K_{MY_j}[Y]^j = K_{MZ_k}[Z]^k$$

A complexation reaction of two ligands X and Y with a central metal ion M can be written as

$$M + iX + jY \rightleftharpoons MX_iY_j$$

where i and j are the stoichiometry numbers. The DeFord and Hume[12] expression for $F_0(X)$ may be extended to give a new function $F_{00}(X, Y)$.

$$F_{00}(X, Y) = \text{antilog } 0.4343 \frac{nF}{RT} \cdot \Delta E_{1/2} + \log \frac{Im}{Ic}$$

where the symbols have their usual meanings[10]. From Leden's function[13]

$$\begin{aligned} F_{00}(X, Y) = & \{\beta_{00} + \beta_{01}[Y] + \beta_{02}[Y]^2 + \beta_{03}[Y]^3\}[X]^0 \\ & + \{\beta_{10} + \beta_{11}[Y] + \beta_{12}[Y]^2\}[X] \\ & + \{\beta_{20} + \beta_{21}[Y] + \beta_{22}[Y]^2\}[X]^2 \\ & + \{\beta_{30} + \beta_{31}[Y]\}[X]^3 \\ & + \{\beta_{40}\}[X]^4 \end{aligned}$$

The function $F_{00}(X, Y) = A + B[X] + C[X]^2 + D[X]^3 + E[X]^4$ where A, B, C, D and E are the constants. The values of all the constants in the above equation can be calculated, if half-wave potentials and diffusion currents of the two series of solutions are measured. The value of A was obtained from the intercept of the plot of $F_{00}(X, Y)$ *vs.* [X]. There was a good agreement between the observed and calculated values of A.

In this method, other functions have been calculated from the following equations:

$$F_{10}(X, Y) = \frac{F_{00}(X, Y) - A}{[X]} = B + C[X] + D[X]^2$$

and

$$F_{20}(X, Y) = \frac{F_{10}(X, Y) - B}{[X]} = C + D[X] + E[X]^2$$

so that the intercept of the plot of $F_{10}(X, Y)$ *vs.* [X] extrapolated to [X] = 0 gives the respective value of B. This procedure is repeated in a similar manner to get C, D and E. From these values stability constants of mixed ligand complexes were evaluated.

EXPERIMENTAL

All the chemicals used were of BDH AnalaR grade and used as such. Sodium perchlorate (E. Merck) was used as a supporting electrolyte to maintain constant ionic strength at 1.0 M. No maximum suppressor was found necessary. All the experimental solutions were prepared in glass distilled water.

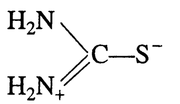
Polarograms were recorded at 25 ± 0.5°C with a Cambridge automatic recording polarograph with a saturated calomel electrode (SCE). The pH measurements were made with the help of a digital pH meter model L-120 (Elico Hyderabad).

The cell resistance was found to be low in all the cases, so no correction by IR drop through the cell was necessary. Deoxygenation of the solutions to be polarographed was achieved by passing purified nitrogen gas. Half-wave potentials were obtained from log plots. The dropping mercury electrode had the following characteristics at 58 cm of mercury head: t = 3.0 sec, m = 1.92 mg/sec. in 1.0 M ($NaClO_4$).

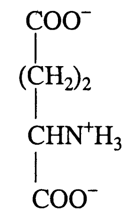
RESULTS AND DISCUSSION

Stability constants of binary complexes: Binary complexes of Pb(II) with thiourea (tu) and glutamate (glu) have been studied polarographically in aqueous medium at 25 ± 0.5°C. All measurements were carried out at constant ionic strength of 1.0 M ($NaClO_4$) and pH 6.80. The reduction of Pb(II) was found to be reversible both in the presence and in the absence of the ligands and diffusion controlled as indicated by the linear plots of i_d *vs.* $\sqrt{h}$ (effective) which passed through the origin. The half-wave potentials of Pb(II) shifted to more negative values on increasing the free ligand concentration indicating complex formation. The relationship between $(-E_{1/2})_c$ and log C_L, where C_L is the concentration of thiourea/glutamate, was not linear but gave a smooth curve showing the existence of more than one complex species. The method of DeFord and Hume[12] was used to calculate the overall stability constants of the binary complexes. Glutamate ion concentration [X] was calculated from the concentration, pK_2 value of glutamic acid (determined at the same ionic strength) and pH of the solution. The thiourea concentration was taken as the analytical concentration.

The normal state of thiourea[14] (tu) is considered to be a Zwitter ion (I) while glutamic acid[15] (glu) is present in the form (II) at pH 6.80



(I)



(II)

Simple systems were investigated here in order to obtain their stabilities *in situ*. The representative data for thiourea and glutamate complexes are set out in Table-1. The overall stability constants of the simple complexes are $\log \beta_1 = 0.48$, $\log \beta_2 = 1.00$, $\log \beta_3 = 0.78$ and $\log \beta_4 = 2.12$ with thiourea; $\log \beta_1 = 4.84$, $\log \beta_2 = 8.38$, $\log \beta_3 = 10.48$ and $\log \beta_4 = 13.80$ with glutamate. The values in case of thiourea system are nearly identical with the reported value[1]. Slight deviations may probably be due to the differences in experimental conditions. The values in thiourea system exhibit the order as $\beta_1 < \beta_2 > \beta_3 < \beta_4$ which supports the order made by Lane *et al.*[1]

The values of stability constants are found to be higher in case of glutamate than with thiourea may be due to the strong chelating ability of glutamate. The trend in values was $\beta_1 < \beta_2 < \beta_3 < \beta_4$. The value of β_1 is nearly identical with the reported value[2]. However, it is not possisble to compare the values of stability constants of glutamate with those obtained by other workers using potentiometric and polarographic methods since the experimental conditions would be widely different.

The complexation reaction of glutamic acid at pH 6.80 may be represented as follows:

$$Pb^{2+} + HL^- \rightleftharpoons Pb(HL)^+$$

$$Pb(HL)^+ + HL^- \rightleftharpoons Pb(HL)_2$$

$$Pb(HL)_2 + HL^- \rightleftharpoons Pb(HL)_3^-$$

$$Pb(HL)_3^- + HL^- \rightleftharpoons Pb(HL)_4^{2-}$$

The value of the overall stability constant of the complex species $\beta_1[Pb(HL)]^+$ is identical with the reported value while $\beta_2[Pb(HL)_2]$ is higher than would be expected[3]. This may probably be due to the neutralization of the charge over the complex species at the particular pH selected in the present investigation.

TABLE-1
REPRESENTATIVE POLAROGRAPHIC DATA FOR Pb(II)-tu AND Pb(II)-glu SYSTEMS:
$-(E_{1/2}) = 0.3880$ v, $(i_d)_s = 6.25$ μA, μ = 1.0 M ($NaClO_4$), T = 25 ± 0.5°C

Conc. of ligand [glu] × 10^{-4} M	−log [glu]	$E_{1/2}$ mV	i_d μA	Conc. of ligand (tu) M	$E_{1/2}$ mV	i_d μA
1.26	3.899	26.0	4.25	0.08	2.5	6.13
2.53	3.597	40.0	4.13	0.16	5.5	6.00
5.06	3.295	54.0	4.00	0.24	10.0	5.75
7.59	3.119	63.5	3.88	0.32	15.0	5.50
8.85	3.053	67.5	3.75	0.40	22.0	5.25
10.12	2.995	70.0	3.63	0.48	29.0	5.25
11.38	2.944	73.5	3.50	0.56	36.0	5.13
12.65	2.898	76.5	3.50	0.64	42.0	5.00
15.18	2.819	82.0	3.38	0.72	46.0	4.85
17.71	2.752	87.0	3.25	0.80	50.5	4.75
20.24	2.694	91.5	3.13	0.88	55.0	4.75
22.77	2.643	96.0	3.00	—	—	—
25.30	2.597	100.0	3.00	—	—	—

Pb(II)-thiourea-glutamate complexes

Polarograms were recorded with solutions containing 1 mM Pb(II), constant glutamate, and increasing concentration of thiourea from 0 to 0.80 M. The two constant concentrations of glutamate 1.00×10^{-4} and 3.15×10^{-4} respectively were so chosen that at lower value 1:1 and at higher value 1:2 complex species predominated in the simple system. In both the sets of the mixed ligand system the reduction waves were found to be well defined, reversible and diffusion controlled both in the presence and absence of the ligands. The half-wave potential of Pb(II) shifted towards more negative values and increasing the thiourea concentration. The shift was found to be more marked than in the simple systems. The relationship between $-(E_{1/2})$ and log C_L for both concentrations of glutamate was not linear but gave a smooth curve showing the existence of more than one complex species (Fig. 1). Schaap and McMasters method[11] was applied for the determination of the overall stability constants of mixed ligand complexes. The half-wave potentials with change in ligand concentration at both the fixed concentrations of glutamate are given in Table-2 along with the observed and calculated $F_{00}(X, Y)$ values (in log form). However, the other F_{ij} functions are not given. The values of A, B, C, D and E (having the usual meaning) and the overall stability constants of mixed ligand complexes are given in Table-3.

TABLE-2
REPRESENTATIVE POLAROGRAPHIC DATA FOR Pb(II)-tu-glu SYSTEM
$-(E_{1/2})_s = 0.3880$ V, $(i_d)_s = 6.25$ μA, μ = 1.0 M ($NaClO_4$), T = 25 ± 0.5°C

Conc. of ligand (tu) M	$-E_{1/2}$ V *vs.* S.C.E.		i_d (μA)	Values of log F_{00}(X, Y)	
	0.00 M [glu]	1.00×10^{-4} [glu]		Observed	Calculated
0.00	—	0.4130	5.75	0.920	0.940
0.08	0.3905	0.4145	5.13	0.981	0.987
0.12	—	0.4155	5.00	1.025	1.041
0.16	0.3935	0.4175	4.88	1.104	1.100
0.20	—	0.4190	4.75	1.167	1.164
0.24	0.3980	0.4205	4.63	1.228	1.230
0.32	0.4030	0.4245	4.63	1.364	1.368
0.40	0.4100	0.4285	4.50	1.511	1.511
0.48	0.4170	0.4325	4.38	1.658	1.655
0.56	0.4240	0.4360	4.25	1.790	1.796
0.64	0.4300	0.4400	4.00	1.951	1.935
0.72	0.4340	0.4445	3.88	2.116	2.068
0.80	0.4385	0.4480	3.88	2.235	2.197
0.96	—	0.4545	3.75	2.469	2.437
		[glu] = 3.15×10^{-4} M			
0.04	—	0.4320	5.00	1.583	1.619
0.08	0.3905	0.4335	4.88	1.645	1.666
0.12	—	0.4350	4.75	1.707	1.716
0.16	0.3935	0.4365	4.63	1.769	1.769
0.20	—	0.4380	4.56	1.826	1.824
0.24	0.3908	0.4395	4.50	1.883	1.880
0.32	0.4030	0.4420	4.50	1.984	1.995
0.40	0.4100	0.4460	4.44	2.108	2.109
0.48	0.4170	0.4490	4.38	2.216	2.224
0.56	0.4240	0.4525	4.38	2.334	2.338
0.64	0.4300	0.4560	4.25	2.465	2.449
0.72	0.4340	0.4590	4.25	2.567	2.559
0.80	0.4385	0.4610	4.25	2.668	2.665
0.96	—	0.4680	4.13	2.883	2.869

TABLE-3
OVERALL STABILITY CONSTANTS OF Pb(II)-(tu)-(glu) SYSTEM

Fixed conc. of [glutamate] M	log A	log B	log C	log D	log E
1.00×10^{-4} [glu]	0.90	1.17	1.90	0.93	2.30
3.15×10^{-4} [glu]	1.58	1.90	2.48	1.00	2.60

log β_{11} = 4.79, log β_{12} = 8.76, log β_{21} = 5.78, log β_{22} = 9.01

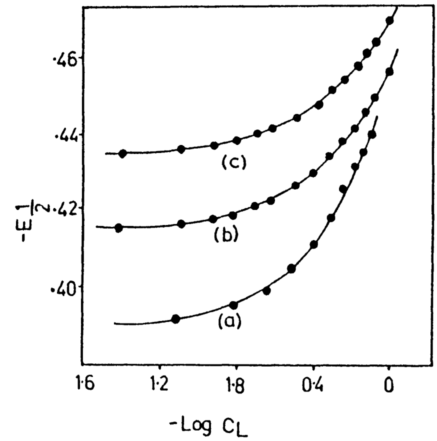


Fig. 1 Plot of $-E_{1/2}$ *vs.* $-\log C_L$ (a) [glu] = 0.00 M; [glu] = 1.00×10^{4} M, and (c) [glu] = 3.15×10^{-4} M.

The values of the stability constants of mixed ligand complexes have been compared with the binary complexes. From the reaction 1,

$$[Pb(tu)]^{2+} + [Pb(glu)]^{+} \rightleftharpoons [Pb(tu)(glu)]^{+} + Pb^{2+} \quad (1)$$

The equilibrium constant $\Delta \log K$ is given by the relation:

$$\Delta \log K = \log \beta_{11} - (\log \beta_{10} + \log \beta_{01})$$

which is found to be –0.53. The negative value of $\Delta \log K$ suggests that the mixed ligand complex species is less stable than the parent monocomplexes. Similarly the value of stabilization constant K_s calculated by using ref. 15 was found to be –0.20, indicating the destabilization of the species (1:1:1) which may probably be due to the unfavourable interaction between the two ligands. However, the value of mixing constant K_m for the reaction $1/2[Pb(tu)_2]^{+} + [1/2\ Pb(glu)_2] = [Pb(tu)(glu)]^{+}$ indicates the relative stability of the mixed complexes in solution as compared to the parent binary complexes. This is given by the reaction

$$K_m = \beta_{11}/\beta_{20}\beta_{02}$$

or

$$\log K_m = \log \beta_{11} - (\log \beta_{20} + \log \beta_{02})$$

The positive value of mixing constant ($\log K_m = 0.1$) observed in the present work suggests that the mixed ligand complexes are comparatively more stable than the simple bis complexes. The values of $\Delta \log K$, $\log K_m$ and $\log K_s$ were found to be positive in case of Cd(II) complexes[10, 16].

Prediction of β values from statistical factors

The statistical factors in the complexation constants were evaluated following the procedure suggested by Watters[17] and Tedesco[18]. The observed values of the stability constants of mixed ligand complexes with the predicted values obtained are represented next page:

Constants	β_{11}	β_{12}	β_{21}	β_{22}
Observed	$10^{4.79}$	$10^{8.76}$	$10^{5.78}$	$10^{9.01}$
Predicted	$10^{4.81}$	$10^{7.72}$	$10^{4.49}$	—
Enhancements	$10^{-0.02}$	$10^{1.04}$	$10^{1.29}$	—

The observed values of the mixed ligand complex species $[Pb(tu)(glu)]^+$ is nearly identical with the predicted value. But in case of $[Pb(tu)_2(glu)]^+$ and $[Pb(tu)(glu)_2]$ the observed values are higher than would be predicted on statistical grounds. This may be due to some weak bonding between unlike bound ligands, the coordination tendencies of Pb(III) ion and the basicity of the oxygen and nitrogen of ligands.

The results were also tested with Van Panthaleon Van Eck equation[19] and the possibility of simultaneous π-bonding between the metal and ligands was established from the non-linear relationship observed in the plots of log K_N *vs.* (N − 1) where N is the coordination number.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. D.B. Ingle, Department of Chemistry, Dr. S.S. Pawar and Dr. M.B. Patil, Department of Biochemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for their helpful suggestions, valuable discussions and necessary help during the progress of the work.

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(*Received: 15 September 1997; Accepted:* 24 March 1998) AJC-1472