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Polarographic Study of Stability Constants of Lead(II) Complexes with β-Picoline, Glycine and Alanine

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The mixed ligand complexes of β-picoline (β-pico), glycine (gly^-) and Alanine (ala^-) with Pb(II) have been studied polarographically at constant ionic strength, $\mu = 1.5$ M ($NaNO_3$) and pH 6.0 at 25.4 ± 0.1°C. The reduction of the complexes at d.m.e. is reversible and diffusion-controlled. Two mixed complexes, $[Pb(gly)(\beta\text{-pico})]^+$ and $[Pb(ala)(\beta\text{-pico})]^+$ are formed and their stability constants at 25.4°C are: $\log \beta_{11} = 5.9515$ and $\log \beta_{11} = 6.0640$ respectively.

Key Words: Stability constants, Lead(II) complexes, β-Picoline, Glycine, Alanine, Polarographic study.

INTRODUCTION

Saxena *et al.*[1] have reported polarographic study of mixed ligand complexes of Pb(II) with pyridoxine amino and amino acids. Singh *et al.*[2,3] have studied the mixed complexes of Pb(II) with imidazole, pyridine and citrate, succinate and tartrate ions. Besides this the survey of literature[4–10] it appears that polarographic studies of mixed complexes of Pb(II) with β-picoline and glycine and alanine are still lacking. The present work reports the studies of mixed ligand complexes of Pb(II) with β-picoline, glycine and alanine.

EXPERIMENTAL

All reagents were analytical grade and their solutions were prepared in conductivity water. The ionic strength was maintained constant at $\mu = 1.5$ using $NaNO_3$ as supporting electrolyte. The concentration of Pb(II) was maintained at 1×10^{-3} M. Polarograms were obtained[11] by means of a manual polarograph (Toshniwal CL 02) in conjunction with Toshniwal polyflex galvanometer (PL 50). All the measurements were made at 25.4 ± 0.1°C and pH 6.0. A saturated calomel electrode (SCE) was used as reference electrode. The d.m.e. had the following characteristics (in 0.1 M $NaNO_3$, open circuit) : $m = 2.219$ mg/s, $t = 3.5$ s, $m^{2/3}t^{1/6} = 2.10$ $mg^{2/3}$ $s^{-1/2}$, $h_{corr} = 40$ cm.

RESULTS AND DISCUSSION

The reduction of Pb(II) in β-picoline, glycine and alanine was found to be reversible and diffusion controlled. The same was true for the mixed system. The slopes of linear plots of $\log i/i_d - i$ *vs.* $E_{d.m.e.}$ were in the range 30–33 mv and the plots of i_d *vs.* $h_{corr}^{1/2}$ were linear and passed through the origin. The stability constants of simple complexes of Pb(II) with β-picoline, glycine and alanine were determined separately prior to the study of mixed ligand system. Identical conditions were maintained in both the simple and mixed systems.

(a) Simple System: The simple systems of Pb(II) with β-picoline, glycine and alanine were studied by the method of Deford and Hume[12]. Identical conditions were maintained in both simple and mixed systems, *i.e.*, 1.5 M sodium nitrate as supporting electrolyte and temperature was maintained contant at 25.4 ± 1°C. The values of stability constants of simple complexes have been tabulated in Table-1.

TABLE-1
STABILITY CONSTANTS OF β-PICOLINE, GLYCINE AND ALANINE WITH Pb(II)

Contents	log β_1	log β_2
β-Picoline	0.903	1.857
Glycine	5.342	9.698
Alanine	5.301	9.778

(b) Mixed System: Glycine (gly$^-$) and alanine (ala$^-$) concentrations were varied from 0.10 M to 0.50 M and that of β-picoline (β-pico) was kept constant at 0.05 M. The $E_{1/2}$ values were greater compared to those obtained in the absence of β-picoline thereby showing the formation of mixed complexes. The system was repeated at another concentration of β-picoline (0.10 M).

Schaap and McMaster's method[18] was used to determine the values of the stability constants of mixed complexes. The polarographic characteristics and F_{ij} [XY] functions of mixed complexes of Pb(II) with β-picoline and glycine and alanine at fixed [β-pico] (0.05 M and 0.10 M) are presented in Tables 2 and 3.

TABLE-2
Pb(II)-GLYCINE-β-PICOLINE SYSTEM
$[Pb^{2+}] = 1 \times 10^{-3}$ M, μ = 1.5 M ($NaNO_3$), pH = 6.00, Temp = 25.4 ± 0.1°C, $(E_{1/2})_s$ = −0.404 volts (SCE)

$[gly]_t$ (M)	$[gly]_f$ ($\times 10^5$ M)	$-E_{1/2}$ V (SCE)	log I_m/I_c	Slope (mv)	F_{00}[X, Y]	F_{10}[X, Y] ($\times 10^{-4}$)	F_{20}[X, Y] ($\times 10^{-9}$)
			Series-I $[\beta\text{-pico}]_t$ = 0.05 M (Fixed)				
0.10	1.7	0.428	0.01631	30	6.70	—	—
0.20	3.3	0.438	0.02087	31	14.75	25.75	—
0.30	4.9	0.448	0.02599	31	32.48	53.53	5.61
0.40	6.6	0.453	0.02599	32	47.92	63.13	5.62
0.50	8.3	0.457	0.03379	33	66.58	72.68	5.62
			Series-II $[\beta\text{-pico}]_t$ = 0.10 M (Fixed)				
0.10	1.7	0.430	0.01637	31	7.83	—	—
0.20	3.3	0.439	0.01985	30	15.90	29.24	—
0.30	4.9	0.450	0.02599	33	37.95	64.69	6.67
0.40	6.6	0.455	0.02909	32	56.38	75.96	6.66
0.50	8.3	0.459	0.03906	33	78.73	87.32	6.66

$[gly]_t$– Total concentration of glycine;
$[gly]_f$– Free ligand concentration of glycine
Series I: log A = 0.795 log B = 5.414 log C = 9.748
Series II: log A = 0.795 log B = 5.505 log C = 9.819

TABLE-3
Pb(II)–ALANINE-β-PICOLINE SYSTEM
$[Pb^{2+}] = 1 \times 10^{-3}$ M, $\mu = 1.5$ M ($NaNO_3$), pH = 6.00, Temp. = 25.4 ± 0.1°C,
$(E_{1/2})_S = -0.404$ volts (SCE)

$[ala]_t$ (M)	$[ala]_f$ ($\times 10^5$ M)	$-E_{1/2}$ V (SCE)	log I_m/I_c	Slope (mv)	$F_{00}[X, Y]$	$F_{10}[X, Y]$ ($\times 10^{-4}$)	$F_{20}[X, Y]$ ($\times 10^{-9}$)
			Series-I [β-pico]$_t$ = 0.05 M (Fixed)				
0.10	1.3	0.427	0.00981	30	6.11	—	—
0.20	2.7	0.437	0.01934	31	13.60	20.74	—
0.30	4.0	0.445	0.02300	32	25.55	43.77	4.96
0.40	5.4	0.449	0.02961	33	35.40	50.74	4.95
0.50	6.7	0.452	0.04431	33	46.24	57.07	4.93
			Series-II [β-pico]$_t$ = 0.10 M (Fixed)				
0.10	1.3	0.429	0.00982	31	7.14	—	—
0.20	2.7	0.440	0.01430	32	16.97	29.51	—
0.30	4.0	0.448	0.02961	33	32.75	59.39	5.34
0.40	5.4	0.452	0.03431	33	45.19	67.01	5.37
0.50	6.7	0.455	0.04431	33	58.39	73.72	5.33

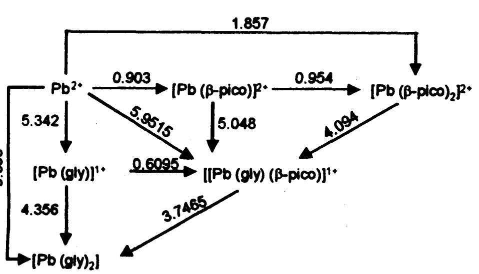
$[ala]_t$– Total concentration of alanine
$[ala]_f$– Free ligand concentration of alanine
Series I : log A = 0.903 log B = 5.380 log C = 9.698
Series II : log A = 0.954 log B = 5.579 log C = 9.732

The stability constants of the mixed complexes were calculated from the constants A, B and C. One mixed complex as is formed in each mixed system:

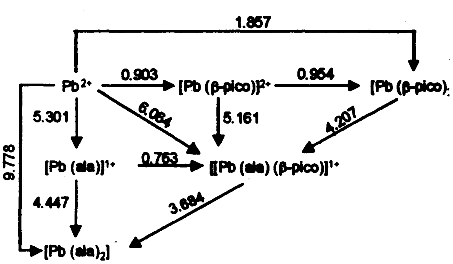
Pb(II)–Glycine–β-picoline system $[Pb(gly)(\beta\text{-pico})]^+$ log $\beta_{11} = 5.9515$

Pb(II)–Alanine–β-picoline system $[Pb(ala)(\beta\text{-pico})]^+$ log $\beta_{11} = 6.0640$

The results of the present study are summarized in the following diagrams (**Schemes I and II**), where the numerical values shown are the logarithms of the equilibrium constants for the reactions indicated:



Scheme-I: Pb(II) Glysine-β-picoline system



Scheme-II: Pb(II) Alanine-β-picoline system

The mixing constant K_M (equilibrium constant) for the reactions:

$$1/2[Pb(gly)_2] + 1/2[Pb(\beta\text{-pico})_2]^{2+} \rightleftharpoons [Pb(gly)(\beta\text{-pico})]^{+} \quad (1)$$

$$1/2[Pb(ala)_2] + 1/2[Pb(\beta\text{-pico})_2]^{2+} \rightleftharpoons [Pb(ala)(\beta\text{-pico})]^{+} \quad (2)$$

is given by the relation

$$\log K_M = \log \beta_{11} - 1/2(\log \beta_{20} + \log \beta_{02})$$

These work out to be +0.181 for reaction 1 and +0.247 for reaction 2. The positive values show that the mixed complexes $[Pb(gly)(\beta\text{-pico})]^+$ and $[Pb(ala)(\beta\text{-pico})]^+$ are more stable than simple complexes: $[Pb(\beta\text{-pico})_2]^{2+}$, $[Pb(gly)_2]$ and $[Pb(ala)_2]$.

The equilibrium constant (log values) for the following disproportion reactions:

$$2[Pb(gly)(\beta\text{-pico})]^{+} \rightleftharpoons [Pb(gly)_2] + [Pb(\beta\text{-pico})_2]^{2+} \quad (3)$$

$$2[Pb(ala)(\beta\text{-pico})]^{+} \rightleftharpoons [Pb(ala)_2] + [Pb(\beta\text{-pico})_2]^{2+} \quad (4)$$

works out to be –0.353 and –0.493 for the disproportion reactions 3 and 4 respectively. The negative log values for the equilibrium constants show that the formation of mixed complexes is favoured over simple ones.

The complex $[Pb(ala)(\beta\text{-pico})]^+$ is more stable than the complex $[Pb(gly)(\beta\text{-pico})]^+$.

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