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Polarographic Studies of Mixed Ligand Complexes of Pb(II) with o-Chloro Benzoyl Glycine and Malonate Ions using $NaNO_3$ as Supporting Electrolyte

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Abstract: Pb(II) mixed ligand complexes with Malonate ion and o -Chloro Benzoyl Glycine (o -chlorohippuric acid) has been studied polarographically and stability constants have been deduced keeping ionic strength constant $\mu=2.0$ ($NaNo_3$) maintaining pH 6.4. at constant temperature 25±0.1℃.

Keywords: Polarographic, Ligand, Complexes, Ions.

Introduction:

Polarographic studies dealing with the complexes of metal ions with Carboxylate ions have been extensively undertaken. Meites and Meites[1-2] have studied the polarographic behavior of Pb(II) in the presence of Oxalate, Tartrate and citrate ions under different experimental conditions and have indicated the formation of complex species of Pb(II) with these ligands. Singh and Kulshrestha[3] have studied the mixed ligand complexes of Pb(II) with Nitrogen donor ligands and carboxylate ions polarographically. Jain and Gaur[4] have reported the formation of three successive format complexes of Pb(II). The single ligand complex of Pb(II) with various carboxylate ions have been studied polarographically by several workers[5-7]. Simple complexes of Pb(II) with various amino acids have been studied polarographically[8-11].Kim et al[12] have studied the mixed complexes of Pb(II) , Cd(II) and Cu(II) with histidine and hydroxide ion in the pH range 9-13 and also determined the composition of the complexes. Gaur et al[13] reported formation of only one mixed complex of Pb(II) with formate and maleate ions. Gupta et al[14] investigated complexes of Cd and Pb with pyridoxine(vitamin B6) at different temperatures and pH. Thermodynamic constants have also been evaluated. Burns and Hume[15] have investigated the formation of three successive complexes of Pb(II) with acetate ion. A precise polarographic determination of the stability constant of complexes of Pb with oxalate and sulfate has been done by Nyholm[17-18]. Complexes of Pb(II) with the Potentially tetradentate ligands have been studied by Bardwell et a1[19].

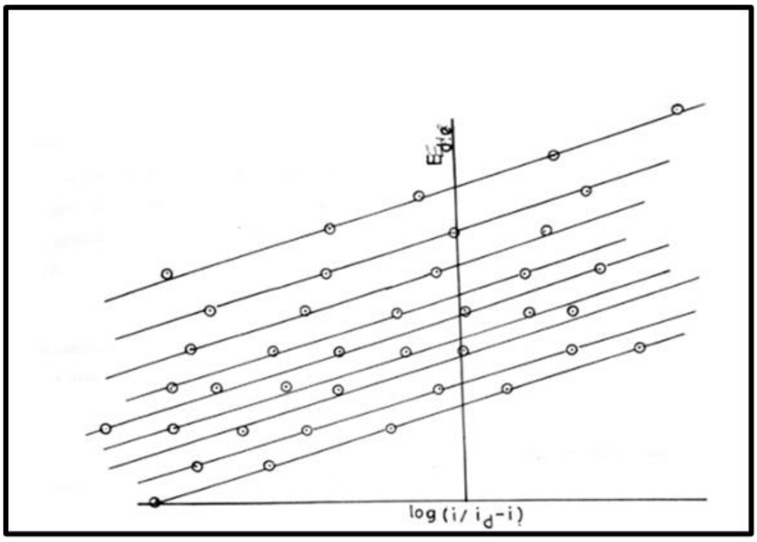
EXPERIMENTS

Nitrogen containing lgand o-Chloro Benzoyl Glycine(o-CBG) was prepared from o-Chloro Benzoyl Chloride. Glycine was dissolved in NaOH and o-Chloro Benzoyl Chloride to obtain o-CBG by standard procedure. Stock solutions of chemicals used were prepared in the conductivity water. The concentration of Pb(II) from $Pb(NO_3)_2$ was maintained at 1.0 x 10^{-3}M taken in the presence of increasing concentration of these ligands at constant ionic strength and pH. All the measurements were made at a constant temperature 25±0.1°C.

The capillary characteristics of the D.M.E have been mentioned in the subsequent tables. The other experimental details such as the pH adjustment calculation of free ligand concentration etc. were also maintained as mentioned in the tables.

The number of electrons involved in the polarographic reduction of Pb(II) in the presence of ligands was determined by the millicoulometric method of Devries. This gave the value of n equal to 2 in each case.

Figure 1: Plots of $\log(i/id - i)$ vs Ed_e for Pb(II)-o-Chloro Benzoyl Glycinate System



RESULTS AND DISCUSSIONS

Pb(II) - Malonate System

Polarographic characteristics of Pb(II)-Malonate shows that with the addition of increasing amounts of Malonate, E1/2 of Pb(II) is shifted to more negative potentials thereby showing the complex formation. The plot of $E_{1/2}$ Vs log $[Mal^{2-}]$ is a smooth curve indicating the formation of successive complexes .The composition and stability constants of the complexes have been determined by Deford and Hume's method Figure 2 shows the degree of formation of various complex species.

Table 1: Polarographic Characteristics and Fj[X] Function of Pb(II)- Malonate System

$[Pb^2+]$ = 1 x 10^{-3} M; µ = 2.0 ($NaNO_3$); pH = 6.4; Temp.= 25 ± 0.1˚C; m = 2.38 mg/sec; t=3.4 Sec., $m^{2/3}$ $t^{1/6}$ = 2.1 $mg^{2/3}$ $sec^{-1/2}$ (in 2.0 M. $NaNO_3$, open circuit); $h_{corr.}$ = 62.5 cm.; [Triton X-100] = 1 x 10^{-3} %.

$[Mal^{2-}]$ M	I_d µA	$-E_{1/2}$ V (S.C.E)	Slope mV	$F_o[X]$ x 10^{-1}	$F_1[X]$ x 10^{-2}	$F_2[X]$ x 10^{-3}	$F_3[X]$ x 10^4
0.00	7.25	.400	30	-	-	-	-
0.10	6.40	.457	30	9.61	9.51	-	-
0.20	6.35	.473	31	33.73	16.81	4.90	-
0.30	6.32	.491	31	137.77	45.88	11.96	3.69
0.40	6.23	.500	32	281.81	70.42	15.85	3.70
0.50	6.19	.507	32	489.37	97.85	19.17	3.68

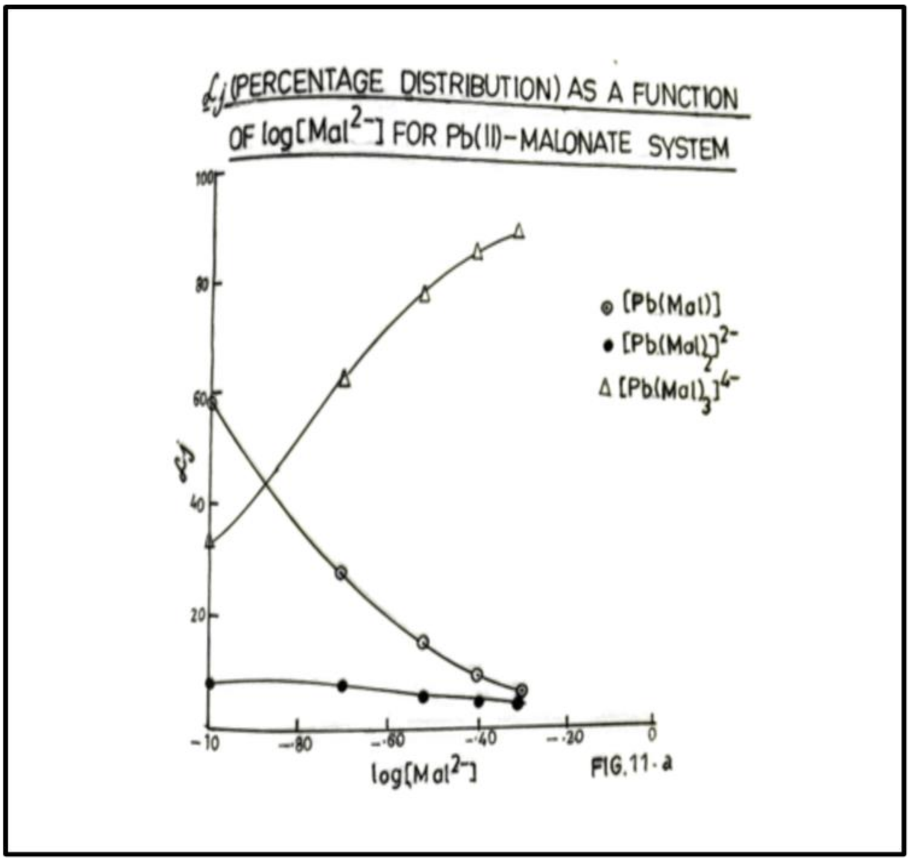


Figure 2

Pb(II) with -o- Chloro Benzoyl Glycinate System

The composition and stability constant of Pb with o-Chloro Benzoyl Glycine was determined prior to the study of mixed complex of Pb (II) with o-CBG and Malonate ions. Identical conditions were maintained in both the simple and mixed ligand systems. Polarogams of the solutions containing 1x10^{-3} M Pb(II) and 0.20M o-Chloro Benzoyl Glycine were taken at 6.4 pH values keeping ionic strength constant at u = 2.0 ($NaNO_3$) with o-chloro Benzoyl glycinate and malonate ions. The $E_{1/2}$ of Pb (II) was measured as a function of pH in the range of 5.0 to 8.0 and it was found that the value of $E_{1/2}$ remains unchanged. This shows that OH- does not enter into coordination with Pb (II) and Pb(II) exists as the Pb^{+2} aqueous ion in the absence of the ligand.

Table 2: Polarographic Characteristics and F_i[X] Function of Pb(II) - o- Chloro Benzoyl Glycinate System

$[Pb^{2+}] = 1 \times 10^{-3}$ M; μ = 2.0 ($NaNO_3$); pH = 6.4; Temp.= 25 ± 0.1°C; m = 2.38 mg/sec; t=3.4 ec., $m^{2/3} t^{1/6} = 2.1$ $mg^{2/3} sec^{-1/2}$ (in 2.0 M. $NaNO_3$, open circuit); $h_{corr.}$ = 62.5 cm.; [Triton X-100] = 1×10^{-3} %.

$[0\text{-}CBG^-]$ M	I_d μA	$-E_{1/2}$ V (S.C.E)	Slope mV	F_o[X]	$F_1[X]$ x 10^{-2}	$F_2[X]$ x 10^{-4}	F3[X] x10^{-6}
0.00	6.60	.400	30	-	-	-	- ,
0.20	5.90	.410	30	2.43			
0.40	5.62	.415	31	3.78	6.95		
0.60	5.58	.424	32	7.67	11.11	14.85	1.60
0.80	5.54	.431	31	13.34	15.42	16.52	1.65
1.00	5.46	.435	31	20.48	19.48	17.28	1.62

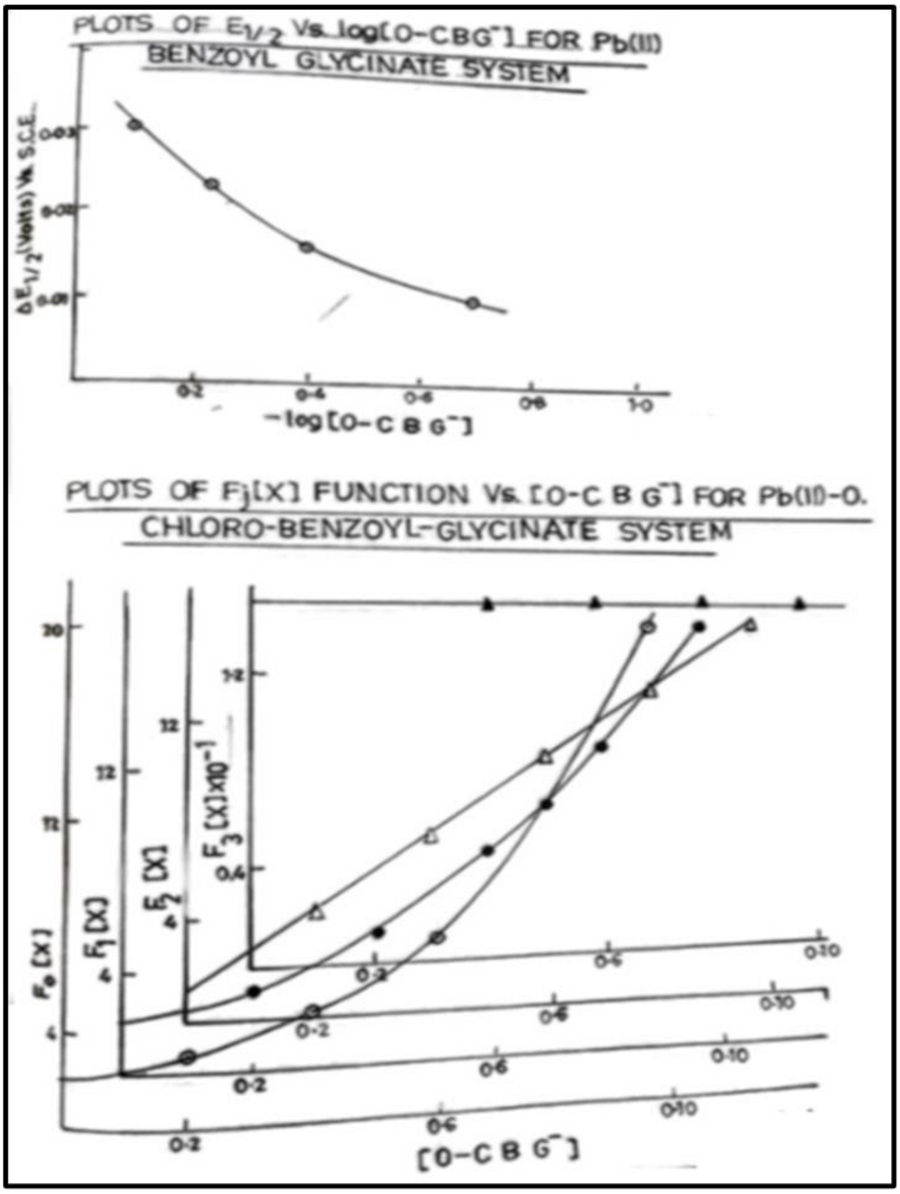


Figure 3

Pb(II)-Malonate-O-Chloro Benzoyl Glycinate System

The concentration of malonate was varied from 0 to .50 M keeping [o-CBG] constant at 0.20 M. The $E_{1/2}$ values were more negative than those obtained in the absence of o-CBG$^-$) thereby showing the formation of mixed ligand complexes. The system is again repeated keeping [o-CBG$^-$] constant at 0.40 M. The polarographic characteristics and F_{ij}[X, Y] functions where (X=Mal^{2-} ,Y=o-CBG) are presented in Table 3.

Table 3: Polarographic Characteristics and F_{ij}[X, Y] Functions of Pb(II) - Malonate-o-Chloro Benzoyl Glycinate System

[Pb^{2+}] = 1 x 10^{-3} M; μ = 2.0 ($NaNO_3$); pH = 6.4; Temp.= 25 ± 0.1°C; m = 2.38 mg/sec; t=3.4 Sec, $m^{2/3}$ $t^{1/6}$ = 2.1 $mg^{2/3}$ $sec^{-1/2}$ (in 2.0 M. $NaNO_3$, open circuit); $h_{corr.}$ = 62.5 cm; [Triton X-100] = 1 x 10^{-3} %.

[Mal 2-$^-$] M	I_d µA	-$E_{1/2}$ V (S.C.E)	Slope mV	F_{00}[X, Y]	F_{10}[X, Y] x 10^{-1}	F_{20}[X, Y] x 10^{-2}	F_{30}[X, Y] x 10^{-4}
[o-CBG$^-$] = 0.20M							
0.10	6.56	0.463	30	12.60	10.52		•10 MD
0.20	6.53	0.479	30	44.01	20.97	8.20	0111••
0.30	6.46	0.493	31	132.21	43.73	13.01	3.62
0.40	6.40	0.503	30	290.21	72.13	17.11	3.69
0.50	6.38	0.511	32	541.10	108.12	20.51	3.68
[o-CBG$^-$]= 0.40M							
0.10	5.90	0.466	31	19.11	18.57	1•• OM	--
0.20	5.88	0.483	31	66.48	32.91	11.62	__
0.30	5.81	0.497	32	200.11	67.04	19.13	5.42
0.40	5.76	0.507	33	439.19	110.21	25.32	5.57
0.50	0.514	0.515	32	820.17	164.11	31.07	5.61

From the plots of F_{ii}[X, Y] data vs [Mal^{2-}] the following intercept values for constant A,B,C and D have been obtained :

Series I: [o-CBG$^-$] = 0.20M

log A = 1.30, log B= 2.72, log C = 3.26, log D = 4.60

Series II: [o-CBG$^-$] = 0.40M D

log A = 0.70, log B= 3.00, log C= 3.51 , log D= 4.75

The stability constants have been obtained from these constants. Two mixed complexes as noted are formed.

[Pb(Mal)(o-CBG)]$^-$; log β_{11}= 3.41

[Pb$(Mal)_2$(o-CBG)]$^{3-}$; log β_{21} = 3.65

The results of the present study have been conveniently summarized in the following diagram. Where the numerical values shown are the logarithms of the equilibrium constants for the reaction indicated. Two mixed complexes existing in the solution have the following equilibria. The equilibrium constant, (log K value) is given in each case for each equilibrium:

Equilibria	**log K**
Pb^{2+} + Mal^{2-} + o-CBG$^-$ ⇌ [Pb(Mal)(o-CBG)]$^-$	3.41
Pb^{2+} + 2Mal^{2-} + o-CBG$^-$ ⇌ [Pb $(Mal)_2$ (o-CBG)]$^{3-}$	3.65
[Pb(Mal)] + o-CBG$^-$ ⇌ [Pb(Mal)(o-CBG)]$^-$	0.56
[Pb$(Mal)_2$] + o-CBG$^-$ ⇌ [Pb$(Mal)_2$(o-CBG)] $^{3-}$	0.66

$[Pb(o\text{-}CBG)]^{+}$ + Mal^{2} ⇌ $[Pb(Mal)(o\text{-}CBG)]^{-}$	3.07
$[Pb(o\text{-}CBG)_2]$ + $Ma1^{2-}$ ⇌ $[Pb(Mal)(o\text{-}CBG)]^{-}$ + o-CBG	2.09

From the above equilibrium constant values the tendency of a ligand to add to a complex and to substitute another ligand may be compared. It is seen that $Ma1^{2-}$ (equilibria 5,6) has a stronger tendency to add to $[Pb(o\text{-}CBG)]^{+}$ and $[Pb(o\text{-}CBG)_2]$ as compared to that of $o\text{-}CBG^{-}$ (equilibria 3,4) to add to [Pb(Mal)] and $[Pb(Mal)_2]^{2-}$. Mal^{2-} can replace $o\text{-}CBG^{-}$ from its simple complexes to form mixed complexes. However, $o\text{-}CBG^{-}$ can not replace $Ma1^{2-}$ from its simple complexes. It seems therefore, $Ma1^{2-}$ is a stronger ligand than $o\text{-}CBG^{-}$.

The mixing constant K_M for the reaction:

1/2 $[Pb(Mal)_2]^{2-}$ +1/2 $[Pb(o\text{-}CBG)_2]$ ⇌ $[Pb(Mal)(o\text{-}CBG)]^{-}$

is given by the relation:

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

This works out to be +1.71. A positive value of $\log K_M$ indicates that the mixed complex, $[Pb(Mal)(o\text{-}CBG)]^{-}$ is more stable than the simple complexes $[Pb(Mal)_2]^{2-}$ and $[Pb(o\text{-}CBG)_2]$. The equilibrium constant for the following disproportionation reactions.

$2[Pb(Mal)(o\text{-}CBG)]^{-}$ ⇌ $[Pb(Mal)_2]^{2-}$ + $[Pb(o\text{-}CBG)_2]$

$2[Pb(Mal)_2(o\text{-}CBG)]^{3-}$ ⇌ $[Pb(Mal)3]^{4-}$ + [Pb(o-CBG)2] + $Ma1^{2-}$

work out to be -3.41 and -2.29 respectively.

The large negative log value of equilibrium constants for these reactions indicate that the formation of mixed complexes $[Pb(Mal)(o\text{-}CBG)]^{-}$ and $[Pb(Mal)_2(o\text{-}CBG)]^{3-}$ are strongly favored over the simple complexes. The variation of α_{ij} with $\log[Ma1^{2-}]$ indicate that with increasing concentration of $Ma1^{2-}$ the degree of formation of 1:1:1 species decreases while that of 1:2:1

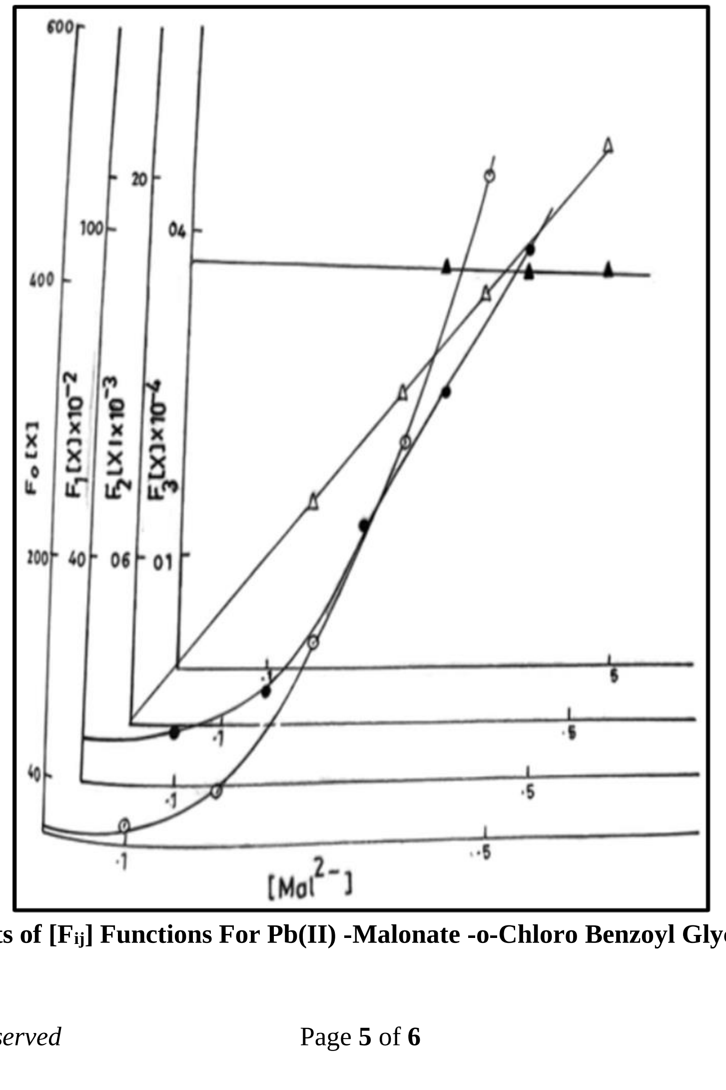


Figure 4: Plots of $[F_{ij}]$ Functions For Pb(II) -Malonate -o-Chloro Benzoyl Glycinate system

CONCLUSION

Ma1^{2-} has a stronger tendency to add to [Pb(o-CBG)]$^{+}$ and [Pb(o-CBG)$_2$] as compared to that of o-CBG^{-} to add to [Pb(Mal)] and [Pb(Mal)$_2$]$^{2-}$. Mal^{2-} can replace o-CBG^{-} from its simple complexes to form mixed complexes. However, o-CBG^{-} can not replace Ma1^{2-} from its simple complexes. It seems therefore, Ma1^{2-} is a stronger ligand than o-CBG^{-}.

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