



Polarographic Studies of Mixed Complexes of Pb(II) with o-Chloro Benzoyl Glycine and Citrate Ions using NaNO₃ as Supporting Electrolyte

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Abstract: *Pb(II) mixed ligand complexes with citrate ion and o-chloro Benzoyl Glycine (o -chlorohippuric glycine) has been studied polarographically and stability constants have been deduced keeping ionic strength constant $\mu=2.0$ (NaNO₃) and at pH 6.4. System has been maintained at a constant temperature of $25\pm 0.1^\circ\text{C}$.*

Keywords: *Mixed Complexes, Polarography, Stability Constant.*

Introduction

Polarographic studies dealing with the complexes of metal ions with Carboxylate ions have been extensively undertaken. Meites and Meites¹⁻² 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 Kulshrestha³ have studied the mixed ligand complexes of Pb(II) with Nitrogen donor ligands and carboxylate ions polarographically. Jain and Gaur⁴ have reported the formation of three successive formate complexes of Pb(II). The single ligand complex of Pb(II) with various carboxylate ions have been studied polarographically by several researchers⁵⁻⁷. Simple complexes of Pb(II) with various amino acids have been studied polarographically⁸⁻¹¹. Kim et al¹² 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 al¹³ reported that formation of only one mixed complex of Pb(II) with formate and maleate ions. Gupta et al¹⁴ investigated complexes of Cd and Pb with pyridoxine (vitamin B6) at different temperatures and pH. Thermodynamic constants have also been evaluated. Burns and Hume¹⁵ 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 sulphate has been done by Nyholm¹⁷⁻¹⁸. Complexes of Pb(II) the Potentially tetradentate ligands have been studied by Bardwell et al¹⁹.

Experiments

All the chemicals used were of Analytical Reagent grade and their stock solutions were prepared in the conductivity water. The concentration of Pb(II) from Pb(NO₃)₂ was maintained at $1.0 \times 10^{-3}\text{M}$. Citric acid was used as the source of Citrate (Cit³⁻). NaNO₃ was used as a Supporting electrolyte and also was 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 $25\pm 0.1^\circ\text{C}$.

The capillary characteristics of the D.M.E have been mentioned in the subsequent tables. The number of electrons n involved in the polarographic reduction of Pb(II) in the Presence of ligands was determined by the milli coulometric method of Devris and Kon.

Preparation of o-Chloro Benzoyl Glycine:

o-Chloro Benzoyl Glycine was prepared from the o-Chloro Benzoyl Chloride. First the o-Chloro Benzoyl Chloride was prepared by adding o-Chloro Benzoic Acid and Chloride, it was converted into the o-Chloro Benzoyl Glycine. It was purified by recrystallisation from hot water.

Thionyl Chloride:

The solution was refluxed and distilled and o-Chloro Benzoyl Chloride was collected at $236-238^\circ\text{C}$. After the preparation of o-Chloro Benzoyl, the polarograms of the solutions were taken in the presence of increasing concentrations of the ligand at constant ionic strength and pH. Triton X-100 ($1 \times 10^{-3}\%$) was used as a maxima suppressor. The measurements were made at a constant temperature ($25 \pm 0.1^\circ\text{C}$). All the current and potential values were corrected for residual current and IR drop of the cell



respectively. Throughout the measurements the current at the end of the drop life (i.e. the maximum current value) was recorded. The capillary characteristics of the d.m.e. have been mentioned in the subsequent tables.

The pH of the solutions was adjusted by adding a very dilute solution of NaOH or HCl by Systronics Digital pH meter (Type 335).

The experimental data obtained on the different systems have been summarized in the following Tables:

Table 1: Polarographic Characteristics and $F_i[X]$ Function of Pb(II)- Citrate System

$[Pb^{2+}] = 1 \times 10^{-3} M$; $\mu = 2.0$ (NaNO₃); pH = 6.4; Temp. = $25 \pm 0.1^\circ C$; $m = 2.38$ mg/sec; $t = 3.4$ Sec., $m^{2/3} t^{1/6} = 2.1$ mg^{2/3} sec^{-1/2} (in 2.0 M. NaNO₃, open circuit); $h_{corr.} = 62.5$ cm.; [Triton X-100] = 1×10^{-3} %.

[Cit ³⁻] M	I _a μA	-E _{1/2} V (S.C.E)	Slope mV	F ₀ [X] x 10 ⁻¹	F ₁ [X] x 10 ⁻²	F ₂ [X] x 10 ⁻³
0.00	7.26	0.400	30	--	--	--
0.10	6.62	0.425	30	7.69	--	--
0.20	6.48	0.444	30	34.51	167.55	--
0.30	6.42	0.456	31	88.71	292.3	8.42
0.40	6.35	0.462	31	143.26	355.66	8.39
0.50	6.37	0.468	32	227.61	453.22	8.11

Table 2: Polarographic Characteristics and $F_{ij}[X, Y]$ Functions of Pb(II) - Citrate-o- Chloro Benzoyl Glycinate System

$[Pb^{2+}] = 1 \times 10^{-3} M$; $\mu = 2.0$ (NaNO₃); pH = 6.4; Temp. = $25 \pm 0.1^\circ C$; $m = 2.38$ mg/sec; $t = 3.4$ Sec., $m^{2/3} t^{1/6} = 2.1$ mg^{2/3} sec^{-1/2} (in 2.0 M. NaNO₃, open circuit); $h_{corr.} = 62.5$ cm.; [Triton X-100] = 1×10^{-3} %.

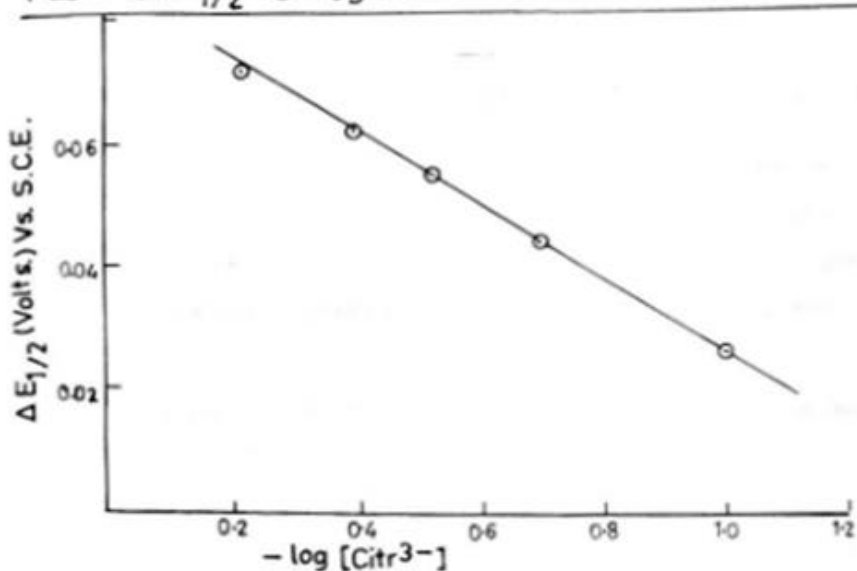
[Cit ³⁻] M	I _a μA	-E _{1/2} V (S.C.E)	Slope mV	F ₀₀ [X, Y]	F ₁₀ [X, Y] x 10 ⁻¹	F ₂₀ [X, Y] x 10 ⁻²
0.10	6.53	0.451	31	55.23	--	--
0.20	6.52	0.459	31	102.04	--	--
0.30	6.46	0.467	33	192.21	49.23	--
0.40	6.40	0.474	33	333.43	72.67	16.02
0.50	6.33	0.479	32	497.51	90.54	16.43
0.60	6.27	0.481	32	634.02	99.43	15.67

Table 3: Polarographic Characteristics and $F_i[X]$ Function of Pb(II) - o- Chloro Benzoyl Glycinate System

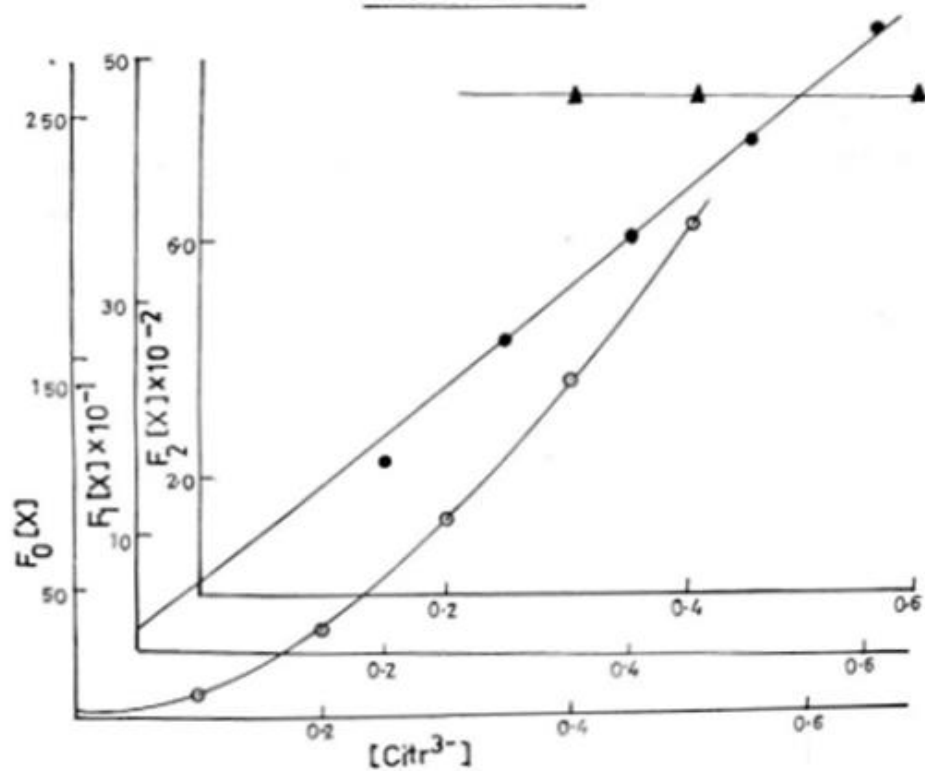
$[0-CBG^-] = 1 \times 10^{-3} M$; $\mu = 2.0$ (NaNO₃); pH = 6.4; Temp. = $25 \pm 0.1^\circ C$; $m = 2.38$ mg/sec; $t = 3.4$ sec, $m^{2/3} t^{1/6} = 2.1$ mg^{2/3} sec^{-1/2} (in 2.0 M. NaNO₃, open circuit); $h_{corr.} = 62.5$ cm.; [Triton X-100] = 1×10^{-3} %.

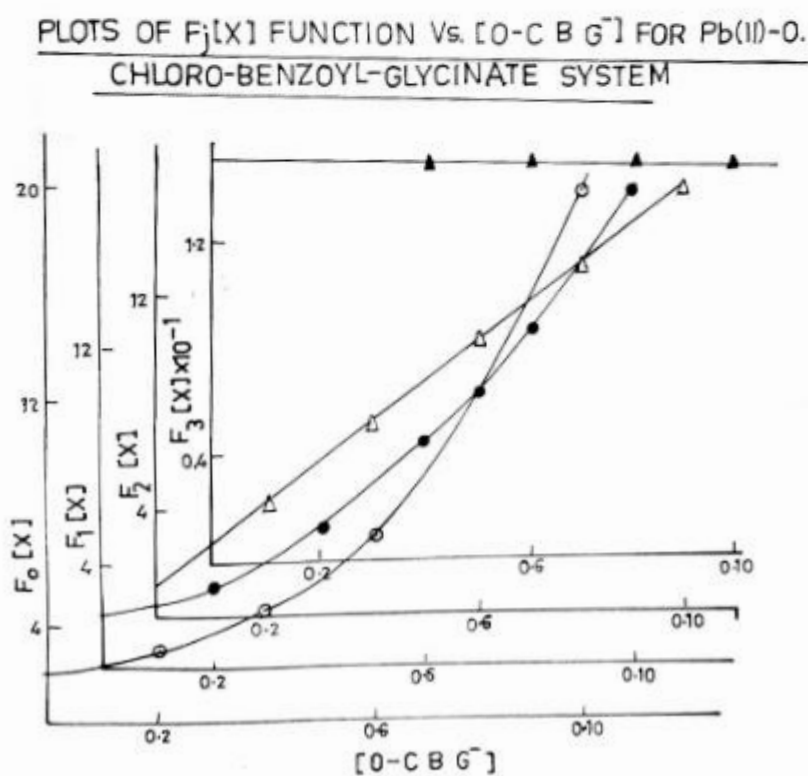
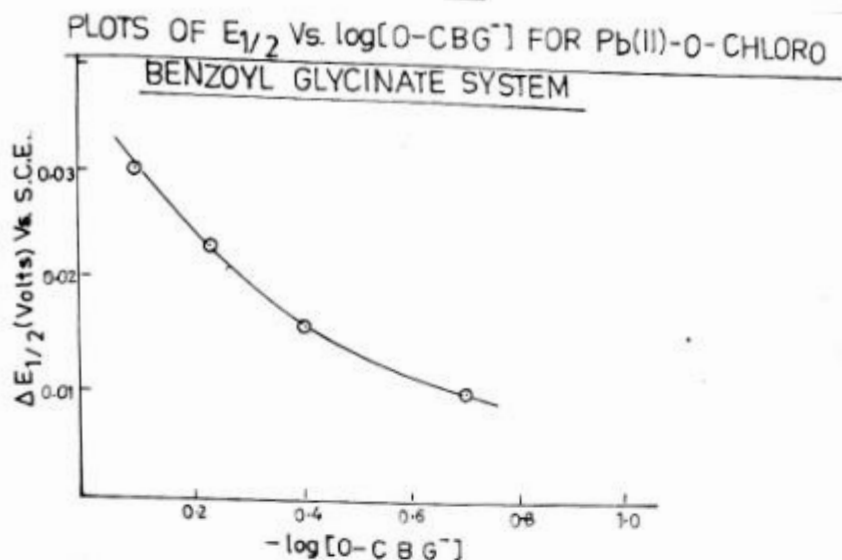
[0-CBG ⁻] M	I _a μA	-E _{1/2} V (S.C.E)	Slope mV	F ₀ [X]	F ₁ [X] x 10 ⁻²	F ₂ [X] x 10 ⁻⁴	F ₃ [X] x 10 ⁻⁶
0.00	6.60	.400	30	-	-	-	-
0.20	5.90	.410	30	2.43			
0.40	5.62	.415	31	3.78	6.95		
0.60	5.58	.424	32	7.67	11.11	14.85	1.60
0.80	5.54	.431	31	13.34	15.42	16.52	1.65
1.00	5.46	.435	31	20.48	19.48	17.28	1.62

PLOTS OF $E_{1/2}$ Vs. $-\log [\text{Cit}r^{3-}]$ FOR Pb(II)-CITRATE SYSTEM



PLOTS OF $F_j[X]$ FUNCTION Vs. $[\text{Cit}r^{3-}]$ FOR Pb(II)-CITRATE SYSTEM





Results and Discussion

The polarographic waves are well defined and diffusion-controlled as evidenced by the linearity of i_d vs $h^{1/2}_{corr}$ plots and their passing through the origin. A perusal of slope values of linear plots of $\log i/i_{d-i}$ vs $-E_{d.e}$ reveals that these lie in the range 30-33 mV thereby showing the reversible nature of the polarographic reduction of Pb(II) in the presence of single as well as mixed ligand systems.

Composition and Stability Constants (Overall) of Simple Complexes of Pb(II) with Citrate and Substituted Benzoyl Glycinate :

The composition and stability constants of simple complexes of Pb(II) with Citrate (Cit^{3-}), o-Chloro Benzoyl Glycine (o-CBG $^-$) were determined separately prior to the study of mixed complexes. Identical conditions were maintained in both the simple and mixed ligand systems.



Polagrams of the solutions containing 10×10^{-3} M Pb(II) and 0.20M o-Chloro Benzoyl Glycine were taken at 6.4 pH values keeping ionic strength constant at $\mu = 2.0$ (NaNO_3) with o-Chloro Benzoyl glycinate and citrate ions. Further, the $E_{1/2}$ of Pb(II) was measured as a function of pH, in the range 5.0 - 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,

An analysis of $F_j[x]$ functions shows the formation of two successive complexes of Pb(II) with Citr^{3-} as follows .

System	Complex Species	Stability Constants
Pb(II)-Citr ³⁻	[Pb(Citr)] ⁻	$\log \beta_1 = 1.5$
	[Pb(Citr) ₂] ⁴⁻	$\log \beta_2 = 2.92$

The degree of formation of 1:1 species decreases with increase in the concentration of the ligand. However, the percentage of the species 1:2 increases as the concentration of the ligand increases.

Pb(II)-o-Chloro Benzoyl Glycinate Systems:

The polarographic characteristics of Pb(II)- o-CBG⁻ system have been presented in table. With the addition of increasing amounts of Benzoyl Glycines $E_{1/2}$ of Pb(II) gets shifted to more negative potentials thereby showing the complex formation. The plots of $E_{1/2}$ vs $\log\text{-CBG}^-$ are smooth curves thereby indicating the formation of successive complexes. The composition and stability constants of the complexes have been determined by Deford and Hume's²⁰ method. The plots of $E_{1/2}$ vs $\log [m\text{-NBG}^-]$ is a straight line (Figure). This shows the formation of a single complex. The composition and stability constant of this complex has been determined by Lingane's²¹ method. An analysis of $F_j[x]$ functions shows the formation of three successive complexes of Pb(II) with o- CBG⁻. The complexes formed are as follows:

System	Complex Species	Stability Constants
Pb(II)- o- CBG ⁻	[Pb(o-CBG)] ⁺	$\log \beta_1 = 0.34$
	[Pb(o-CBG) ₂]	$\log \beta_2 = 1.08$
	[Pb(o-CBG) ₃] ⁻	$\log \beta_3 = 1.18$

Composition and Stability Constants of Mixed Complexes:

The method of Schaap and McMaster has been applied to determine the composition and stability constants of the mixed ligand systems discussed below. Polarographic reduction of Pb(II) in all the mixed ligand systems is reversible and diffusion-controlled. All these systems have been studied under the same experimental conditions as those maintained in simple ones.

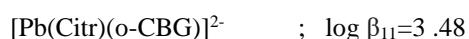
Pb(II)-Citrate -o-Chloro Benzoyl Glycinate System:

The concentration of Citr^{3-} was varied from 0 to 0.60 M keeping $[\text{o-CBG}^-]$ constant at 0.20 M. The values were more negative than those obtained in the absence of $[\text{o-CBG}^-]$ thereby showing the formation of mixed ligand complexes. The polarographic characteristics and $F_{ij}[X, Y]$ functions ($X = \text{Citr}^{3-}$, $Y = \text{o-CBG}^-$) are presented. From the plots of $F_{ii}[X, Y]$ data vs $[\text{Citr}^{3-}]$ the following intercept values for constant A, B and C have been obtained :

Series I: $[\text{o-CBG}^-] = 0.20\text{M}$

$\log A = 1.65$, $\log B = 1.90$, $\log C = 2.20$

The stability constant has been obtained from these constants. Only one mixed complex as noted below is formed.



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: Mixed complexes existing in the solution has the following equilibria. The equilibrium constant ($\log K$ value) is given for each equilibrium:



Equilibria	log K
1. $\text{Pb}^{2+} + \text{Citr}^{3-} + \text{o-CBG} \rightleftharpoons [\text{Pb}(\text{Citr})(\text{o-CBG})]^{2-}$	3.48
2. $[\text{Pb}(\text{Citr})]^{-} + \text{o-CBG} \rightleftharpoons [\text{Pb}(\text{Citr})(\text{o-CBG})]^{2-}$	1.98
3. $[\text{Pb}(\text{Citr})_2]^{4+} + \text{o-CBG} \rightleftharpoons [\text{Pb}(\text{Citr})(\text{o-CBG})]^{2-} + \text{Citr}^{3-}$	0.56
4. $[\text{Pb}(\text{o-CBG})]^{+} + \text{Citr}^{3-} \rightleftharpoons [\text{Pb}(\text{Citr})(\text{o-CBG})]^{2-}$	3.14
5. $[\text{Pb}(\text{o-CBG})_2] + \text{Citr}^{3-} \rightleftharpoons [\text{Pb}(\text{Citr})(\text{o-CBG})]^{2-} + \text{Citr}^{3-}$	3.06

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 Citr^{3-} (equilibria-4) has a stronger tendency to add to $[\text{Pb}(\text{o-CBG})]^{+}$ as compared to o-CBG (equilibria-2) to add to $[\text{Pb}(\text{Citr})]^{-}$. It is also seen that Citr^{3-} can replace o-CBG^{-} (equilibria 5) from its simple complex $[\text{Pb}(\text{o-CBG})_2]$, to form mixed complex $[\text{Pb}(\text{Citr})(\text{o-CBG})]^{2-}$ more easily as compared to o-CBG^{-} .

It seems therefore, that Citr^{3-} is a stronger ligand than o-CBG^{-} . The mixing constant K_M for the reaction:

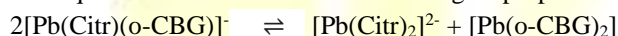


is given by the relation.

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

This works out to be +1.98. A positive value indicates that the mixed complex is more stable than the simple complexes.

The equilibrium constant for the following disproportionation reaction



works out to be -3.61. The large negative log value of equilibrium constant for this reaction indicates that the formation of mixed complexes is strongly favored over the simple complexes.

CONCLUSION

Two successive complexes of Pb(II) with Citrate ions are formed. The equilibrium constant values show that Citrate has a stronger tendency to add to $[\text{Pb}(\text{o-CBG})]^{+}$ as compared to o-CBG to add to $[\text{Pb}(\text{o-CBG})_2]$ to form mixed complex $[\text{Pb}(\text{Citr})(\text{o-CBG})]^{2-}$. Study shows Citr^{3-} is a stronger ligand than o-CBG .

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