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POLAROGRAPHIC STUDY OF MIXED-LIGAND COMPLEX AND STABILITY CONSTANTS OF Pb(II) WITH o-CHLORO BENZOYL GLYCINE [N-(2-CHLOROBENZOYL)-GLYCINE] AND SUCCINATE ION

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Abstract

Stability constants of the binary species Pb(II) -o-chloro benzoyl glycine,Pb(II)-succinate and mixed-ligand complex of Pb (II) -succinate-o-chloro benzoyl glycine have been determined polarographically by the method of Schapp and Mc Masters at temperature 25 ± 0.1°C; The positive values of the mixing constants for the mixed-ligand complexes indicate that the mixed-ligand complexes are more stable than simple binary complexes. The reduction of the simple and mixed complexes is irreversible at a dropping mercury electrode.

Keywords: Mixed Ligand Complexes, Mixing Constants; Stabilization Constants.

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 condition and have indicated the formation of complex species of the 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 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 that 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. Sreenivasulu and co-workers [16] have studied the polarographic determination of stability constants of Pb(II) -4-amino-antipyrine complexes.

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) the Potentially tetradentate ligands have been studied by Bardwell et a1 [19].

The present paper deals with the polarographic investigation of the binary and ternary complexes formed by Pb(II) with)(N-(2-Chlorobenzoyl)-glycine) and succinate ligands.

Experimental

Analytical grade reagents were used to prepare stock solutions in the conductivity water. The concentration of Pb(II) from $Pb(NO_3)2$ was maintained at 1.0×10^{-3}M. Succinic acid was used as the source of succinate[Succ2-]. $NaNo_3$ was used

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as a Supporting electrolyte in the presence of increasing concentration of these ligand at constant ionic strength and pH.

Apparatus and Procedure

Polarograms in all instances were recorded at 25±0.1°C. with a manual polarography (Toshniwal CL02) in conjunction with a polyplex galvanometer (Toshniwal PL 50). A saturated calomel electrode (SCE) was used as the reference electrode. 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. pH of 6.4 was adjusted.

The capillary characteristics of the D.M.E have been mentioned in the subsequent tables. pH of 6.4 was adjusted. The number of electrons n involved in the polarographic reduction of Pb(II) in the Presence of ligands was determined by the millicoulometric method of Devries and Kroon. This gave the value of n equal to 2 in each case.

Results and Discussions

Pb(II)- Succinate System and Pb(II)-o-Chloro Benzoyl Glycine System

The polarographic characteristics of Pb(II)-Succ2- shows that with the addition of increasing amounts of carboxylate ion (Succ2-) E1/2 of Pb(II) is shifted to more negative potentials thereby showing the complex formation. The plot of E1/2 vs log[Succ2], are smooth curves indicating the formation of successive complexes. The composition and stability constants of the complexes were determined by Deford and Humne's [20] method.

The composition and stability constants of simple complexes of Pb(II) with Succinate (Succ2-), o-Chloro Benzoyl Glycine (o-CBG-), were determined separately prior to the study of mixed complexes of Pb(II) with substituted Benzoyl Glycinate and (Succ2-), identical conditions were maintained in both the simple and mixed ligand systems. Polagrams of the solutions containing 10x10-3 M Pb(II) and 0.20M o-Chloro Benzoyl Glycine were taken at 6.4 pH values keeping ionic strength constant at $\mu = 2.0$ ($NaNO_3$) Further, the E1/2 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 E1/2 remains unchanged. This shows that OH- does not enter into coordination with Pb(II) and Pb(II) exists as the Pb2+ aqueous ion in the absence of the ligand.

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

Pb2+] = 1 x 10-3 M; μ = 2.0 (NaNO3); pH = 6.4; Temp.= 25 ± 0.1°C; m = 2.38 mg/sec; t=3.4 Sec., m2/3 t1/6 = 2.1 mg2/3 sec-1/2 (in 2.0 M. $NaNO_3$, open circuit); hcorr. = 62.5 cm; [Triton X-100] = 1 x 10-3 %.

[Citr3-] M	Id μA	-E1/2 V (S.C.E)	Slope mV	Fo[X]	F1[X] x 10^{-2}	F2[X] x 10^{-3}
0.00	7.10	0.400	30	--	--	--
0.10	6.36	0.449	30	53.0	--	--
0.20	6.28	0.468	31	220.9	109.9	--
0.30	6.15	0.478	32	580.7	19.,2	56.42
0.40	6.07	0.489	32	1190.5	297.4	68.39
0.50	5.97	0.496	32	2105.7	421.9	79.11

An analysis of Fj[x] functions show the formation of three successive complexes of Pb(II) with succ2- as follows:

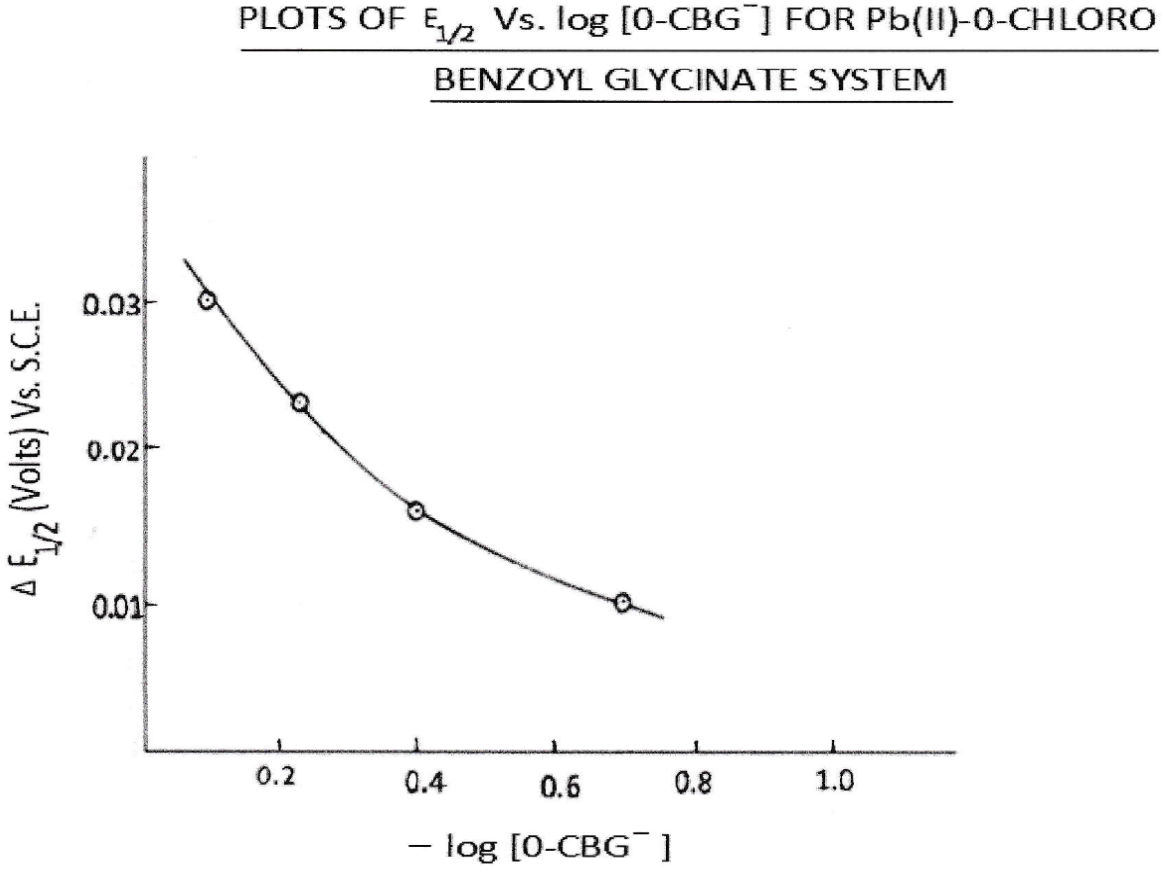
Pb(II)-$Succ^{2-}$System	Complex Species	Stability Constants
	[Pb(Succ)]	log β1 = 2.36
	$[Pb(Succ)_2]^{2-}$	log β2 = 3.32
	$[Pb(Succ)_3]^{4-}$	log β3 = 4.08

The degree of formation α (%) of various complex species as a function of log [Succ2-] shows that the degree of formation (percentage) of 1:1 species decreases as the concentration of Succ2- increases. On the other hand, the percentage of species 1:2 increases with increasing concentration of Succ2- but beyond a certain concentration of the ligand, the degree of formation of this species gets retarded. However, the percentage of the species 1:3 goes on increasing as the concentration of the ligand increases.

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

[Pb2+] = 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., m2/3 t1/6 = 2.1 mg2/3 sec-1/2 (in 2.0 M. $NaNO_3$, open circuit); hcorr. = 62.5 cm; [Triton X-100] = 1 x 10-3 %.

[0-CBG-] M	Id μA	-E1/2 V (S.C.E)	Slope mV	Fo[X]	F1[X] x 10^{-2}	F2[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	0.424	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



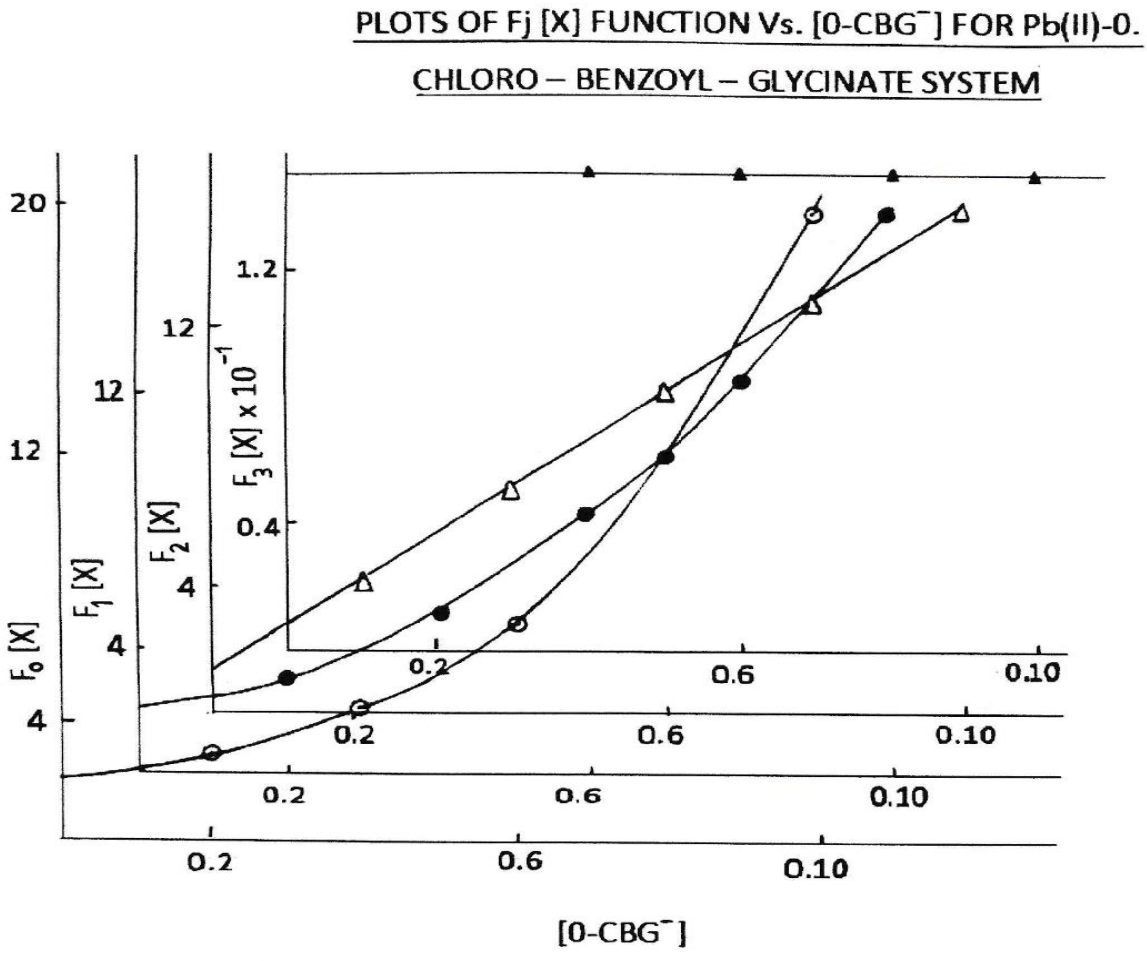


Table 3: Polarographic Characteristics and F_{ij}[X, Y] Functions of Pb(II)-Succinate-o-Chloro Benzoyl Glycinate System

[Pb2+] = 1 x 10-3 M; μ = 2.0 (NaNO3); pH = 6.4; Temp.= 25 ± 0.1°C; m = 2.38 mg/sec; t = 3.4 Sec., m2/3 t1/6 = 2.1 mg2/3 sec-1/2 (in 2.0 M. NaNO3, open circuit); hcorr. = 62.5 cm; [Triton X-100] = 1 x 10-3 %.

[Succ2-] M	Id μA	-E1/2 V (S.C.E)	Slope mV	F00[X, Y]	F10[X, Y] x 10^{-1}	F20[X, Y] x 10^{-2}	F30[X, Y] x10^{-4}
[o-CBG-] = 0.20M							
0.10	6.40	0.453	31	74.20	-	-	-
0.20	6.10	0.472	31	341.61	171.10	-	-
0.30	6.01	0.486	31	882.00	295.09	81.52	-
0.40	6.01	0.493	31	152.42	37.59	8.71	1.4
0.50	5.91	0.501	32	289.01	57.56	10.91	1.5
[o-CBG-] = 0.40M							
0.10	6.80	0.453	31	7.01	-	-	-
0.20	6.63	0.472	31	31.85	14.87	-	-
0.30	6.57	0.487	32	81.71	26.71	4.81	1.25
0.40	6.42	0.493	32	143.01	35.32	5.71	1.21
0.50	6.41	0.498	33	246.31	48.91	7.30	1.26

The of C-V curves of Pb (II) in the presence of single as well as mixed ligand systems show that in each case the polarographic waves are well defined and diffusion-controlled as evidenced by the linearity of id vs h1/2corr plots and their passing through the origin. A perusal of slope values of linear plots of logi/id-i vs – Ed.e reveals that these lie in the range 30-33 mV thereby showing the reversible nature of the polarogaphic reduction of Pb(II) in the presence of single as well as mixed ligand systems.

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

After studying simple complexes of Pb(I1) with o-chloro benzoyl glycine and succinate separately, attempts have been made to study the mixed complexes of Pb(II) with [o-CBG-] and succinate present together. The concentration of Succ2 was varied from 0 to 0.60 M keeping [o-CBG-] constant at 0.20 M. The E1/2 values were more negative than those obtained in the absence of [o-CBG-] (table) thereby showing the formation of mixed ligand complexes. The system is again repeated keeping o-CBG- constant at 0.40 M. The polarographic characteristic and Fij[X, Y] functions (X = Succ2-,Y = o-CBG-) are presented in Table From the plots of Fij[X, Y] data vs functions [Succ2-]) the following intercept values for constant A,B,C and D have been obtained :

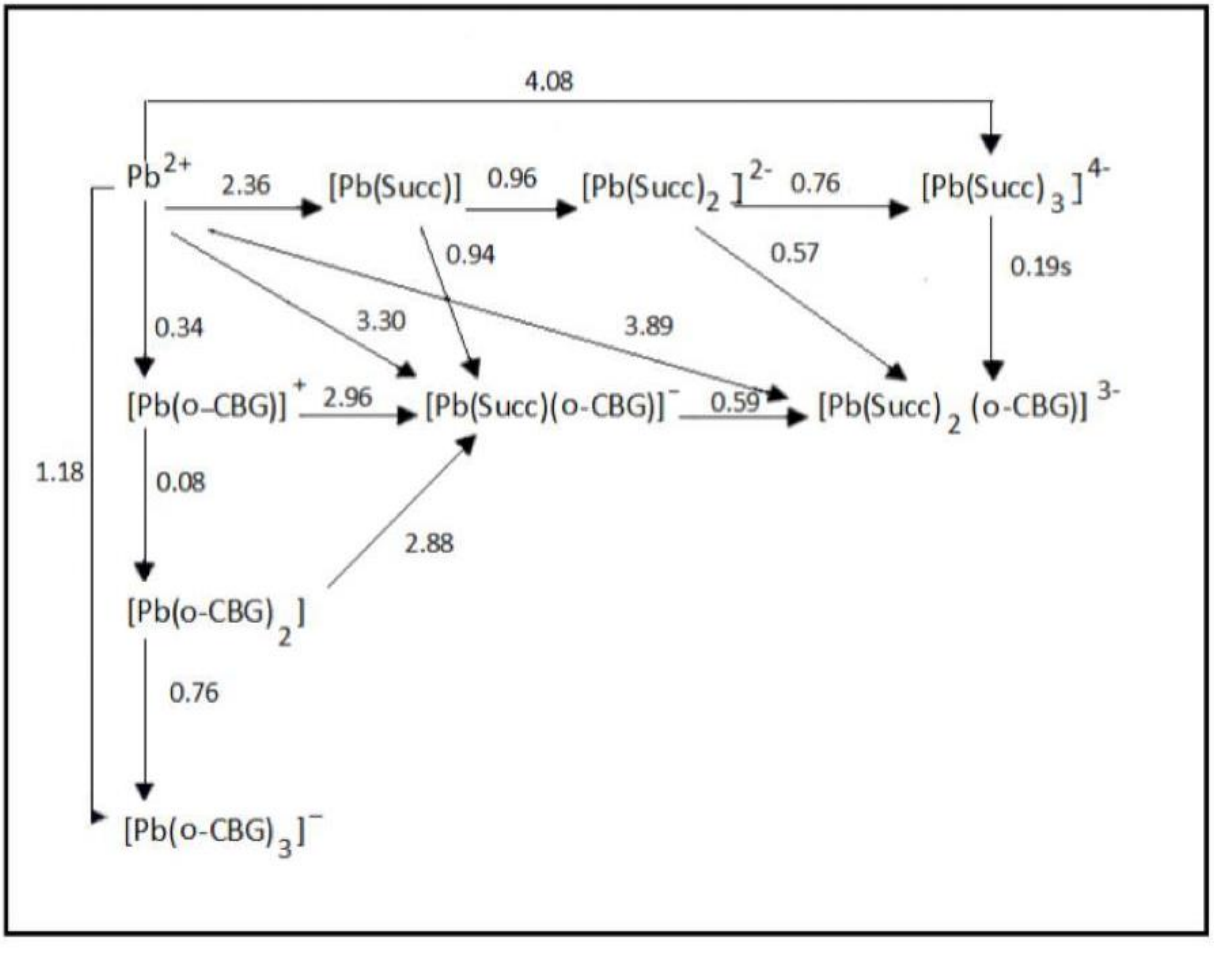
Series I: [o-CBG-] = 0.20 M, log A = 0.30, log B = 2.70, log C = 3.56, log D = 4.20

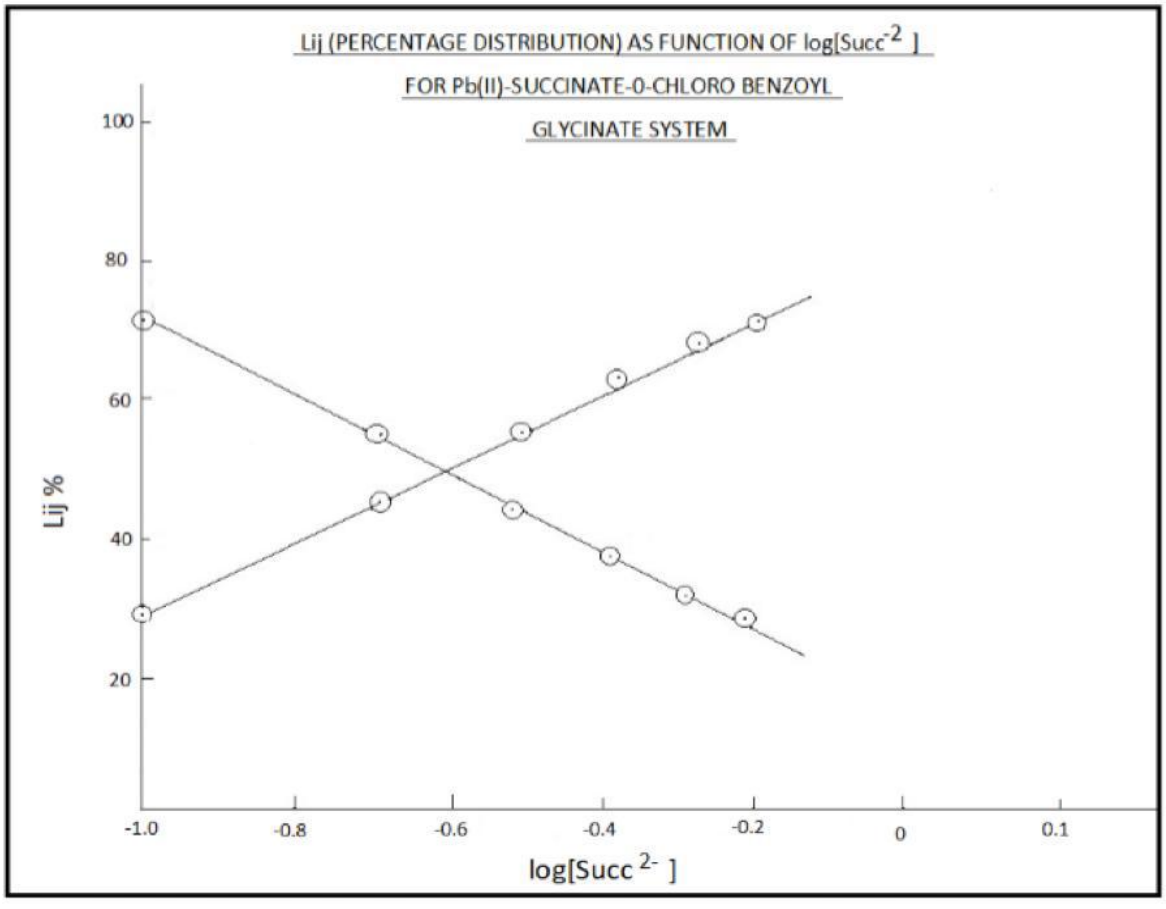
Series II: [o-CBG-] = 0.40 M, log A = 1.30, log B = 2.78, log C = 3.65, log D = 4.20

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

[Pb(succ)(o-CBG)]- ; log β11 = 3.30
[Pb(Succ)2(0-CBG)]3 ; log β21 = 3.89

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 for





The mixed complexes existing in the solution have the following eqilibria. The equilibrium constant (log K) value is given in each case for each equilibrium.

Equilibrium			**log K**
Pb2+ + Succ2- + o-CBG-	⇌	[Pb(Succ)(o-CBG)]-	3.30
Pb2+ +2Succ2- + o-CBG-	⇌	[Pb(Succ)2(o-CBG)]3-	3.89
[Pb(Succ)] + o-CBG-	⇌	[Pb(Succ)(o-CBG)]-	0.94
[Pb(Succ)2]2- + o-CBG-	⇌	[Pb(Succ)2(o-CBG)2]3-	0.57
[Pb(o-CBG)]+ + Succ2-	⇌	[Pb(Succ)(o--CBG)]	2.96
[Pb(o-CBG)2] + Succ2-	⇌	[Pb(Succ)(o--CBG)]- + o-CBG-	2.88

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 Succinate (equilibrium 5&6) has a stronger tendency to add to [Pb(o-CBG)]+ as compared to that of o-CBG- to add to [Pb(Succ)]. Succ2- can replace o-CBG- from its simple complexes to form mixed complexes. However, o-CBG- can not replace Succ2- from its simple complexes. It seems therefore, that Succ2- is a stronger ligand than o-CBG-.

The mixing constant KM for the relation
½[Pb(Succ)2]2- + ½[Pb(o-CBG)2] ⇌ [Pb(Succ)(o-CBG)]-

is given by the relation:

$\log KM = \log \beta 11 - \frac{1}{2} (\log \beta 20 + \log \beta 02)$

This works out to be +1.43. A positive value of logKM indicates that the mixed complex [Pb(Succ)(o-CBG]- is more stable than the simple complexes, [Pb(Succ)2]2- and [Pb(o-CBG)2].

The equilibrium constant for the following disproportionation reactions
2[Pb(Succ)(o-CBG)]- ⇌ [Pb(Succ)2]2- + [Pb(o-CBG)2]
2[Pb(Succ)2(o-CBG)]3- ⇌ [Pb(Succ)314- +[Pb(o-CBG)2]+Succ2-
work out to be -2.86 and -3.28 respectively.

The variation of αij, with log[Succ2-] indicate that with increasing concentration of Succ2- the percentage of both the species tend to become the same.

Conclusion

The study indicates that the formation of mixed complexes, [Pb(Succ)(o-CBG)]- and $[Pb(Succ)_{2(}o\text{-}CBG)]^{3-}$ are strongly favored over the simple complexes Further, the complex species $[Pb(Succ)_2(o\text{-}CBG)]^{3-}$ is more stable than the species $[Pb(Succ)(o\text{-}CBG)]^{-}$].

The variation of αij, with log[$Succ^{2-}$] indicate that with increasing concentration of $Succ^{2-}$ the percentage of both the species tend to become the same.

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