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POLAROGRAPHIC STUDIES OF MIXED COMPLEXES OF Cd(II) WITH o-NITRO BENZOYL GLYCINE AND SUCCINATE IONS USING KCI AS A SUPPORTING ELECTROLYTE

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Abstract

Stability constants of the binary species Cd(II) -o- Nitro benzoyl glycine, Cd(II)-succinate and mixed-ligand complex of Cd(II) -succinate-o-Nitro 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, Stability Constants.

Introduction

Cadmium, which is not an essential trace element in biological systems, is highly toxic. The liver and kidney are the two main organs where cadmium accumulates. The half-life of cadmium in Mall has been estimated to be 16 -33 years (Kellstrom and Norberg, 1978) and with constant exposure, accumulation may take place over a lifetime. The survey of literature on cadmium toxicity clearly shows that this heavy metal is implicated as a causative agent of several pathological disorders in human beings. Brief exposure develops a persistent cough and chest pain. Heating of cadmium metal or alloys causes cadmium poisoning. Dusts or fumes produced during the smelting of cadmium ores. Paints and alloys containing cadmium are also poisonous. poisoning by cadmium may also cause dermatitis, skin ulceration and teeth decolorization. The removal of metal by proper complex formation is the only possible treatment for cadmium poisoning. Cadmium forms several complexes with various ligands. In the human body there are numerous ligands to compete and as such mixed ligands complex formation is favored. Thus, the problem of cadmium removal is a problem of mixed ligand complex formation.

The studies on the mixed ligand complexes of cadmium with bicarboxylates, polycarboxylates, thiocynates thiosulphates, salicylates vitamins and amino acids have been carried out polarographically by many workers [1-16] Taneja and coworkers [17-18] investigated mixed ligand complexes of cadmium with reactive methylene compounds of malonamic acid series and carboxylic acid.

The complexation of Cd(II) and Zn(II) with solo chrome mordant dye were studied by Gupta and Raina [19]. The mixed ligand complexes of Cu(II) and Cd(II) with acids and 2- amino-3-hydroxy pyridine were studied by Bansal and co-workers [20]. Agarwal and Kumar [21] investigated the polarographic behavior of Cd(II) and Pb(II) with 2-amino-3- hydroxy pyridine. Thermodynamic parameters have been evaluated in the mixed ligand complexes of propylene diamine and malonate, succinate by Gaur et. al. [22-26]. Abdul Hamid and co-workers [27] carried out polarographic study of binary and ternary complexes of Cd(II) salicylidene tris methyl amine chloride. Singh and co-workers [28] studied polar graphically the mixed ligand complexes of Cd(II) with picolines and carboxylate ions. A mixed system of cadmium with bicarboxylic acids, amino acids with O, N containing donor atoms have been studied by Gupta and co-workers [29-31].

A literature survey reveals that simple complexes of Cd(II) with Hippuric acid have been studied palaeographically and reported. The study of complexes of Cd(II) with o-Nitro Benzoyl glycine (2-Nitro Hippuric acid) and succinate could add to understand the possibility of complex formations in the biochemical systems.

Experimental

All the chemicals used were of analytical reagent grade and their stock solutions were prepared in conducting water. The concentration of Cd(II) (from $CdCl_2$) was maintained at 1.0 x 10^{-3} M. Sodium salts of succinic acid were used as sources of Succinate ($Succ^{2-)}$, KCl was used as a supporting electrolyte and also to maintain a constant ionic strength of ($\mu = 2.0$).

For preparing o-NBG first o-Nitro Benzoic acid was added in dry Benzene and Thionyl Chloride. The solution was then refluxed for about 2.5 hours on a boiling water bath until the evolution of gases ceased. Excess Benzene was distilled off and the residual acid chloride was used for preparing o-Nitro Benzoyl glycine. Glycine was dissolved in

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sodium hydroxide and o-Nitro Benzoyl Chloride was added in small portions and the flask was shaken vigorously after each addition. After this o-NBG was precipitated by the slow addition of conc. HCl. The product was collected under suction and recrystallized from hot water yielding shining white needles.

The polarograms of the solutions were taken in the presence of increasing concentrations of the ligand at constant ionic strength and pH according to the standard procedure. Triton X-100 (1 x 10^{-3} %) was used as a maxima suppressor. The measurements were made at a constant temperature (25 ± 0.1 °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).

Table 1: Polarographic Characteristics and $F_j[X]$ Function of Cd(II) - Succinate System

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

[Succ2-] M	I_d µA	$E_{1/2}$ Vs (S.C.E)	Slope mV	$F_{00}[X]$	$F_{10}[X]$ x 10^{2-}	F_{20} [X] x 10^{3-}	F_{30} [X] x 10^{-4}
0.00	9.80	0.600	30	--	--	--	--
0.02	9.48	0.630	30	10.67	--	--	--
0.05	9.21	0.648	31	44.57	8.71	--	--
0.1	8.75	0.665	31	176.28	17.52	1.25	--
0.2	8.35	0.667	32	1024.5	51.17	2.30	--
0.3	8.07	0.700	32	2920.11	97.30	3.07	7.60
0.4	7.75	0.710	33	6615.15	165.36	4.01	7.52
0.5	7.75	0.718	33	12357.3	247.12	4.84	7.70
0.6	7.61	0.724	32	20041.7	334.01	5.48	7.48

Table 2: Polarographic Characteristics and Fj[X] Function of Cd(II)- o-Nitro Benzoyl Glycinate System

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

[o-NBG] M	I_d µA	E1/2 Vs (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	8.45	0.600	32	-	-	-	-
0.002	8.20	0.626	33	7.80	-	-	-
0.005	8.15	0.636	31	17.08	32.16	4.32	-
0.01	7.81	0.647	31	42.00	41.00	11.00	4.00
0.02	7.07	0.658	32	109.19	54.09	12.04	4.02
0.03	6.69	0.668	33	251.39	83.46	17.82	4.60
0.04	6.58	0.674	30	407.6	104.65	22.66	4.60

Polarograrm of solution containing (i) 1.0 x 10^{-3} M Cd(II) and 0.005M o-NBG^{-} and was taken at different pH values keeping ionic strength constant at µ= 2.0(KCl).

It was found that the negative shift in E1/2 was maximum at pH 6.4. Hence this pH was chosen for studying the simple and mixed systems.

Results and Discussion

The morphology of C-V curves of Cd(II) in the presence of single as well as mixed ligand systems. In each case polarographic waves are well defined. Plots of id VS h_{corr} ½ are linear and pass through the origin showing that the polarographic wave are diffusion- controlled.

Slope values of linear plots of log i/(id-i) vs E d.e. reveal that these lie in the range 30-33 mV thereby showing the reversible nature of the polarographic reduction of Cd(II) in the presence of single as well as mixed ligand systems.

Composition and Stability Constants (Overall) of Simple Complexes of Cd(II) with Succinate and o-Nitro Benzoyl Glycine

The composition and stability constant of simple complexes of Cd(II) with o- Nitro Benzoyl glycinate (o-NBG) and Succinate ($Succ^{2-}$), were determined separately prior to the study of mixed complexes. Identical conditions were maintained in both the simple and mixed ligand systems.

Cd (II)- Carboxylate Ion Systems

The polarographic characteristics of Cd(II)-$Succ^{2-}$ show that with the addition of increasing amounts of the carboxylate ions, $E_{1/2}$ of Cd(II) is shifted, in each case, to more negative potentials thereby showing the formation of complexes.

In Cd(II)-$Succ^{2-}$ system The plots of $E_{1/2}$ vs concentration of carboxylate ion are smooth curves thereby indicating the formation of successive complexes

The composition and stability constants of the complexes have been determined by Deford & Hume's method by Lingane's method. An analysis of F_j [X] functions show the formation of following complexes of Cd(II) with $Succ^{2-}$ as detailed below

System	Complex Species	Stability Constant
Cd(II)- $Succ^{2-}$	[Cd(Succ)] $[Cd(Succ)]^{2-}$ $[Cd(Succ)_3]^{4-}$	**Log β_1** = 2.6 **Log β_2** = 3.9 **Log β_3** = 4.8

The result shows that the values of Log β_1, Log β_2 and Log β_3 in respect of Cd(II)- succinate system are in close agreement with the values reported by Schaap and Mc-Masters on this system. These values (log) at 25°C and µ = 1.0 are 2.61 ± 0.1, 4.41±0.1 and 5.04 ± 0.1 respectively. The degree of formation αj(%) of various complexes species as a function of logarithum of [Succ 2-] shows that percentage of 1:1 species decreases as the concentration of carboxylate ion increases. On the other hand, the percentage of species 1:2 increases with increasing concentration of carboxylate ions 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 carboxylate ion increases.

$E_{1/2}$ of Cd(II) gets shifted to more negative potentials in the Polarographic characteristics of Cd (II) -o-NBG system with the increasing amount of Benzoyl Glycinates. thereby showing the complex formation. The plots of $E_{1/2}$ vs log[o-NBG^{-}] and l are smooth curves, thereby indicating the formation of successive complexes. The composition and stability constants of the successively formed complexes have been determined by Lingane's method. An analysis of F_j[X] functions reveal the formation of successive complexes of Cd(II) with o-$NBG^{-\cdot}$ as detailed below:

System	Complex Species	Stability Constant
Cd(II)-o- NBG^{-}	$[Cd(o\text{-}NBG)]^{+}$ $[Cd(o\text{-}NBG)_2]$ $[Cd(o\text{-}NBG)_3]^{-}$	**Log β_1** = 3.4 **Log β_2** = 4.7 **Log β_3** = 6.6

The degree of formation (%) of various complexes species as a function of log of [o--NBG^{-}] show that as the concentration of ligand increases, the degree of formation of 1:1 and 1:2 species decreases as that of 1:3 increases.

Composition and Stability Constants (Overall) of Mixed Complexes

The method of Schaap and Mc-Master has been applied to determine the composition and stability constants of the mixed ligand system of **Cd(II)-Succinate-o-Nitro Benzoyl glycine** polarographic reduction of Cd(II) in studied mixed ligand systems is reversible and diffusion controlled.

Cd(II)-Succinate-o-Nitro Benzoyl Glycine System

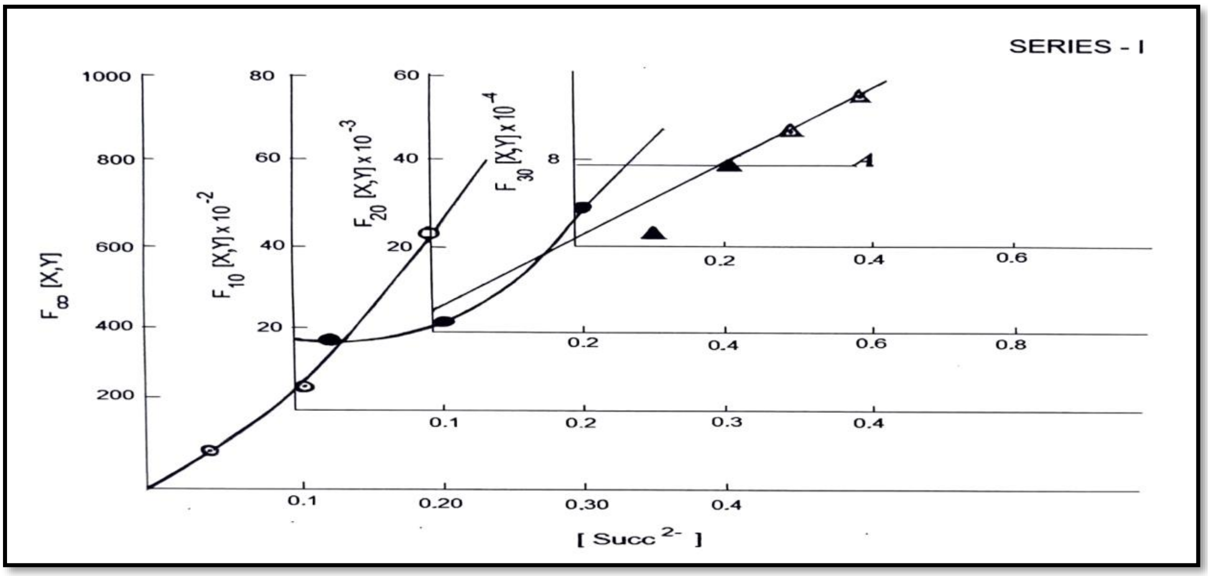
Table 3: Polarographic Characteristics and F_{ij}[X, Y] Function of Cd(II)- Succinate-o-Nitro Benzoyl Glycinate System

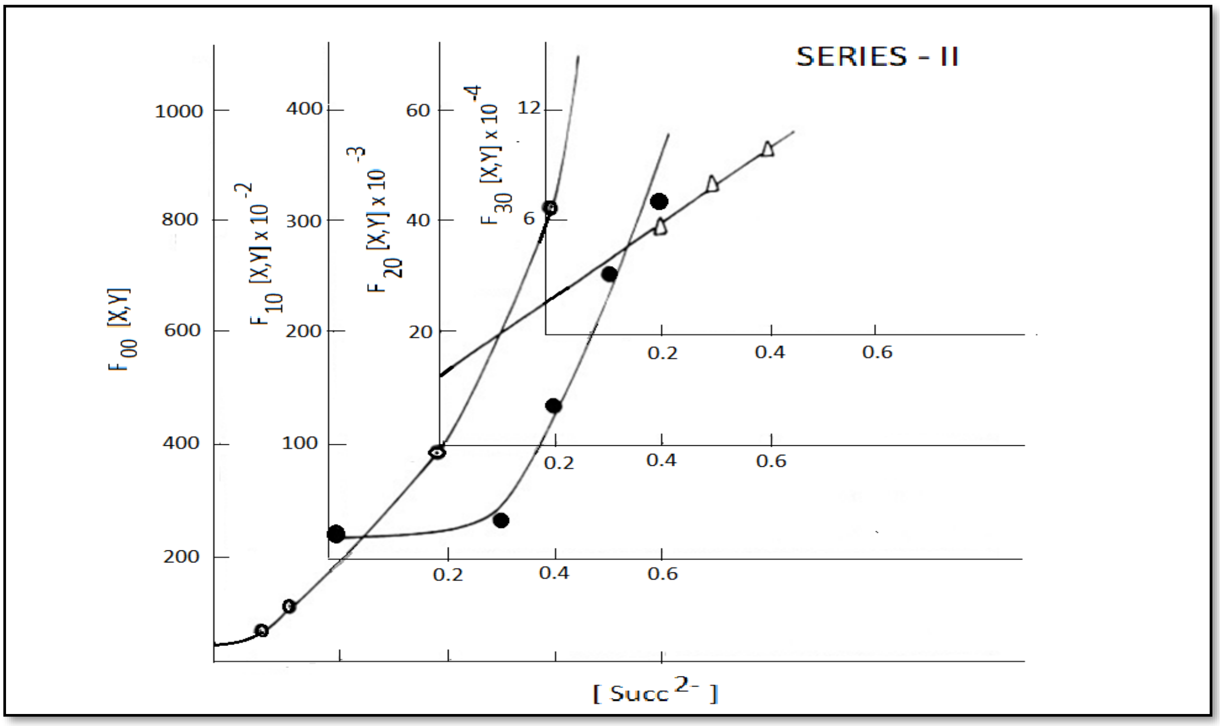
[Cd^{2+}] = 1 x 10^{-3} M; μ = 2.0 (KCl); pH = 6.4; Temp.= 25 ± 0.1°C; m = 2.38 mg/sec; $m^{2/3}$ t $^{1/6}$ = 2.1 $mg^{2/3}$ $sec^{-1/2}$ (in 2.0 M.KCl, open circuit); h_{corr} = 62.5 cm; [Triton X-100] = 1 x 10^{-3} %.

[Succ2-] M	ld µA	-E1/2 V (S.C.E)	Slope mV	F_{00}[X, Y]	F_{10}[X, Y] x 10^{-2}	F_{20}[X, Y] x 10^{-3}	F_{30}[X, Y] x 10^{-4}
Series-I [o-NBG-] = 0.005 M							
0.00	8.42	0.650	31	49.01	--	--	--
0.10	8.02	0.672	32	240.71	21.97	--	--
0.20	7.32	0.682	31	625.17	30.25	--	--
0.30	6.01	0.701	32	2558.58	84.62	22.87	--
0.40	5.75	0.712	33	6621.09	165.02	37.25	7.30
0.50	5.62	0.720	33	12551.6	250.63	46.93	7.78
0.60	5.55	0.726	33	20197.6	336.29	53.38	7.56
Series-I [o-NBG-] = 0.01 M							
0.02	8.45	0.651	31	53.01	--		-
0.05	8.35	0.660	32	108.10	--	-	__
0.10	8.22	0.670	33	238.77	--		__
0.20	8.08	0.676	31	308.38	--		--
0.30	7.88	0.685	31	802.63	26.72	39.06	
0.40	7.68	0.710	32	5766.86	144.14	32.28	7.21
0.50	7.55	0.720	32	12781.7	255.61	48.1	7.82
0.60	7.45	0.725	33	19118.3	318.62	50.6	7.71

The concentration of $Succ^{2-}$ varied from 0 to 0.6M, keeping [$o-NBG^{-}$] constant at .005M. The $E_{1/2}$ values were more negative than those obtained in the absence of $Succ^{2-}$ thereby showing the formation of mixed complexes. The system was repeated at another concentration of $o-NBG^{-}$ (0.01M). Polarographic characteristics and F_{ij}[X, Y] functions (X = $Succ^{2-}$, Y = $o-NBG^{-}$) of this system at fixed concentrations of $o-NBG^{-}$ (0.005M and 0.01M) have been presented in Table 3. From the plots of F_{ij}[X, Y] data vs $Succ^{2-}$ the following intercept values for constants A, B, C and D are obtained.

PLOTS OF Fij [X, Y] FUNCTION FOR Cd (II)- SUCCINATE o-NITRO BENZOYL GLYCINATE





Series I: [o-NBG] = 0.005M(Fixed)
log A = 1.30; log B = 3.20; log C = 3.77; log D = 4.92

Series II: [o-NBG] = 0.01M(Fixed)
log A = 1.60; log B = 3.30; log C = 3.69; log D = 4.84

The satiability has been obtained from these constants.

The mixed complexes as noted below are formed:
$[Cd(Succ)(o\text{-}NBG)]^{-}$ **$^{log}\beta_{11}= 5.72$**
$[Cd(Succ)_2(o\text{-}NBG)]^{3-}$ **$^{log}\beta_{21}= 4.66$**

Cd(II) is hexa co-ordinated. Three mixed complexes existing in the solution have following equilibria. The equilibrium constant, K (log value) is given in each case for each equilibrium

SNo	**Equilibria**	**logK**
1	$Cd^{2+} + Succ^{2-} + o\text{-}NBG^{-} \rightleftharpoons [Cd(Succ)(o\text{-}NBG)]$	5.72
2	$Cd^{2+} + 2\ Succ^{2-} + o\text{-}NBG \rightleftharpoons [Cd(Succ)_2\ (o\text{-}NBG)]^{3-}$	4.66
3	$[Cd(o\text{-}NBG)]^{+} + Succ^{2-} \rightleftharpoons [Cd(Succ)\ (o\text{-}NBG)]^{-}$	2.32
4	$[Cd(Succ)] + o\text{-}NBG^{-} \rightleftharpoons [Cd(Succ)(0\text{-}NBG)]^{-}$	3.12
5	$[Cd(Succ)\text{-}_2]^{2-} + o\text{-}NBG^{-} \rightleftharpoons [Cd(Succ)_2\ (o\text{-}NBG)]^{3-}$	0.76
6	$[Cd(o\text{-}NBG)_2] + Succ^{2-} \rightleftharpoons [Cd(Succ)\ (o\text{-}NBG)]^{-} + o\text{-}NBG^{-}$	1.02

From the above equilibrium constant values the tendency of a ligand to add to a complex and to substitute another ligand may be compared. The relative tendencies of $Succ^{2-}$ and $o\text{-}NBG^{-}$ to add to $[Cd(o\text{-}NBG)]^{+}$ $[Cd(Succ)]$ and $[Cd(Succ)_2\ ]^{2}$. (equilibrium 3-5) can be compared, it is seen that $Succ^{2-}$ has a stronger tendency to add to $[Cd(o\text{-}NBG)]^{+}$ and $[Cd(o\text{-}NBG)_2]$ as compared to that of o-NBG. to add to $[Cd(Succ)]$ and $[Cd(Succ)_2]^{2-}$ and that $Succ^{2-}$ can replace o-NBG from its simple complexes. Therefore, it seems that $Succ^{2-}$ is a stronger ligand than $o\text{-}NBG^{-}$.

The mixing constant Km for the reaction

$1/2[Cd(Succ)_2]^{2-} + 1/2[Cd(o\text{-}NBG)_2] \rightleftharpoons [Cd(Succ)(o\text{-}NBG)]^{-}$ is given by the relation:

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

and works out to be +1.42.

The positive value of log K_M shows that the mixed complex $[Cd\ (Succ)(o\text{-}NBG)]^{-}$ is more stable than the simple binary complexes **$[Cd(Succ)_2]^{2-}$ and $[Cd(Succ)_2(o\text{-}CBG)]^{3-}$**

The equilibrium constant for the following disproportionation reactions

$2[Cd\ (Succ)(o\text{-}NBG)]^- \rightleftharpoons [Cd\ (Succ)_2]^{2-} + [Cd(o\text{-}NBG)_2]$

$2[Cd\ (Succ)_2(o\text{-}NBG)]^{3-} \rightleftharpoons [Cd\ (Succ)_3]^{4-} + [Cd(o\text{-}NBG)_2] + Succ^{2-}$

Work out to be -2.84 and-0.18 respectively. The large negative log values of equilibrium constants for these reaction indicates the formation of mixed complexes $[Cd(Succ)(o\text{-}NBG)]^-$ and $2[Cd\ (Succ)_2(o\text{-}NBG)]^{3-}$.

Conclusion

Stability constants of the binary species Cd (II) -o-Nitro benzoyl glycine, Cd(II)-succinate and mixed-ligand complex of Cd(II) -succinate-o-Nitro benzoyl glycine have been determined. The positive value of log K_M shows that the mixed complex **$[Cd\ (Succ)(o\text{-}NBG)]^-$** is more stable than the simple binary complexes **$[Cd(Succ)_2]^{2-}$ and $[Cd(Succ)_2(o\text{-}CBG)]^{3-}$**.

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