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Polarographic study of ternary complexes of Cd (II) - malonamic and carboxylic acid

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ABSTRACT

The mixed system Cd (II) Malonamate-Oxalate has been studied polarographically at constant ionic strength μ=2.0 ($NaNO_3$) and constant pH 5.6. The reduction of the complexes at d.m.e is reversible and diffusion - controlled. Two mixed complexes viz $[Cd(OX)\ (EPM)_2]^{2-}$ and $[Cd\ (OX)_2\ (EPM)]^{3-}$ are formed. Their overall stability constant at 25°C are log b12= 9.95 and log b21 = 8.75 respectively.

Simple complexes of Cd (II) Malonamate and Oxalate has been studied polarographically but the mixed complexes with the said ligands have not been reported so far. With this end in view, the present study has been under taken.

Key words: Polarography-Oxalic acid and Malonamic acid

INTRODUCTION

A number of worker[1-5] have investigated the mixed complexes of Cd (II) with various ligands. The stability constant of mixed ligand complexes of Cd (II) with Malonic acid and some amino acid were determined by Ramanujam and Krishna[6]. Kumaretal[7-8] Rao[9] and Sharma *et al.*,[10] have been reported the polarography of mixed complexes of various metals. Paliwal[11] has reported the polarographic studies of mixed ligand complexes of Cd (II) with propylene diamine the polarographic studies of mixed polarographic studies of mixed complexes of Cd (II) with oxalate and N-(2-ethoxy) phenyl melanomata are still lacking. The communication deals with the studies of mixed ligand complexes of Cd (II) with oxalate and N-(2-ethoxy) phenyl melanomata.

Experimental

All the chemicals used, were analytical Reagent grade. Their stock solutions were prepared in conductivity water. The ionic strength was maintained constant μ=2.0 using KCl as supporting elerolyte. The concentration of Cd (II) was kept constant i.e 1×10^{-3} M. Polarogram were obtained by means of a manual polarography (Toshniwal CLO-2A) in conjunction with Toshniwal polyflex galvanometer (PL-50). Purified nitrogen was used for reference electrode. The d.m.e had the following characteristics in (2.0 MK Cl, open circuit); m = 2.404 mg/sec, t = 3.4sec, $m^{2/3} t^{1/6} = 2.2\ mg^{2/3}\ sec^{-1/2}$, h_{corr} = 64.8 cm.

RESULTS AND DISCUSSION

The reduction of Cd (II) is reversible and diffusion controlled. The polarogram of the solutions containing depolariser and the ligands were recorded at different pH values. It was found that the maximum shift occrued at pH = 5.6. Hence this pH was selected for the study. The ionic strength was kept at μ=2.0 to enable the addition of larger concentration of ligands ions.

Stability constants of simple complexes of Cd (II) with melanomata and oxalate ions were determined separately prior to the study of mixed ligand system. Identical conditions were maintained in both the simple and mixed system.

Cu(II)-Oxalate system

A series of polarograms were obtained at variying concentrations of at constant ionic strength μ=2.0 and at constat pH = 5.6. A plot of $E_{½}$ Vs log [OX^{2-}] was a smooth case which indicated the formation of successive complexes Deford and Humes[3] method was applied for the determination of composition and stability of the complexes. An analysis of Fj[X] function (Table 1) reveals the formation of there successive viz [Cd(OX)], $[Cd(OX)_2]^{2-}$ and $[Cd(OX)_3]^{4-}$ with stability constant $\log\beta_1$= 3.0 $\log\beta_2$=5.5 respectively.

Cd (II)-N-(2-ethoxy) Malonanate system)

A series of polarograms were obtained at varying concentraitons of EPM^- at μ=2.0 and at pH = 5.6. A plot of $E_{½}$ Vs log [EPM^-] was straight line which indicated the formation of single complex in each case. The composition and stability constant of the this complex had been determined by Lingane's[4] method. The Fj [x] functions of simple complex of Cd (II) with EPM^- have been presented in Table 2. The composition of single complex of Cd (II) with EPM^- workout be $[Cd(EPM)_2]$ with stability constant log β_2 = 6.92.

Table 1: Polarographic charactersitcs and F_j [x] functions of Cd (II) - Oxalate system

[Cd^{2+}] - 1×10^{-3}M, μ = 2.0 ($NaNO_3$), pH =5.6, Temp = 25 ± 0.1°C, h_{corr}= 64.8 cm, m = 2.404 mg/sec, t = 3.4 sec, $m^{2/3}$ $t^{1/6}$ = 2.2 $mg^{2/3}$ $sec^{-1/2}$ (in 2.0 M $NaNO_3$, open circuit)

[OX^{2-}] M	i_d µ.A	$-E_{½}$V (S.C.E.)	Slope mV	F_0[x]	F_1[x] x10^{-2}	F_2[x] x10^{-4}	F_3[x] x10^{-4}
0.00	10.30	0.600	30	-	-	-	-
0.02	7.46	0.630	30	1.87	-	-	-
0.05	7.20	0.648	31	45.78	8.95	-	-
0.10	6.74	0.665	31	183.88	18.28	1.82	-
0.20	6.34	0.687	32	1082.80	53.10	2.44	7.1
0.30	6.00	0.700	32	3110.35	103.64	3.26	7.6
0.40	5.74	0.709	33	6631.00	163.73	4.00	7.5
0.50	5.69	0.719	32	12358.00	247.14	4.83	7.5

Table 2: Polarographic charactersitcs and F_j [x] functions of Cd (II) -N-(2-ethoxy) Phenyl Malonamate system

[Cd^{2+}] - 1×10^{-3}M, μ = 2.0 ($NaNO_3$), pH =5.6, Temp = 25 ± 0.1°C, h_{corr}= 64.8 cm, m = 2.404 mg/sec, t = 3.4 sec, $m^{2/3}$ $t^{1/6}$ = 2.2 $mg^{2/3}$ $sec^{-1/2}$ (in 2.0 M $NaNO_3$, open circuit)

[EPM M	id µ.A	$-E_{½}$V (S.C.E)	Slope mV
0.0000	10.30	0.600	30
0.0005	5.75	0.615	31
0.001	5.45	0.630	32
0.002	5.15	0.647	31
0.004	5.00	0.665	30
0.008	4.90	0.685	33

Cd(II)-Oxalate-N-(2-ethoxy) Phenyl Malonamate system

This system has been investigated at constant pH = 5.6 and μ = 2.0. The concentration of OX^{2-} was varied from 0 to 0.30 M Keeping [EPM^-] constant at 0.0005M. The waves obtained were diffusion-controlled and reversible. The $E_{½}$ value were more negative than those obtained in the absence of EPM^- thereby showing the formation of mixed complexes. The Schaap and Mc Masters[5] method was used for the determination of composition and stability constant of mixed complexes. The polarographic characteristics and F_{ij}[x,y] functions of mixed complexes of Cd (II) with

EMP^- and oxalate at fixed $[EPM]^-$ and oxalate at fixed $[EPM]^-$ (0.0005M to 0.001M) has been presented in table 3. The stability constant of the mixed complexes have been calculated from the constant A, B, C and D at two different fixed concentrations of EPM^- These are following.

Series 1: $[EPM^-]$ = 0.0005 [fixed]
log A = 0.98, log B = 2.79, log C = 5.00 and log D = 4.97

Series 2: $[EPM^-]$ = 0.0001M [fixed]
log A = 1.08, log B = 3.25, log C = 5.17 and log D = 4.99

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

$[Cd\ (OX)\ (EPM)_2]^{2-}$ $\log \beta_{12} = 9.95$
$[Cd\ (OX)_2(EPM)^{3-}$ $\log \beta_{21} = 8.75$

The results of the present study have been conventently summarised in the following diagram. Where the numerical values shown are the logarithams of the equilibrium constnats for the reaction indicated.

Two mixed complex existing in the solution have the following equilibria. The equilibrium constant, K (log value) is given for each equilibrium.

Equilibria	log K
1.$Cd^{2+}+OX^{2-}+2EPM^- \rightleftharpoons [Cd(OX)(EPM)_2]^{2-}$	9.95
2.$Cd^{2+}+2OX^{2-}+EPM^- \rightleftharpoons [Cd(OX)_2(EPM)_2]^{3-}$	6.95
3.$[Cd(EPM)_2]+OX^{2-} \rightleftharpoons [Cd(OX)(EPM)_2]^{2-}$	3.03
4.$[Cd(OX_3)^{4-}+EPM^- \rightleftharpoons [Cd(OX)_2(EPM)_2]^{3-}+OX^{2-}$	3.25
5.$[Cd(OX_2]^{2-}+EPM^- \rightleftharpoons [Cd(OX)_2(EPM)_2]^{3-}$	4.25

The quilibrium constant log values for the following desproportionation rection.

$2[Cd(OX)EPM_2]^{2-}$ $[Cd(OX)_2]^{2-}+Cd(EPM)_2]+2EPM^-$

$2[Cd(OX)_2EPM]^{3-}$ $[Cd(OX)_3]^{4-}+Cd(EPM)_2]+OX^{2-}$

Works out to be -6.51 and 4.75 respectively. The large negative value of the equilibriam constnat indicates that the formation of mixed complex is strongly favoured over the simple ones.

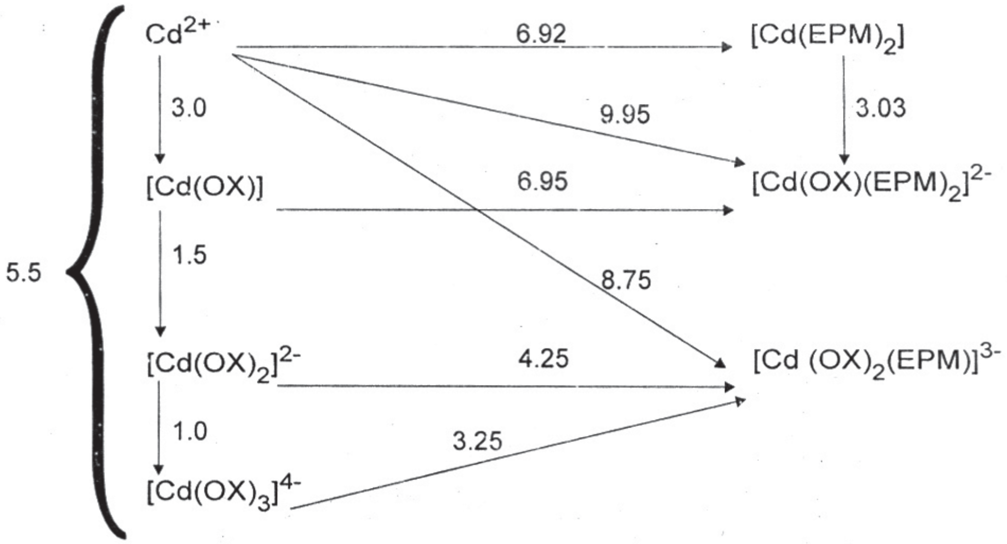
The stability of the two complexes as seen from their overall stability constants follows the order.

$$[Cd(OX)(EPM)_2]^{2-} > [Cd(OX)_2](EPM)]^{3-}$$

Table 3: Polarographic charactersitcs and F_{ij} [x,y] functions of Cd (II) - Oxalate -N-(2-ethoxy) Mamonamate system($E_{½}$) = 0.600 V (S.C.E.)

$[Cd^{2+}]$ - 1×10^{-3}M, μ = 2.0 ($NaNO_3$), pH =5.6, Temp = 25 ± 0.1°C, h_{corr}= 64.8 cm, m = 2.404 mg/sec, t = 3.4 sec, $m^{2/3}\ t^{1/6}$ = 2.2 $mg^{2/3}\ sec^{-1/2}$ (in 2.0 M $NaNO_3$, open circuit)

$[OX^{2-}]$ M	i_d μ.A	$-E_{½}V$ (S.C.E.)	Slope mV	F_{00}[x,y]	F_{10}[x,y] $\times10^{-2}$	F_2[x,y] $\times10^{-4}$	F_3[x,y] $\times10^{-4}$
Series I [EPM] = 0.0005 M							
0.02	8.95	0.650	30	6.08	26.20	-	-
0.05	8.84	0.671	31	323.20	63.10	11.48	9.0
0.10	8.25	0.685	31	1264.70	125.50	11.95	9.5
0.20	8.10	0.705	32	5277.00	263.30	12.94	9.5
0.30	7.95	0.715	30	12650.20	421.30	13.80	9.4
Series II [EPM] = 0.001 M							
0.02	8.62	0.658	31	79.95	35.41	-	-
0.05	8.58	0.675	32	404.10	78.41	12.50	9.7
0.10	8.30	0.694	30	1470.30	145.92	12.91	9.9
0.20	7.72	0.715	31	5929.30	295.65	14.00	9.9
0.30	7.40	0.725	31	13641.50	454.001	14.60	9.8



Scheme 1

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