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# ELECTRO-CHEMICAL BEHAVIOUR OF THE MIXED LIGAND COMPLEXES OF Cd(II) – MALONAMIC ACID AND OXALIC ACID

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The mixed ligand complexes of Cd (II) with 1-Naphthyl malonamate ($NM^-$) and Oxalate ($Ox^{2-}$) has been studied polarographically at constant ionic strength $\mu$ = 2.0 ($NaNO_3$) and Constant pH 5.6 at 25 ± 0.1°C. The reduction of simple and mixed complexes have been found to be reversible and diffusion-controlled. The stability constants of the mixed ligand complexes viz $[Cd(OX)(NM)_2]^{2-}$ and $[Cd(OX)_2(NM)]^{3-}$ are found to be $\log \beta_{12}$ = 10 .50 and $\log \beta_{21}$= 7.98 respectively. Oxalate and 1-Naphthyl malonamate are abbreviated as ($Ox^{2-}$) and ($NM^-$) respectively.

## Introduction

Thermodynamic parameters have been evaluated in the mixed ligand complexes of propylene diamine and malonamate/succinate by Gaur *et al* [1-2]. Deford [3], Lingane [4] and Schaap [5] have reported the mixed ligand complexes of various metals. Pratihar *et al* [6] have polarographic studies of several mixed ligand complexes of Cd (II), In (III) and Pb (II) with 3, 6 dimethyl-2 picolinate. Several co-workers [7-13] have studied of mixed ligand complexes of Cd (II) with propylene diamine, tyrosine and arginine. Resently Avdhesh and co-workers [14] have studied of Cd (II) of ternary complexes of malonamic acid series and carboxylic acid. Simple complexes of Cd (II) with malonamate and carboxylic acids have been studied polarographically, but the mixed complexes said ligand have not been studied so far. With this and in view the present study has been undertaken.

## Experimental (Appratus, Chemical and Reagent)

All the chemicals used, were analytical Reagent grade. Their stock solutions were prepared in conductivity water. The ionic strength was maintained constant $\mu$ = 2.0 using KCl as supporting elecrolyte. The concentration of Cd (II) was kept constant *i.e.* $1 \times 10^{-3}$ M. Polarograms were obtained by means of a manual polarograph (Toshniwal CLO-2A) in conjunction with Toshniwal polyflex galvanometer (PL-50). Purified nitrogen was used for removing the dissolved oxygen. All the measurements were taken at temp. 25 ± 0.1°C and pH 5.6. Secondary calomel electode (S.C.E.) was used as a reference electrode. The d.m.e. had the following characteristics (in 2.0 M KCl, open circuit); m = 2.404 mg/sec, t = 3.4 sec, $m^{2/3}t^{1/6}$ = 2.2 $mg^{2/3}$ $sec^{-1/2}$, $h_{corr}$ = 64.8 cm.

## RESULT AND DISCUSSIONS

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

Stability constants of simple complexes of Cd(II) with malonamate 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.

### POLAROGRAPHIC STUDY OF OXALIC ACID

**Cd(II)-Oxalate System-** A series of polarograms were obtained at varying concentrations of at F=2.0 and at constant pH =5.6. A plot of $E_{1/2}$ Vs log $[OX^{2-}]$ was a smooth case which showing the formation of successive complexes Deford and Humes [3] method was applied for the determination of composition and stability constant of the complexes. An analysis of $F_j[X]$ function (Table-1) reveals the formation of three successive complexes were formed [Cd(OX)], $[Cd(OX)_2]^{2-}$ and $[Cd(OX)_3]^{4-}$ with stability constant log $\beta_1$ = 3.0 log $\beta_2$ = 4.5 and log $\beta_3$ = 5.5 respectively.

### POLAROGRAPHIC STUDY OF MALONAMIC ACID

**Cd(II)-1-Naphthyl Malonanate System-** A Series of polarograms were obtained at varying concentrations of $NM^-$ at ionic strength $\mu$ = 2.0 and at constant pH = 5.6. A plot of $E_{1/2}$ Vs log $[NM^-]$ 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 $F_J$ [$x$] functions of simple complex of Cd(II) with $NM^-$ have been presented in Table 2. The composition of single complex of Cd(II) with $NM^-$ workout be $[Cd(NM)_2]$ with stability constant log $\beta_2$ = 9.13.

### POLAROGRAPHIC STUDY OF CARBOXYLIC AND MALONAMIC ACID

**Cd(II) - Oxalate 1-Naphthyl Malonanate System-** $[OX^{2-}]$ was varied from 0 to 0.30 M Keeping $[NM^-]$ constant at 0.0001M. The $E_{1/2}$ value were more negative than those obtained in the absence of $NM^-$ tables 1 & 2 hence showing the formation of mixed complexes. The systems have repeated at other concentration of $[NM^-]$ (0.0002 M). The polarographic characteristics and *Fij* [$x$, $y$] functions data Vs $[OX^{2-}]$. The following intercept values for the constants A, B, C and D are obtained.

Series I : $[NM^-]$ = 0.0001M [fixed]

log A = 1.00, log B = 2.80, log C = 4.24 and log D = 4.92

Series II : $[NM^-]$ = 0.0002M [fixed]

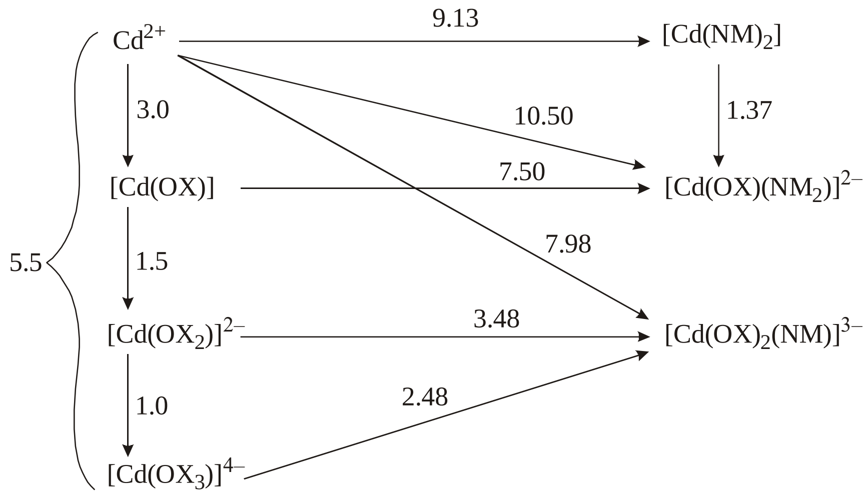
log A = 1.09, log B = 2.90, log C = 4.35 and log D = 4.94

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

$[Cd(OX)(NM)_2]^{2-}$ ; $\log \beta_{12} = 10.50$

$[Cd(OX)_2(NM)]^{3-}$ ; $\log \beta_{21} = 7.98$

The results of the present study have been conveniently summarised in the following diagram, where the numerical values shown are the logarithams of the equilibrium constants 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. | $Cd^{2+} + OX^{2-} + 2NM^{-} \rightleftharpoons [Cd(OX)(NM)_2]^{2-}$ | 10.50 |
| 2. | $Cd^{2+} + 2OX^{2-} + NM^{-} \rightleftharpoons [Cd(OX)_2(NM)]^{3-}$ | 7.98 |
| 3. | $[Cd(NM)_2] + OX^{2-} \rightleftharpoons [Cd(Ox)(NM)_2]^{2-}$ | 1.37 |
| 4. | $[Cd(OX)_3]^{4-} + NM^{-} \rightleftharpoons [Cd(OX)2(NM)]^{3-} + OX^{2-}$ | 2.48 |
| 5. | $[Cd(OX)_2]^{2-} + NM^{-} \rightleftharpoons [Cd(OX)_2(NM)]^{3-}$ | 3.48 |

The equilibrium constant log values for the following disproportionation reactions

$$2[Cd(OX)(NM)_2]^{2-} \rightleftharpoons [Cd(OX)_2]^{2-} + [Cd(NM)_2] + 2NM^{-}$$

$$2[Cd(OX)_2(NM)]^{3-} \rightleftharpoons [Cd(OX)_3]^{4-} + [Cd(NM)_2] + OX^{2-}$$

Works out to be – 5.87 and 1.57 respectively. The large negative value of the equilibriam constants indicates that the formation of mixed complex is strongly favoured over the simple ones.

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

**Table-1. Polarographic Characteristics and $F_j[x]$ function of Cd(II)-Oxalate System :**

$[Cd^{2+}] = 1 \times 10^{-3}$ M; $\mu = 2.0$ ($NaNO_3$); 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 | $-E_{1/2}$ V (S.C.E.) | Slope mV | $F_0[x]$ | $F_1[x]$ $\times 10^{-2}$ | $F_2[x]$ $\times 10^{-4}$ | $F_3[x]$ $\times 10^{-4}$ |
|---|---|---|---|---|---|---|---|
| 0.00 | 10.30 | 0.600 | 30 | – | – | – | – |
| 0.02 | 7.46 | 0.630 | 30 | 10.87 | – | – | – |
| 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 | 3110.65 | 103.64 | 3.26 | 7.6 |
| 0.40 | 5.74 | 0.709 | 33 | 6631.00 | 163.73 | 4.00 | 7.5 |

**Table 2. Polarographic Characteristics and *Fj*[x] function of Cd(II) - 1-Naphthyl Malonamate System :**

$[Cd^{2+}] = 1 \times 10^{-3}$ M; $\mu = 2.0$ ($NaNO_3$); 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);

| [NM] M | Id μ.A | –E1/2 V (S.C.E.) | Slope mV |
|---|---|---|---|
| 0.0000 | 10.30 | 0.600 | 30 |
| 0.0001 | 8.30 | 0.615 | 33 |
| 0.0002 | 8.15 | 0.635 | 32 |
| 0.0004 | 8.00 | 0.655 | 32 |
| 0.0008 | 7.60 | 0.680 | 30 |
| 0.001 | 6.80 | 0.686 | 31 |

**Table 3. Polarographic Characteristics and $F_{ij}$ [x, y] functions of Cd(II)-Oxalate-1-Naphthyl Malonamate Systems :**

$[Cd^{2+}] = 1 \times 10^{-3}$ M; $\mu$ =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);
($E_{1/2}$) = – 0.600 V (S.C.E.)

| $[OX^{2-}]$ M | $I_d$ μ.A | $-E_{1/2}$ V (S.C.E.) | Slope mV | $F_{00}[x,y]$ | $F_{10}[x,y]$ $\times 10^{-2}$ | $F_{20}[x,y]$ $\times 10^{-4}$ | $F_{30}[x,y]$ $\times 10^{-4}$ |
|---|---|---|---|---|---|---|---|
| Series I [NM] = 0.0001 M | | | | | | | |
| 0.02 | 8.42 | 0.630 | 30 | 13.65 | - | - | - |
| 0.05 | 8.00 | 0.645 | 33 | 52.32 | 8.54 | - | - |
| 0.10 | 7.85 | 0.665 | 30 | 250.00 | 26.00 | 2.50 | 8.30 |
| 0.20 | 7.80 | 0.690 | 31 | 1427.50 | 70.85 | 3.31 | 8.3 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 0.30 | 7.55 | 0.700 | 30 | 3981.00 | 132.32 | 4.21 | 8.4 |
| Series II [NM] = 0.0002 M | | | | | | | |
| 0.02 | 8.43 | 0.635 | 32 | 20.10 | - | - | - |
| 0.05 | 8.00 | 0.650 | 30 | 77.20 | 14.00 | - | - |
| 0.10 | 7.85 | 0.672 | 30 | 368.92 | 35.65 | 3.00 | 8.5 |
| 0.20 | 7.80 | 0.690 | 30 | 1664.10 | 82.50 | 3.85 | 8.4 |
| 0.30 | 7.51 | 0.706 | 31 | 4651.452 | 154.52 | 4.95 | 9.0 |

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