

**Polarographic Study of  
Mixed Ligand Complexes:  
Cd(II)-Oxalate-Phthalate System**

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The mixed ligand complexation of oxalate (Ox) and phthalate ions with Cd(II) has been studied polarographically in aqueous medium at  $25^\circ \pm 0.5^\circ$  and  $\mu = 1.0M$  (KNO<sub>3</sub>). The formation of three complex species [Cd(Ox)(phthalate)]<sup>2-</sup>, [Cd(Ox)<sub>2</sub>(phthalate)]<sup>4-</sup> and [Cd(Ox)(phthalate)<sub>2</sub>]<sup>4-</sup> is observed. By applying Schaap and McMasters treatment the stability constants of these complexes are found to be  $\log \beta_{11} = 3.75$ ,  $\log \beta_{21} = 5.02$  and  $\log \beta_{12} = 3.89$  respectively. The complexation constants of these species were also evaluated following the procedure suggested by Watters.

In recent years polarographic technique has received considerable attention in the study of mixed ligand complexes after the notable work of Schaap and McMasters<sup>1</sup>. The present note is in continuation of an earlier publication<sup>2</sup> from our laboratories describing the polarographic determination of stability constants of mixed ligand complexes of oxalate and salicylate ions with Cd(II).

Cadmium nitrate was of BDH (AR) grade. Oxalate (Ox) and phthalic acids were used in the form of their potassium salts, which were recrystallized from doubly distilled water. All the solutions were prepared in a doubly distilled water. The polarograms of deaerated solutions were recorded at  $25^\circ \pm 0.5^\circ$  and  $\mu = 1.0M$  (KNO<sub>3</sub>) with the help of a Cambridge Pen recording polarograph. The d.m.e. had the following characteristics:  $t = 3.2$  sec, in 0.1M (open circuit); and  $m = 1.97$  mg sec<sup>-1</sup>. SCE used as a reference electrode had negligible cell resistance. Half-wave potential values were obtained from log plots. The polarograms were recorded at a fixed concentration of Cd(II) (1 mM) and varying concentration of oxalate (0.02-0.5M) and phthalate (0.02-1.0M).

The conditions maintained for Cd(II)-oxalate-phthalate-mixed system were similar to those reported<sup>1-3</sup> for Cd(II)-oxalate and Cd(II)-phthalate systems.

For the system Cd(II)-oxalate, the plot of  $-(E_{1/2})_c$  vs  $\log C_L$  (where  $C_L$  = oxalate ion concentrations) indicates the presence of 1:1, 1:2 and 1:3 Cd(II)-oxalate complex species. The DeFord and Hume treatment<sup>4</sup> was applied to determine the stability constants of these species and the values are:  $\log \beta_{1,0} = 2.70 \pm 0.04$ ,  $\log \beta_{2,0} = 4.07 \pm 0.15$  and  $\log \beta_{3,0} = 5.14 \pm 0.06$ . These values are in good agreement with those obtained by Schaap and McMasters<sup>1</sup> and Kanemura and Watters<sup>5</sup>.

The application of DeFord and Hume method<sup>4</sup> for Cd(II)-phthalate system suggested the formation of 1:1, 1:2 and 1:3 complex species. The stability constants thus obtained are:  $\log \beta_{0,1} = 1.90$

TABLE 1 — VALUES OF  $E_{1/2}$  AND THE SLOPES OF THE PLOTS OF  $E_{dc}$  VERSUS  $\log [i/(i_d - i)]$

[Cd(II) = 1 mM;  $\mu = 1.0M$  (KNO<sub>3</sub>); temp.  $25^\circ \pm 0.5^\circ$ ;  
 $-(E_{1/2})_s = 0.5850$  V]

[Ox] M	$-E_{1/2}$ (vs SCE) at		$\log I_m/I_c$	Slope (mV)
	0.0M [phthalate]	0.08M [phthalate]		
0.02	0.6180	0.6300	0.0615	30.0
0.04	0.6338	0.6420	0.0906	30.0
0.06	0.6425	0.6485	0.0706	30.0
0.08	0.6490	0.6550	0.0806	30.0
0.10	0.6535	0.6620	0.0706	32.5
0.15	0.6670	0.6690	0.1007	33.6
0.20	0.6780	0.6810	0.1007	33.3
0.30	0.6900	0.6950	0.1007	30.0
0.40	0.7000	0.7026	0.1007	30.0
0.50	0.7075	0.7100	0.1007	33.0

TABLE 2 — VALUES OF  $E_{1/2}$  AND THE SLOPES OF THE PLOTS OF  $E_{dc}$  VERSUS  $\log i/(i_d - i)$

[Cd(II) = 1 mM;  $\mu = 1.0M$  (KNO<sub>3</sub>); temp.  $25^\circ \pm 0.5^\circ$ ;  
 $-(E_{1/2})_s = 0.5850$  V]

[Ox] M	$-E_{1/2}$ (vs SCE) at		$\log I_m/I_c$	Slope (mV)
	0.0M [phthalate]	0.16M [phthalate]		
0.02	0.6180	0.6400	0.1007	32.4
0.04	0.6338	0.6478	0.1007	30.9
0.06	0.6425	0.6540	0.1133	30.0
0.08	0.6490	0.6588	0.1222	30.0
0.10	0.6535	0.6655	0.1007	30.1
0.15	0.6670	0.6735	0.1007	32.0
0.20	0.6780	0.6840	0.1007	31.1
0.30	0.6900	0.6950	0.1007	33.0
0.40	0.7000	0.7030	0.1222	30.0
0.50	0.7075	0.7100	0.1222	30.0

$\pm 0.11$ ,  $\log \beta_{0,2} = 2.25 \pm 0.12$  and  $\log \beta_{0,3} = 3.44 \pm 0.04$ .

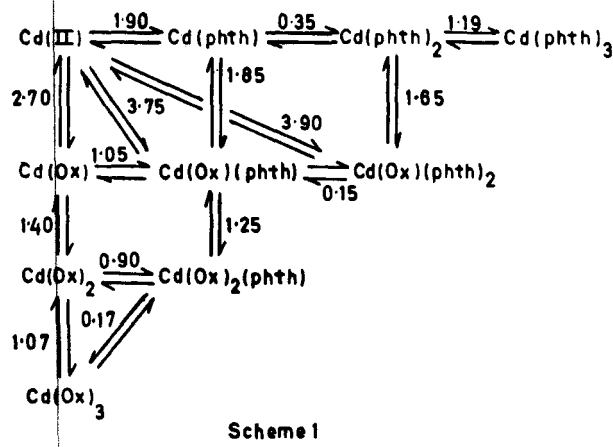
In the mixed ligand system, the concentrations of phthalate ion were constant at 0.08M and 0.16M because at these concentrations 1:1 and 1:2 Cd(II)-phthalate complex species were found to be predominant.

In the first set, the solutions ( $\mu = 1.0M$ ) containing 1 mM Cd(II), 0.08M potassium phthalate and different concentrations of oxalate were polarographed. The same procedure was adopted in the second set in which phthalate ion concentration was kept constant at 0.16M.

In all the systems, a well-defined and diffusion-controlled single wave was observed. The linear relationship between  $E_{dc}$  vs  $\log i/(i_d - i)$  with slope values in the range of 30-33 mV indicated a reversible reduction involving two electrons.

The values of  $-(E_{1/2})_c$  and the slopes at these two concentrations of phthalate ions are given in Tables 1 and 2.

The shift in half-wave potential of Cd(II) in the presence of the mixture of phthalate and oxalate ions is greater than that of in oxalate ion alone. This suggests the formation of Cd(II)-oxalate-phthalate mixed complexes.



The method of Schaap and McMasters<sup>1</sup> was applied to evaluate the coefficients  $A$ ,  $B$ ,  $C$  and  $D$  in both the sets. The values of these coefficients are given below:

At 0.08M phthalate:  $\log A = 1.30$ ;  $\log B = 3.0 \pm 0.09$ ;  $\log C = 4.30 \pm 0.09$ ; and  $\log D = 5.17 \pm 0.06$

At 0.16M phthalate:  $\log A = 1.78$ ;  $\log B = 3.20 \pm 0.03$ ;  $\log C = 4.47 \pm 0.03$ ; and  $\log D = 5.17 \pm 0.08$

The mean value of  $\log D = 5.17$  agrees well with the  $\log \beta_{30} = 5.14$ , the stability constant of  $[\text{Cd}(\text{Ox})_3]^{4-}$ .

The values of  $A$ ,  $B$ ,  $C$  and  $D$  were used in calculating the stability constants of mixed species. The mixed complex species  $[\text{Cd}(\text{Ox})(\text{phthalate})]^{2-}$ ,  $[\text{Cd}(\text{Ox})_2(\text{phthalate})]^{4-}$  and  $[\text{Cd}(\text{Ox})(\text{phthalate})_2]^{4-}$  were found to have the stability constants  $\log \beta_{11} = 3.75$ ,  $\log \beta_{21} = 5.02$  and  $\log \beta_{12} = 3.89$  respectively.

The observed stability constants of the mixed complexes have been compared with calculated from those of the simple complexes following the procedure suggested by Watters<sup>6</sup>. The calculated values for complexation constants are: (i)  $3 \times \beta_{2,0}^{2/3} \times \beta_{0,3}^{1/3} = 10^{4.35}$  as compared to  $10^{5.02}$  observed for  $[\text{Cd}(\text{Ox})_2(\text{phthalate})]^{4-}$  and (ii)  $3 \times \beta_{3,0}^{1/3} \times \beta_{0,2}^{2/3} = 10^{3.69}$  as compared to  $10^{3.89}$  of  $[\text{Cd}(\text{Ox})(\text{phthalate})_2]^{4-}$ . The increase in the values for these species were respectively  $10^{+0.67}$  and  $10^{+0.20}$ .

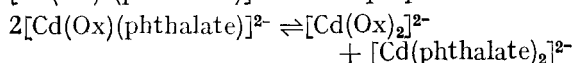
The statistical factor favouring the formation of mixed complex  $[\text{Cd}(\text{Ox})(\text{phthalate})]^{2-}$  is two. The observed value ( $10^{3.75}$ ) is larger than the calculated ( $10^{3.46}$ ) by  $10^{+0.29}$ . The greatest enhancement is observed for the  $[\text{Cd}(\text{Ox})_2(\text{phthalate})]^{4-}$  complex.

The various complexation reactions along with their log stepwise stability constants are shown in Scheme 1.

log  $K$  value for  $[\text{Cd}(\text{Ox})]$  to  $[\text{Cd}(\text{Ox})_2]^{2-}$  is 1.40 while the value for  $\text{Cd}(\text{phthalate})$  to  $[\text{Cd}(\text{Ox})(\text{phthalate})]^{2-}$  is 1.85. The larger value of log  $K$  for the later reaction shows that the formation of mixed species is favoured. A similar argument holds good for the mixed complex  $[\text{Cd}(\text{Ox})(\text{phthalate})]^{2-}$  when formed from  $[\text{Cd}(\text{Ox})]$ . It is seen that log  $K$  value in the formation of  $[\text{Cd}(\text{Ox})(\text{phthalate})]^{2-}$  from  $[\text{Cd}(\text{Ox})]$  is much higher than in the formation

of  $[\text{Cd}(\text{phthalate})_2]^{2-}$  from  $[\text{Cd}(\text{phthalate})]$  being 1.05 in the former and 0.35 in the latter case.

One of the modes in which mixed ligand complex  $[\text{Cd}(\text{Ox})(\text{phthalate})]^{2-}$  can disproportionate is:



and reaction has the  $\log K = -1.18$  in the direction written which clearly shows that the formation of the mixed complex is preferred.

That the saturated mixed complexes  $[\text{Cd}(\text{Ox})_2(\text{phthalate})]^{4-}$  and  $[\text{Cd}(\text{Ox})(\text{phthalate})_2]^{4-}$  are favoured can be seen by comparing the formation constants for the addition of oxalate anion as a third ligand to  $[\text{Cd}(\text{Ox})_2]^{2-}$ ,  $[\text{Cd}(\text{Ox})(\text{phthalate})]^{2-}$  and  $[\text{Cd}(\text{phthalate})_2]^{2-}$ . Log  $K$  values are respectively 1.07, 1.25 and 1.65.

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#### A Study of Cu(II) Monochloroacetate & Trichloroacetate at d.m.e.

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**Copper(II) mono- and trichloroacetates have been observed to undergo diffusion-controlled, irreversible reduction at d.m.e. in 25% ethanol and 25% acetone. But in aqueous medium copper(II) monochloroacetate undergoes diffusion-controlled reversible single-electron electroreduction while the other shows irreversible electroreduction. Kinetic parameters of all irreversible electrode processes have been evaluated along with other polarographic characteristics.**

**C**OPPER(II) monochloroacetate exhibits metal-metal exchange interaction, while Cu(II) trichloroacetate shows normal magnetic properties of a paramagnetic complex in solid state<sup>1</sup>. Such a typical behaviour of these two alkanooates has also been established in organic solvents<sup>2</sup> of low dielectric constant and having less coordinating ability than water. In aqueous solution, the dimerization reaction appears to be destroyed. These conclusions have been arrived at on the basis of spectral and magnetic properties of these alkanooates. Recent polarographic investigations<sup>3</sup> show that Cu(II) monochloroacetate gives double wave