Polarographic Study of Mixed Ligand Complex: Cd (II)–Imidazole–Succinate System

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THE mixed ligand complexes of Imidazole (Im) and succinate (Succ) with Cd(II) have been studied polarographically at constant ionic strength, $\mu = 2.0$ ($NaNO_3$) and at temperature 25 ± 0.1°C. The reduction of the complexes at d.m.e. is reversible and diffusion—controlled. Four mixed complexes viz., $[Cd(Im)_n(Succ)]$; $[Cd(Im)(Succ)_2]^{2-}$; $[Cd(Im)_4(Succ)_2]^{2-}$ and [Cd(Im) (Succ)] are formed. Their overall stability constants at 25°C are : log β_{11}=2.7, log β_{12}=4.7, log β_{22}=6.6 and log β_{31}=5.7 respectively.

In a previous publication[1] we have reported the polarographic study of mixed complexes of Cd(II) with imidazole and tartrate ions. This paper describes the results of our investigations on the polarographic study of mixed complexes of Cd (II) with imidazole and succinate ions. This system has not been studied polarographically so far.

EXPERIMENTAL

Materials and Methods : All the chemicals used were of analytical reagent grade and their solutions were prepared in conductivity water. The ionic strength was maintained constant at $\mu = 2.0$ using $NaNO_3$ as supporting electrolyte. Imidazole and potassium succinate were used as ligands. The concentration of Cd (II) was kept at 1×10^{-3} M. Polarograms were obtained by means of a manual polarograph (Toshniwal CLO2) in conjunction with Toshniwal polyflex galvanometer (PL 50). Purified nitrogen was used for removing the dissolved oxygen. All the measurements were made at 25 ± 0.1°C. SCE was used as reference electrode. The dme had the following characteristics : m = 1.5 mg/sec, t = 2.75 sec, (in 0.1 M $NaNO_3$ open circuit) at h_{corr} = 52 cms.

RESULTS AND DISCUSSIONS

The reduction of Cd (II) in imidazole and succinate media, seperately, was found to be reversible and diffusion controlled. The same was true in the case of the mixed system. The slopes of linear plots of $\log\frac{i}{id-i}$ vs. E_{dr} were of the order of 30 mV and the plots of i_d vs. h_{corr} were linear and passed through the origin.

Stability constants of simple complexes of Cd (II) with imidazole and succinate : The stability constants of simple complexes of Cd (II) with imidazole and succinate were determined separately prior to the study of mixed ligand system Identical conditions were maintained in both the simple and mixed systems.

(1) Cd (II) – Imidazole system : A plot of $E_{\frac{1}{2}}$ vs. log [Im] is a smooth curve (Fig. 1) thereby showing the formation of successive complexes. DeFord and Hume's[2] method has been applied to determine the stability constants of successive complexes. The polarographic characteristics and F_i [x] functions of Cd (II) - Imidazole system have been listed in Table 1. Four complexes, viz., $[Cd(Im)]^{2+}$, $[Cd(Im)_2]^{2+}$, $[Cd(Im)_3]^{2+}$ and $[Cd(Im)_4]^{2+}$ with stability constants log β_{10}=2.69, log β_{20} = 4.0, log β_{30} = 5.3 and log β_{40} = 7.0 are formed. The percentage distribution of Cd (II) in its various forms as are function of [Im] has been presented in Fig. 3

FIG 1

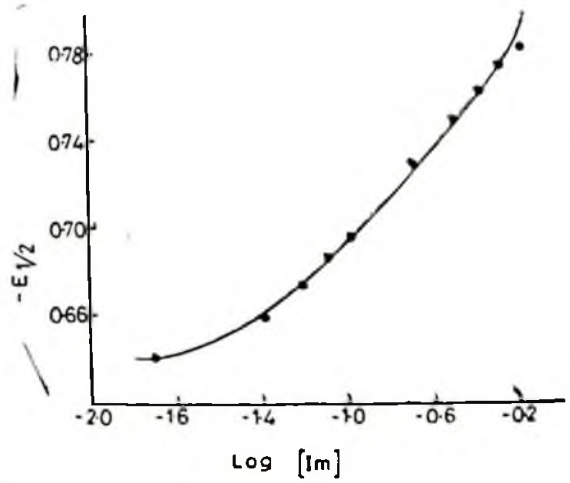


Fig. 1 Plots of $E_{\frac{1}{2}}$ vs. log [Im] for Cd(II)-Imidazole system

Table : 1 *Cd (II)—Imidazole System*
$[Cd^{2+}] = 1 \times 10^{-3}M$, $\mu = 2.0$ ($NaNO_3$) ; Temp. = 25°C ; pH 8 ;

[Im] M	$-E_{\frac{1}{2}}$ V (S.C.E.)	i_d div.	$F_0[X]$	$F_1[X]$ $\times 10^{-2}$	$F_2[X]$ $\times 10^{-3}$	$F_3[X]$ $\times 10^{-5}$	$F_4[X]$ $\times 10^{-6}$
0.00	0.605	113					
0.02	0.641	110	16.97	7.98			
0.04	0 660	110	74.61	18.40	33.50	5.87	
0.06	0.675	110	240.20	39.10	58.10	8.01	
0.08	0.687	108	622.90	77.73	90.91	10.11	10.13
0.10	0.697	106	1384.00	138.38	133.30	12.33	10.33
0.20	0.730	104	18450.00	922.45	458.72	22.43	10.20
0.30	0.752	104	87680.00	2922.63	972.54	32.08	10.02
0.40	0.764	104	260600.00	6514 97	1627.49	40.43	9.60
0.50	0.776	104	664700.00	13293.98	2657.79	52.95	10.59
0.60	0.784	97	1329410.00	22156.80	3691.96	61.36	10 00

(2) Cd (II)–succinate system : A plot of $E_{\frac{1}{2}}$ vs. log $[Succ^{2-}]$ is a smooth curve (Fig. 2) thereby showing the formation of successive complexes. DeFord and Hume's method has been applied to determine the stability constants of successive complexes. The polarographic characteristics $F_j[X]$ functions of Cd (II)-succinate system have been presented in Table 2. Three complexes viz., [Cd (Succ)] , $[Cd(Succ)_2]^{2-}$ and $[Cd(Succ)_3]^{4-}$ with stability constants log $\beta_{01} = 1.30$, log $\beta_{02} = 2.0$ and log $\beta_{03} = 3.0$ are formed. The percentage distribution of Cd (II) in its various forms as a function of $[Succ^{2-}]$ has been presented in Fig. 4

FIG 2

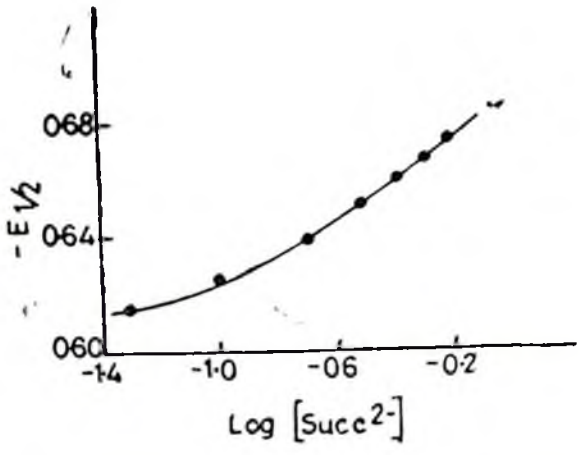


Fig. 2 Plots of $E_{\frac{1}{2}}$ vs. log $[Succ^{2-}]$ for Cd(II)-Succinate system

FIG 3

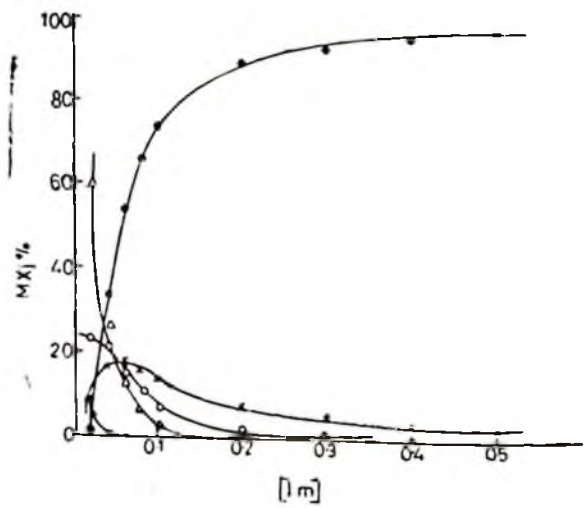


Fig 3 : Percentage distribution of Cd (II) in its various forms as a function of Imidazole

- ■ - Cd^{2+}
- △ - $[Cd(Im)]^{2+}$
- ○ - $[Cd(Im)_2]^{2+}$
- × - $[Cd(Im)_3]^{2+}$
- ● - $[Cd(Im)_4^{2+}]$

Table 2 : *Cd (II) - Succinate System*

$[Cd^{2+}] = 1 \times 10^{-3}$ M; $\mu = 2.0$ ($NaNO_3$), Temp. = 25°C; pH 8

$[Succ^{2-}]$ M	$-E_{\frac{1}{2}}$ V (S.CE.)	i_d div	$F_0[x]$	$F_1[x]$	$F_2[x]$ $\times 10^{-1}$	$F_3[x]$ $\times 10^{-2}$
0.00	0.605	110				
0.05	0.615	101	2.37	27.40	14.80	
0.10	0,625	101	5.17	41.70	21.70	
0.20	0.639	91	17.03	80.15	30.07	10.00
0.30	0.651	90	44.09	143.63	41.21	10.40
0.40	0.660	89	89.89	222.22	50.35	10.13
0.50	0.667	82	168.40	334.80	62.96	10.50
0.60	0.673	82	268.70	446.16	71.02	10.17

FIG 4

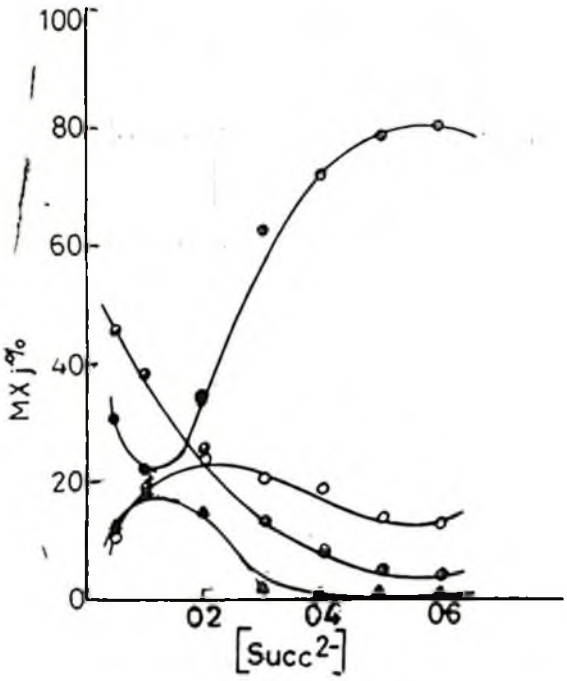


Fig. 4: Percentage distribution of Cd (II) in its various forms as a function of succinate

-▲-Cd^{2+}
-◐-[Cd(Succ]
-○-$[Cd(Succ)_2]^{2-}$
-●-$[Cd(Succ)_3]^{4-}$

(3) Cd (II)—Imidazole — succinate — mixed system : Imidazole concentration was varied from 0–0.10 M and that of succinate was kept constant at 0.10 M. It was found that the $E_{\frac{1}{2}}$ values were greater as compared to those obtained in the absence of succinate thereby showing the formation of mixed complexes. The system was repeated at another concentration of succinate (0.20 M).

The method of Schaap and McMasters[3] has been used to determine the composition and values stability constants of mixed complexes. The polarographic characteristics and $F_{ij}[XY]$ functions of mixed complexes of Cd (II) with imidazole and succinate at fixed $[Succ^{2-}]$ (0.10 M and 0.20 M) have been presented in Table 3.

From plots of F_{ij} data vs. [Im] the following intercept values of constants[4] A, B, C D, and E have been obtained :

For series 1 : log A = 0.7, log B = 3.0, log C = 4.3, log D = 5.4 and log E = 7.0

For series 2 . log A = 1.3, log B = 3.4, log C = 5.0, log D = 5.5 and log E = 7.3

Table 3 : *Values of $F_{ij}[XY]$ Functions for Cd (II) - Imidazole - Succinate System*

[Im] M	$-E_{1/2}$ V (S.C.E)	i_d div	$F_{00}[XY]$	$F_{10}[XY]$ $\times10^{-2}$	$F_{20}[XY]$ $\times10^{-3}$	$F_{30}[XY]$ $\times10^{-4}$	$F_{40}[XY]$ $\times10^{-6}$
Series I : Concentration of the Succinate ($Succ^{2-}$) = 0.10 M							
0.00	0.605	110					
0.02	0.655	102	53.07	24.03			
0.04	0.665	101	116.80	27.95	44.87	62.17	9.54
0.06	0.678	100	324.80	53.63	72.71	87.85	10.64
0.08	0.689	99	773.20	96.02	107.52	109.40	10.67
0.10	0.699	98	1693.00	168.80	158.80	138.80	11.40
Series II : Concentration of the succinate ($Succ^{2-}$) = 0.20 M							
0.00	0.605	110					
0.02	0.667	100	114.00	47.00	115.00		
0.04	0.679	96	365.80	86 45	156.12	115.30	21.32
0.06	0.691	98	912.80	148.80	208.00	163.33	22.16
0.08	0.701	97	2009.00	248.62	281.02	213.77	22.71
0.10	0.710	97	3970.00	395.00	371.00	261.00	23.10

The stability constants of the mixed complexes have been determined from the values of A, B, C, D and E. Four mixed complexes, viz., [Cd(Im) (Succ)], [Cd(Im) $(Succ)_2]^{2-}$, $[Cd(Im)_2$ $(Succ)_2]^{2-}$ and $[Cd(Im)_3$ (Succ)] with stabitily constants log $\beta_{11} = 2.7$, log $\beta_{12} = 4.7$, log $\beta_{22} = 6.6$ and log $\beta_{31} = 5.7$ respectively are formed.

The mixing constant K_M (equilibrium constant) for reaction :

$$1/2[Cd(Im)_2] + 1/2[Cd(Succ)_2]^{2-} \rightleftharpoons [Cd(Im)(Succ)] \quad \ldots\ldots (1)$$

is a measure of relative stability of mixed complexes in solution as compared to parent binary complexes This is given by the following relation.[5-6]

$$K_M = \beta_{11} / \sqrt{\beta_{20}\,\beta_{02}}$$

This comes out to be -0.3 for the above reaction. The negative value shows that the simple binary complexes, $[Cd(Im)_2]^{2+}$ and $[Cd(Succ)_2]^{2-}$ are somewhat more stable than the mixed complex species [Cd(Im) (Succ)].

Disproportionation constant for the reactions :

$$2\,[Cd(Im)\,(Succ)] \rightleftharpoons [Cd(Im)_2]^{2+} + [Cd(Succ)_2]^{2-} \quad \ldots\ldots\ldots (2)$$

$$2\,[Cd(Im)_2(Succ)_2]^{2-} \rightleftharpoons [Cd(Im)_2]^{2+} + [Cd(Succ)_2]^{2-} + 2Im + 2\,succ^{2-} \quad \ldots\ldots (3)$$

works out to be +0.6 and −7.2 respectively. The positive value clearly indicates' the preferential tendency of Cd(II) to form simple binary complexes over the mixed complex species, [Cd(Im) (Succ)]. This conclusion is in harmony with that obtained on the basis of mixing constant. The negative value of disproportionation constant in the second case clearly shows the preferential tendency of Cd (II) to form the mixed complex species, $[Cd(Im)_2(Succ)_2]^{2-}$ over the simple binary complexes.

Cd (II) is hexa coordinated. Four mixed complexes existing in solution have the following equilibria (Table 4). The equilibrium constants (log values) have been calculated and written in front of each equilibrium.

Table 4: *Equilibria Involved in Four mixed complexes and equilibrium constant (K) values.*

	Equilibria			log K at 25°C
1.	$Cd^{2+} + Im + Succ^{2-}$	⇌	$[Cd\ (Im)\ (Succ)]$	2.7
2.	$Cd^{2+} + Im + 2Succ^{-2}$	⇌	$[Cd\ (Im)\ (Succ)_2]^{2-}$	4.7
3.	$Cd^{2+} + 2Im + 2Succ^{2-}$	⇌	$[Cd\ (Im)_2\ (Succ)_2]^{2-}$	6.6
4.	$Cd^{2+} + 3Im + Succ^{2-}$	⇌	$[Cd\ (Im)_3\ (Succ)]$	5.7
5.	$[Cd\ (Im)\ (Succ)] + 2Im$	⇌	$[Cd\ (Im)_3\ (Succ)]$	3.0
6.	$[Cd\ (Im)\ (Succ)] + Succ^{2-}$	⇌	$[Cd\ (Im)\ (Succ)_2]^{2-}$	2.0
7.	$[Cd\ (Im)\ (Succ)_2]^{2-} + 2Im$	⇌	$[Cd\ (Im)_3\ (Succ)] + Succ^{2-}$	1.0
8.	$[Cd\ (Im)_3\ (Succ)] + Succ^{2-}$	⇌	$[Cd\ (Im)_2\ (Succ)_2]^{2-} + Im$	0.9
9.	$[Cd\ (Im)_3\ (Succ)] + Im$	⇌	$[Cd\ (Im)_4]^{2+} + Succ^{2-}$	1.3
10.	$[Cd\ (Im)_2]^{2+} + 2Succ^{2-}$	⇌	$[Cd\ (Im)_2\ (Succ)_2]^{2-}$	2.6
11.	$[Cd\ (Succ)_2]^{2-} + Im$	⇌	$[Cd\ (Im)\ (Succ)_2]^{2-}$	2.7
12.	$[Cd\ (Succ)_2]^{2-} + 2Im$	⇌	$[Cd\ (Im)_2\ (Succ)_2]^{2-}$	4.0
13.	$[Cd\ (Im)]^{2+} + Succ^{2-}$	⇌	$[Cd\ (Im)\ (Succ)]$	0.01
14.	$[Cd\ (Succ)] + Im$	⇌	$[Cd\ (Im)\ (Succ)]$	1.4
15.	$[Cd\ (Succ)_2]^{2-} + Im$	⇌	$[Cd\ (Im)\ (Succ)_2]^{2-}$	0.7
16.	$[Cd\ (Succ)_3]^{4-} + Im$	⇌	$[Cd\ (Im)\ (Succ)_2]^{2-} + Succ^{2-}$	1.7
17.	$[Cd\ (Succ)_2]^{2-} + 3Im$	⇌	$[Cd\ (Im)_3\ (Succ)] + Succ^{2-}$	3.7

From the equilibrium constant values, the tendency of a ligand to add to a complex and to substitute another may be compared. It is seen that Im adds readily to [Cd(Im)(Succ)] as compared to $Succ^{2-}$ (Equilibria 5-6). It is also observed that mixed complex, $[Cd(Im)_3(Succ)]$ can accommodate Im more readily than $Succ^{2-}$ (Equilibria 7-8)

From equilibria 10, 12, 13, and 14 it is clear that complexing tendency of Im is much more than $Succ^{2-}$. The same conclusion may be drawn from the substitution of Im in place of $Succ^{2-}$ in equilibria 16 and 17.

The stability of four mixed complexes as seen from their overall stability constant follows the order :

$[Cd(Im)_2(Succ)_2]^{2-} > [Cd(Im)_3\ (Succ)] >$
$[Cd(Im)\ (succ)_2]^{2-} > [Cd(Im)(Succ)]$

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