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Polarographic study of mixed ligand complexes: Pb(II)-succinate-imidazole system

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Abstract. The mixed ligand complexes of succinate ($Succ^{2-}$) and Imidazole (Im) with Pb(II) have been studied polarographically at constant ionic strength, $\mu = 2.0$ ($NaNO_3$) and at pH 6. The system has been studied at constant temperature, $25 \pm 0.1°$ C. The reduction of the complexes at dropping mercury electrode is reversible and diffusion-controlled. Three mixed complexes, *viz.*, [Pb(Succ)(Im)]: [Pb(Succ)$(Im)_2$] and [Pb$(Succ)_2$(Im)]$^{2-}$ are formed.

Keywords. Polarographic study; mixed ligand complexes; succinate imidazole system.

1. Introduction

In the previous publication (Madhu and Mukhtar Singh 1981a,b,c) polarographic studies on simple and mixed complexes of Cd(II) with imidazole and tartrate, melonate and succinate have been reported. A survey of literature reveals that polarographic studies of the complexes of Pb(II) except Pb(II) succinate system (Gaur and Palrecha 1968) with imidazole have not been undertaken so far. But so far no polarographic study of mixed complexes of Pb(II) with imidazole and succinate ions has been made. With this aim in view a polarographic study of Pb(II)-imidazole-succinate system has been undertaken at a constant ionic strength, $\mu = 2.0$ ($NaNO_3$) and pH 6.

2. 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 $\mu = 2.0$ ($NaNO_3$). Imidazole and potassium succinate were used as ligands. The concentration of Pb(II) was kept at 1×10^{-3} M. Polarograms were obtained by means of a manual polarograph (Toshniwal CL 02) in conjunction with Toshniwal polyflex galvanometer (PL 50). Purified nitrogen was used for removing the dissolved oxygen. All the measurements were made at $25 \pm 0.1°$ C. Saturated calomel electrode (SCE) was used as reference electrode. The dme had the following characteristics (0.1 M $NaNO_3$, open circuit): $m = 1.5$ mg/sec, $t = 2.7$ sec, $m^{2/3}\, t^{1/6} = 1.55$ $mg^{2/3}\, sec^{-1/2}$, $h_{corr} = 52$ cm.

3. Results and discussion

The reduction of Pb(II) in succinate and imidazole media, separately, was found to be reversible and diffusion-controlled. The same was true in the case of the mixed

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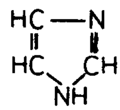
system. The slopes on the linear plots of log $i/i_d - i$ vs $E_{d.e.}$ were of the order of 30 mV and the plots of i_d vs. h_{corr} were linear and passed through the origin.

As imidazole (Im) (structure: ) is a base, it gets protonated in aqueous medium according to the following equilibrium:

$$\mathrm{Im} + \mathrm{H_2O} \rightleftharpoons \mathrm{ImH^+} + \mathrm{OH} \quad (1)$$

Since hydrogen bound(protonated) base does not enter into complexation, the amount of the "free base" (*i.e.* unprotonated) only has to be taken for the concentration of the ligand. This can be calculated from the pH and pK_a value of the base as per the following equilibrium:

$$\mathrm{ImH^+} \rightleftharpoons \mathrm{Im} + \mathrm{H^+} \quad (2)$$

$$K_a = \frac{[\mathrm{Im}]\ [\mathrm{H^+}]}{[\mathrm{ImH^+}]}$$

or

$$\log\ [\mathrm{Im}] = \log\ [\mathrm{ImH^+}] + \mathrm{pH} - \mathrm{p}K_a$$

The pK_a value of imidazole at $25 \pm 0.1°$ C and at $\mu = 2.0$ ($NaNO_3$) has been determined by the titration method using glass electrode (Chaberek and Martell 1953). This worked out to be 7.09.

3. Pb(II)-succinate and Pb(II)-imidazole systems

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

A plot of $E_{1/2}$ vs log [$Succ^{2-}$] and vs log [Im] (figure 1) gave smooth curves thereby showing the formation of successive complexes. DeFord and Hume's

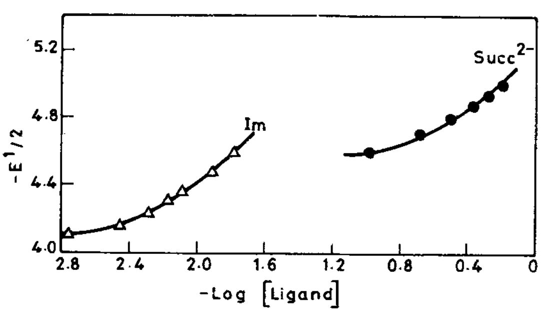


Figure 1. Plots of $E_{1/2}$ vs. log[$Succ^{2-}$] and log[Im] for Pb(II)-succinate and imidazole systems.

Table 1. Pb(II)-succinate system.
$[Pb^{2+}] = 1 \times 10^{-3}$ M; $\mu = 2.0$ ($NaNO_3$); pH 6; Temp. $25 \pm 0.1°$ C

$[Succ^{2-}]$ M	$-E_{1/2}$ V (SCE)	i_d div	$F_0[X]$	$F_1[X]$ x10^{-2}	$F_2[X]$ x10^{-4}	$F_3[X]$ x10^{-6}
0.00	0.400	100	-	-	-	-
0.10	0.460	90	119.30	11.83	-	-
0.20	0.470	89	263.10	13.10	40.52	7.76
0.30	0.480	88	580.10	19.30	47.66	7.55
0.40	0.488	87	1095.00	27.35	55.85	7.71
0.50	0.494	85	1788.00	35.74	61.48	7.29
0.60	0.500	85	2855.00	47.56	70.93	7.60

Table 2. Pb(II)-imidazole system.
$[Pb^{2+}] = 1 \times 10^{-3}$M; $\mu = 2.0$ ($NaNO_3$); pH 6; Temp. $= 0.1°$ C

[Im] (Free ligand) M	$-E_{1/2}$ V (SCE)	i_d div	$F_0[X]$	$F_1[X]$ x10^{-2}	$F_2[X]$ x10^{-4}	$F_3[X]$ x10^{-6}
0	0.400	100	-	-	-	-
0.0016	0.411	90	2.61	-	-	-
0.0032	0.416	86	4.04	9.50	4.68	-
0.0047	0.423	85	7.06	12.89	10.40	-
0.0064	0.430	85	12.20	17.50	14.84	2.00
0.0079	0.436	83	19.93	23.96	20.20	2.33
0.0120	0.448	82	51.41	42.00	28.33	2.19
0.0162	0.458	81	113.40	69.38	37.08	2.21

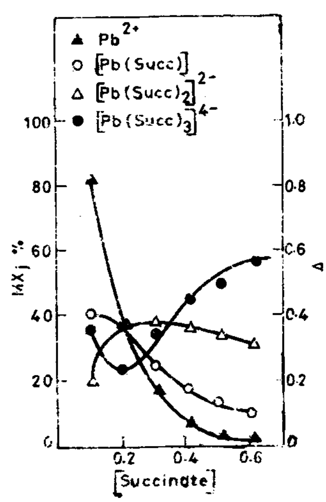


Figure 2. Percentage distribution of Pb(II) in its various forms as a function of $[Succinate^{2-}]$

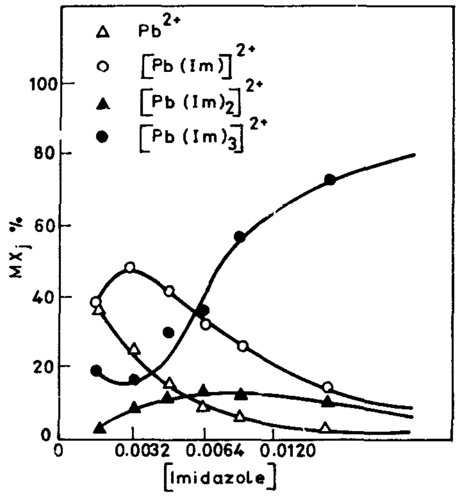


Figure 3. Percentage distribution of Pb(II) in its various forms as a function of [Im].

(1951) method has been applied to determine the stability constants of the successive complexes. The polarographic characteristics and $F_i[X]$ and $F_j[X]$ functions of Pb(II)- succinate and Pb(II)-imidazole systems have been presented in tables 1 and 2. Pb(II) forms three complexes with both the ligands. These are: [Pb(Succ)], $[Pb(Succ)_2]^{2-}$ and $[Pb(Succ)_3]^{4-}$ with stability constants log $\beta_{10} = 2.7$, log $\beta_{20} = 3.4$ and log $\beta_{30} = 3.9$; and $[Pb(Im)]^{2+}$, $[Pb(Im)_2]^{2+}$ and $[Pb(Im)_3]^{2+}$ with stability constants $\beta_{01} = 2.90$, log $\beta_{02} = 4.30$ and log $\beta_{03} = 6.30$. The percentage distribution of Pb(II) in its various forms as a function of $[Succ^{2-}]$ and [Im] has been presented in figures 2 and 3.

3.2 *Pb(II)-succinate-imidazole system*

$[Succ^{2-}]$ was varied from 0–0.6 M [Im] was kept constant at 0.0032 M. It was found that the $E_{1/2}$ values were more negative than those obtained in the absence of imidazole thereby showing the formation of mixed complexes. The system was repeated at another concentration of imidazole (0.0064 M). The method of Schaap and McMasters (1961) was applied to determine the values of the stability constants of mixed complexes. The polarographic characteristics and $F_{ij}[X, Y]$ functions of the system have been presented in table 3. From the plots of F_{ij} data *vs* $[Succ^{2-}]$ (representative figure 4 for series 1) the following intercept values of constants (Crow 1963) A, B, C and D have been obtained which involve an error of ±0.5%. For series 1: log $A = 0.7$, log $B = 2.9$, log $C = 3.8$ and log $D = 3.9$. For series 2: log $A = 1.3$, log $B = 3.1$, log $C = 3.9$ and log $D = 4.1$.

The stability constants of the mixed complexes have been determined from the values of A, B, C and D. Three mixed complexes, *viz* [Pb(Succ)(Im)], $[Pb(Succ)(Im)_2]$ and $[Pb(Succ)_2(Im)]^{2-}$ with stability constants log $\beta_{11} = 4.9$ log $\beta_{12} = 6.7$ and log $\beta_{21} = 6.0$ respectively are formed. The mixing constant K_M (equilibrium constant) for the reaction:

$$1/2[Pb(Im)_2]^{2+} + 1/2[Pb(Succ)_2]^{2-} \rightleftharpoons [Pb(Succ)(Im)] \quad (5)$$

indicates the relative stability of mixed complexes in solution as compared to parent

Table 3. Values of $F_{ij}[X,Y]$ functions for Pb(II)-succinate-imidazole system.

$[Succ^{2-}]$ M	$-E^{1/2}$ V (SCE)	i_d div.	$F_{00}[X,Y]$	$F_{10}[X,Y]$ $\times 10^{-2}$	$F_{20}[X,Y]$ $\times 10^{-3}$	$F_{30}[X,Y]$ $\times 10^{-3}$
Series 1 - Concentration of Imidazole, [Im] = 0.0032 M						
0.00	0.400	100	-	-	-	-
0.05	0.455	88	82.64	15.52	-	-
0.10	0.463	86	157.80	15.28	72.50	-
0.20	0.477	84	480.90	23.54	77.70	8.85
0.30	0.487	84	1053.00	34.94	89.76	8.92
0.40	0.494	83	1831.00	45.65	94.12	8.53
0.50	0.500	82	2959.00	59.08	102.16	8.43
0.60	0.505	81	4423.00	73.65	109.38	8.23
Series 2 - Concentration of Imidazole, [Im] = 0.0064 M						
0.00	0.400	100	-	-	-	-
0.50	0.460	85	126.20	21.64	-	-
0.10	0.467	81	228.80	20.88	88.80	-
0.20	0.480	82	625.50	30.27	91.35	-
0.30	0.490	81	1374.00	45.13	110.43	11.80
0.40	0.496	80	2095.00	64.37	130.92	13.98
0.50	0.504	80	4143.00	78.86	133.72	11.74
0.60	0.509	78	6273.00	101.20	148.66	12.27

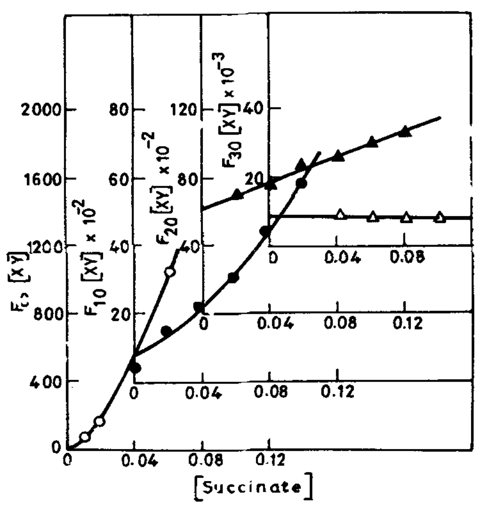


Figure 4. Plots of $F_{ij}[X,Y]$ *vs* $[Succinate^{2-}]$ for Pb(II)-succinate-imidazole system.

binary complexes, this is given by

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

The value of log K_M works out to be +1.1 for the reaction (5). The positive value of log K_M shows that the mixed complex [Pb(Succ)(Im)] is more stable than the simple binary complexes, $[Pb(Succ)_2]^{2-}$ and $[Pb(Im)_2]^{2+}$.

Table 4. Equilibria involved in three mixed complexes and equilibrium constant (K) values.

	Equilibria	log K at 25° C
1.	$Pb^{2+} + Succ^{2-} + Im \rightleftharpoons [Pb(Succ)(Im)]$	4.9
2.	$Pb^{2+} + Succ^{2-} + 2Im \rightleftharpoons [Pb(Succ)(Im)_2]$	6.7
3.	$Pb^{2+} + Succ^{2-} + Im \rightleftharpoons [Pb(Succ)_2(Im)]^{2-}$	6.0
4.	$[Pb(Succ)(Im)] + Im \rightleftharpoons [Pb(Succ)(Im)_2]$	1.8
5.	$[Pb(Succ)(Im)] + Succ^{2-} \rightleftharpoons [Pb(Succ)_2(Im)_2]^{2-}$	1.1
6.	$[Pb(Succ)_2(Im)]^{2-} + Im \rightleftharpoons [Pb(Succ)(Im)_2] + Succ^{2-}$	0.7
7.	$[Pb(Succ)] + Im \rightleftharpoons [Pb(Succ)(Im)]$	2.2
8.	$[Pb(Succ)_2]^{2-} + Im \rightleftharpoons [Pb(Succ)_2(Im)_2]^{2-}$	2.6
9.	$[Pb(Succ)] + 2Im \rightleftharpoons [Pb(Succ)(Im)_2]$	2.6
10.	$[Pb(Im)]^{2+} + Succ^{2-} \rightleftharpoons [Pb(Succ)(Im)]$	2.0
11.	$[Pb(IM)]^{2+} + 2Succ^{2-} \rightleftharpoons [Pb(Succ)_2(Im)]$	3.1
12.	$[Pb(Succ)_2]^{2-} + Im \rightleftharpoons [Pb(Succ)_2(Im)] + Succ^{2-}$	1.5
13.	$[Pb(Succ)_3]^{4-} + Im \rightleftharpoons [Pb(Succ)_2(Im)]^{2-} + Succ$	2.1
14.	$[Pb(Im)_2]^{2+} + 2Succ^{2-} \rightleftharpoons [Pb(Succ)_2(Im)]^{2-} + Im$	1.7

Disproportionation constant (Δlog K) for the equilibria:

$$2\ [Pb(Succ)(Im)] \rightleftharpoons [Pb(Succ)_2]^{2-} + [Pb(Im)_2]^{2+} \quad (6)$$

$$2\ [Pb(Succ)(Im)_2] \rightleftharpoons [Pb(Succ)_2]^{2-} + [Pb(Im)_2]^{2+} + 2Im \quad (7)$$

$$2\ [Pb(Succ)_2(Im)] \rightleftharpoons [Pb(Succ)_2]^{2-} + [Pb(Im)_2]^{2+} + Succ^{2-} \quad (8)$$

works out to be -2.1, -5.7 and -4.3 respectively. The positive value of Δ log K for (6) shows that the mixed complex species, [Pb(Succ)(Im)] is less stable than the simple binary complexes, $[Pb(Succ)_2]^{2-}$ and $[Pb(Im)_2]^{2+}$. On the other hand negative values of Δ log K for equilibrium (6)(7) (Bidkar *et al* 1977) show that the mixed species [Pb(Succ) (Im)], $[Pb(Succ)(Im)_2]$ and $[Pb(Succ)_2(Im)]^{2-}$ are more stable than the simple binary complexes, $[Pb(Succ)_2]^{2-}$ and $[Pb(Im)_2]^{2+}$.

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

From the equilibrium constant values, the relative tendency of $Succ^{2-}$ and Im to add to the mixed complex species, [Pb(Succ)(Im)] can be compared. It is seen that Im adds readily to [Pb(Succ)(Im)] as compared to $Succ^{2-}$ (equilibria 4 and 5). It is also seen that Im can replace $Succ^{2-}$ from the mixed complex, $[Pb(Succ)_2(Im)]^-$ Equilibria 10, 11, 12 and 13 indicate that complexing tendency of Im is much more than $Succ^{2-}$.

The stability of three mixed complexes as seen from their overall stability constants follows the order:

$$[Pb(Succ)(Im)_2] > [Pb(Succ)_2(Im)]^{2-} > [Pb(Succ)(Im)]$$

4. Conclusion

Pb(II) can be determined polarographically in the presence of both $Succ^{2-}$ and imidazole.

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