Polarography of Mixed Ligand Complexes of Cu(II), Cd(II) and Pb(II) with Phthalic Acid and 1,2 Propylenediamine

J.K. Garg* , P.S. Verma** and D.S. Jain**

* Postgraduate Department of Chemistry
Government College, Ajmer-305001, India

** Department of Chemistry,
University of Rajasthan, Jaipur-302004, India

The mixed complexes of Cu(II), Cd(II) and Pb(II) with phthalic acid as primary ligand and 1,2 propylenediamine as secondary ligand have been studied by polargraphy. The stability constants of the various species formed have been evaluated using the method of Schaap and McMasters. The values of equilibrium constants are correlated and discussed in terms of statistical consideration, charge neutralization etc.

In continuation of our earlier work [1-4] on the polarographic study of different metal ions with carboxylic acids and diamine, studies on the formation of mixed ligand complexes by Cu(II), Cd(II) and Pb(II) with phthalic acid (phth) as primary ligand and 1,2 propylenediamine (pn) as secondary ligand are reported in this paper. It is observed that highest complex of Cu (II) is 1:2 while that of Cd(II) and Pb(II) is found to be 1:3.

EXPERIMENTAL

Experimental details are same as described earlier (2-3). In the study of mixed ligand complexes of Cd (II), the ionic strengths of all the solutions were maintained at 1.0 (KNO_3). The acid dissociation constants of the ligands were determined under the present experimental conditions by the method of Albert and Serjeant (6). The pK_1 and pK_2 values are (7.00, 9.78) and (2.92, 5,43) respectively for 1,2 propylenediamine and phthalic acid. The concentration of the free ligands were calculated from the pH and the total amount present using determined values of dissociation constants of the ligand.

RESULTS AND DISCUSSIONS

THE SIMPLE SYSTEM

The reductions of Cu(II), Cd(II) and Pb(II) in all the systems were found to be diffusion controlled and reversible involving two electrons as indicated by the linear plots of i_d versus $h_{eff}^{1/2}$ passing through the origin.The plots of log $i/(i_d-i)$ versus $E_{d.e}$, were linear with a slope of 31 ± 2 mV. No maximum suppressor was needed in these systems. The overall formation constants of simple complexes have been evaluated by DeFord and Hume's method (6). The computed values of log β_1 log β_2 are given in Table 1. The uncertainty in the above reported stability constants is ± 0.05.

THE MIXED (TERNARY) SYSTEMS

Polarograms were taken with solution containing 0.5 mM Cu II in 1 M KNO_3 , Cr 0.5 mM Cd II in 1 $MKNO_3$, Cr 0.5 mM Pb in 0.5 $MKNO_3$ with varying concentration of 1,2 propylenediamine and fixed concentration of phthalate (0.20 M in case of Cu(II), 0.20 M and 0.25 M and in case of Cd (II) or 0.20 M and 0.24 M in case of Pb (II). The pH was maintained at 8.0 because at this pH it is much easier to hold the concentration of phthalate and to vary the concentration of propylenediamine. The corresponding binary systems were also determined under identical pH values and experimental conditions. The equilibrium concentration of stronger ligand (pn) was determined from pH of solution and determined pK values. A shift in $E_{1/2}$ to more negative potential with increasing propylenediamine concentration was observed in all the cases. This shift is greater in presence of weaker ligand (phthalate) than in its absence. It signifies the formation of mixed ligand complexes. The Schaap and McMaster's (7) treatment was applied to the $E_{1/2}$ data and F_{io} functions evaluated. Leaden's (8) graphical extrapolation method was applied to calculate A, B, C and D (Table 2). The observed values of formation constants (log β_{11} ,log β_{12} and log β_{21}) are also included in this Table. The uncertainty in the reported overall formation constants is ± 0.06. It can be noted that log $B_{20}$and log C in case of Cu complexes and log B_{30} and log D incase of Cd and Pb complexes agree as predicted by theory.

A number of interesting observations are worth mentioning. The log K values for addition of a phth group to $[Cu(phth)]^2$ and $[Cu(pn)]^{2+}$ are 2.10, 3.20. The corresponding tendency to add pn to [Cu(phth)] and $[Cu(pn)]^{2+}$ are 10.61, 6.44. These observations suggest that mixed ligand formation is favoured.

TABLE 1

LOG STABILITY CONSTANTS OF DIFFERENT BINARY COMPLEXES

μ = 1.0 M KNO_3

	Log of β_{10}	β_{20}	β_{30}	β_{01}	β_{02}	β_{03}
CuPn	13.00	19.44	-	-	-	-
CuPhth	-	-		5.59	7.69	-
CdPn	5.04	9.08	12.89	-	-	-
CdPhth	-	-	-	2.99	4.21	4.98
PbPn	5.06	8.20	10.96	-	-	-
PbPhth	-	-	-	2.99	3.76	4.48

The log K values for addition of phth to [Cd(phth)] and $[Cd(pn)]^{2}$ are 1.22, 2.45. Likewise the tendency to add pn to [Cd(phth)] and $[Cd(pn)]^{2+}$ are 4.50,4.04. The log K values obtained for the addition of neutral propylenediamine molecule as third ligand to $[Cd(phth)_2]^{2-}$, [Cd(pn)(phth)] and $[Cd(pn)_2]^{2+}$ are 4.44, 3.51,3.81. The log K values for the addition of a phthalate ion as third ligand to $[Cd(phth)_2]^{2-}$, [Cd(pn)(phth)] and $[Cd(pn)_2]^{2+}$ are 0.74, 1.16, 1.92.

The tendency of [Pb(phth)] and $[Pb(pn)]^{2+}$ to add a phthalate anion is given by log K values of 0.77, 1.77. Again the difference is much larger than the statistical factor of 2 would predict showing the effect of charge neutrlization. The addition of uncharged propylenediamine ligand to each of the above complexes gives rise to log K values of 3.84 and 3.14. These observations also suggest that formation of mixed complex is favoured. The log K values for the addition of propylenediamine as third ligand to $[Pb(phth)_2]^{2-}$ [Pb(pn)(phth)] and $[Pb(pn)_2]^{2+}$ are 3.27, 2.37 and 2.76 which shows that addition of a stronger ligand viz pn is preferred to a weaker ligand viz phth. The log K values for the addition of phthalate anion as third ligand to $[Pb(phth)_2]^{2-}$, [Pb(pn)(phth)] and $[Pb(pn)_2]^{2+}$ are 0.72, 0.20 and 1.00 which suggests that the addition of phthalate anion is preferred to $[Pb(phth)_2]^{2-}$ and $[Pb(pn)_2]^{2+}$ as compared to [Pb(pn)(phth)].

The relative stability of a mixed complex over the parent binary complex and the compatibility between the ligands, indicated by the "mixing constant" K_M and the enhanced (or sometime decreased) stability due to factor other than statistical given by "stabilization constant" K_S are calculated by the expression of Marcus and Eliezer [9].

$$K_{M(x,y)} = \beta_{xy} \cdot \beta_{m,0}^{-x/m} \cdot \beta_{0,m}^{-y/m} \qquad (x+y = m)$$

$$\text{and} \quad \log K_S = \log K_M - \log (m!/x!.y!)$$

The observed values of K_M and K_S of these ternary systems are given in Table 3.

The positive values of mixing constant and stabilization constant show that the mixed complex is more stable than the simple bis complexes. The positive value of stabilization constant has also been observed by Brookes and Pettit [10], Gergely and Sovago [11], Ting and Nancollas [12] and Jain and Kapoor [13].

The extent of stabilization of ternary complexes also can be inferred from the value of $\Delta \log K$. For any complex $[M(pn)_r (phth)_s]$, the $\Delta \log K_{rs}$ values can be obtained by using the generalized equation:

$$\log K_{rs} = \log \beta_{rs} - (\log \beta_{ro} + \log \beta_{os})$$

Where M is Cu(II) or Cd (II) or Pb (II), r is the number of moles of propylenediamine and s is the number of moles of phthalate. Sigel [14] has shown that when both the ligands are bidentate, the statistical value of $\Delta \log K$ is -0.4 for octahedral complexes. According to Sigel [14] the statistical values of $\Delta \log K$ for metal ions like Cu(II) forming distorted octahedral complexes will be lower. The $\Delta \log K$ values obtained in the present study are shown in Table 4.

TABLE 2

MIXED LIGAND CONSTANTS PARAMETERS AT 298 ± 0.5° K , pH = 8.0

System	KNO_3	[Phthalate]	A calculated	B	C	D	log C_{av}	log D_{av}	log B_{11}	log B_{12}	log B_{21}
Cu-pn-phth	1.0	0.20M	31.57×10^{5}	32.00×10^{14}	5.52×10^{19}	-	19.74	-	16.20	-	-
Cd-pn-phth	1.0	0.20M	15.65×10^{2}	24.0×10^{6}	2.10×10^{10}	7.22×10^{12}	-	12.86	7.49	8.65	11.00
		0.25M	26.62×10^{2}	35.5×10^{6}	2.59×10^{10}	7.82×10^{12}	-	12.89	-	-	-
Pb-pn-phth	1.5	0.20M	6.66×10^{2}	190.0×10^{4}	4.80×10^{8}	8.38×10^{10}	-	10.92	6.83	7.03	9.20
		0.24M	9.80×10^{2}	236.0×10^{4}	5.44×10^{8}	8.62×10^{10}	-	10.94	-	-	-

TABLE 3

Ternary system	log $K_{M_{11}}$	log $K_{M_{12}}$	log $K_{M_{21}}$	log $K_{S_{11}}$	log $K_{S_{12}}$	log $K_{S_{24}}$
Cu-pn-phth	2.64	-	-	2.34	-	-
Cd-pn-phth	0.85	1.13	0.86	0.55	0.65	0.38
Pb-pn-phth	0.85	0.49	0.53	0.55	0.01	0.05

Sigel [15] has also reported that as far as possible log X(= 2 log K_M) should be used for the estimation of stability of unknown mixed ligand complex.

Watter and DeWitt [16] and Tadesco and Martinez [17] have duduced that for a mixed ligand system in which three mixed complexes are formed, it is possible to predict on statistical basis that the value of formation constant β_{11} would be $2[4/9\ \beta_{02} \times \beta_{20}]^{1/2}$, β_{12} would be $3[\beta_{30}^{1/3} \times \beta_{03}^{2/3}]$ and β_{21} would be $3[\beta_{30}^{2/3} \times \beta_{03}^{1/3}]$.

The values of stability constants calculated from the above expressions are (6.77, 8.07, 10.72) and (6.10,7.11,9.28) for the Cd-pn-phth and Pb-pn-phth system respectively. The experimental values for the mixed complex species [Cd(pn)(phth)] or [Pb(pn)(phth)] is higher than the statistically calculated value. This has been explained by many workers [16-17] considering the enhancement due to some weak bonding between unlike bound ligand. This may also be accounted for due to the neutralization of charge [13].

The formation of neutral ternary complexes from the parent complexes can be represented as follows:

$$[M(pn)_2]^{2+} + [M(phth)_2]^{2-} \rightleftharpoons 2[M(pn)(phth)]$$

Where M is Cu(II) or Cd(II) or Pb(II).

Many workers [18-20] have observed that charge neutralization favours formation of mixed ligand complexes. In addition to coulombic effects, such a neutralization of charge would be expected to be accompanied by a positive entropy change due to decreased orientation of the solvent molecule (desolvation of the charged species). Our results are in agreement with this postulation.

It is observed that Cu(II) or Cd(II) or Pb(II) forms with phthalate and propylenediamine a mixed ligand complex having one five - and one seven - membered ring.

On comparison of the formation constants data for mixed ligand complexes of Copper (II), Cadmium (II) and Lead (II) with the ratio 1:1:1, it is observed that among these, the copper complexes are most stable. From the values of overall stability constants data for mixed ligand species of Cd(II) and Pb(II) with the ratio 1:1:2 it is observed that stability of $[Cd - (pn) - (phth)_2]^{-2}$ $[Pb - (pn) - (phth)_2]^{2-}$. Likewise it is also observed that the stability of $[Cd(pn)_2\ (phth)]$ $>[Pb(pn)\ (phth)]$.

TABLE 4

Ternary system	Δ log K_{11}	Δlog K_{12}	Δ log K_{21}
Cu-pn-phth	- 2.39	-	-
Cd-pn-phth	- 0.54	- 0.60	- 1.08
Pb-pn-phth	- 1.22	- 1.79	- 1.99

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