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Study of Mixed Complexes of Cu(II) with Propylene Diamine, Malonate and Maleate Ions using Polarographic Technique

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The mixed ligand complexes of propylene diamine (pn), malonate (mal) and maleate (male) with Cu(II) have been studied polarographically at constant ionic strength, $\mu = 1.5$ M ($NaNO_3$) and pH 6.43 at 25.0 ± 0.1 ºC. The reduction of the complexes at d.m.e. is reversible and diffusion-controlled. One mixed complex [Cu(pn)(mal)] and [Cu(pn)(male)] is formed in each case with stability constants log $\beta_{11} = 16.69$ and 16.585 respectively.

Key Words: Polarography, Mixed complexes, Stability constants.

INTRODUCTION

The mixed ligand complexes are important in analytical, biochemical and pharmaceutical field. Therefore several workers have studied such type of complexes polarographically during the last few decade[1-13]. However from the survey of literature, it appears that polarographic studies of mixed complexes of Cu(II) with propylene diamine, malonate and maleate ions are still lacking. The present communication deals with the studies of mixed ligand complexes of Cu(II) with propylene diamine, malonate and maleate ions.

EXPERIMENTAL

All reagents were analytical grade and their solutions were prepared in conductivity water. The ionic strength was maintained constant at $\mu = 1.5$ M using $NaNO_3$ as supporting electrolyte. The concentration of Cu(II) was maintained at 1×10^{-3} M. Polarograms[14] were obtained by means of a manual polarograph (Toshniwal CL 02) in conjunction with Toshniwal polyflex galvanometer (PL 50). All the measurements were made at 25 ± 0.1 ºC and pH 6.43. A saturated calomel electrode (SCE) was used as reference electrode. The d.m.e. had the following characteristics (in 0.1 M $NaNO_3$, open circuit): $\mu = 2.219$ mg/s, $t = 3.5$ s, $m^{2/3} t^{1/6} = 2.10$ mg$^{2/3}$ s$^{-1/2}$, $h_{corr} = 40$ cm.

RESULTS AND DISCUSSION

Simple system: The simple systems of Cu(II) with propylene diamine and Cu(II) with malonate and maleate ions were studied by the method of Deford and Hume[15]. The results are in good agreement with the previous studies. Identical conditions were maintained in both simple and mixed systems *i.e.* 1.5 M sodium nitrate as supporting electrolyte and Triton-X-100 = 2×10^{-3} as maxima superior. The values of stability constants of simple complexes have been tabulated in Table-1.

TABLE-1
STABILITY CONSTANTS OF PROPYLENEDIAMINE, MALONATE AND MALEATE WITH Cu(II)

System	log β_1	log β_2
Cu(II)-Propylenediamine	14.84	20.97
Cu(II)-Malonate	4.78	6.70
Cu(II)-Maleate	3.18	4.51

Mixed system: Propylenediamine concentration was varied from 0.01 to 0.10 M and that of malonate or maleate was kept constant at 0.10 M. The $E_{1/2}$ values were greater compared to those obtained in the absence of malonate or maleate ions thereby showing the formation of mixed complexes. The system was repeated at another concentration of malonate or maleate ions (0.20 M).

The method of Schaap and McMaster[16] was used to determine the values of the stability constants of mixed complexes. The polarographic characteristic and $F_{ij}[XY]$ functions of mixed complexes of Cu(II) with propylenediamine and malonate or maleate at fixed [mal^{2-}] or [$male^{2-}$] (0.10 and 0.20 M) are presented in Tables 2 and 3.

The stability constants of the mixed complexes were calculated from the constants A, B and C. One mixed complex as mentioned in Tables 2 or 3 is formed in each mixed system.

The results of the present study are summarized in the following **Schemes I** and **II**, where the numerical values shown are the logarithisms of the equilibrium constants for the reactions indicated.

The mixing constant K_M (equilibrium constant) for the reactions:

$$\tfrac{1}{2}[Cu(pn)_2]^{2+} + \tfrac{1}{2}[Cu(mal)_2]^{2-} \rightleftharpoons [Cu(pn)(mal)] \quad (1)$$

$$\tfrac{1}{2}[Cu(pn)_2]^{2+} + \tfrac{1}{2}[Cu(male)_2]^{2-} \rightleftharpoons [Cu(pn)(male)] \quad (2)$$

is given by the relation.

$$\log K_{M(1)} = \log \beta_{11} - \tfrac{1}{2}(\log \beta_{20} + \log \beta_{02})$$

These works out to be +2.85 for reaction 1 and +3.85 for reaction 2. The positive value shows that the mixed complexes [Cu(pn)(mal)] and [Cu(pn)(male)] are more stable than their simple complexes: $[Cu(pn)_2]^{2+}$, $[Cu(mal)_2]^{2-}$ and $[Cu(male)_2]^{2-}$.

TABLE-2

Cu(II)-PROPYLENEDIAMINE-MALONATE SYSTEM $[Cu^{2-}] = 1 \times 10^{-3}$ M, $\mu = 1.5$ M ($NaNO_3$), pH = 6.43, Temp. = 25 ± 0.1 ºC, $(E_{½})_S = -0.018$ Volts (SCE)

$[pn]_t$ M	$[pn]_f \times 10^{-6}$ M	$-E_{1/2}$ V (SCE)	log I_m/I_c	Slope mv	F_{00} [X,Y] $\times 10^{-9}$	F_{10} [X,Y] $\times 10^{-15}$	F_{20} [X,Y] $\times 10^{-20}$
Series-I $[mal^{2-}] = 0.1$ M (Fixed)							
0.01	1.2	0.292	0.03846	30	33.21	11.01	–
0.02	2.4	0.298	0.04249	31	53.65	14.02	20.4
0.03	3.6	0.303	0.04249	32	80.70	16.90	29.0
0.04	4.8	0.308	0.05060	32	119.12	20.60	30.5
0.06	7.2	0.314	0.06328	31	211.50	26.60	28.5
0.08	9.6	0.321	0.07625	33	347.70	34.10	29.3
0.10	12.0	0.326	0.07625	32	513.20	41.10	29.3
Series-II $[mal^{2-}] = 0.2$ M (Fixed)							
0.01	1.2	0.297	0.03846	31	49.1	13.5	28.9
0.02	2.4	0.302	0.04657	30	74.0	17.1	29.9
0.03	3.6	0.307	0.05484	31	111.3	21.7	32.5
0.04	4.8	0.312	0.06756	32	156.4	25.7	32.7
0.06	7.2	0.318	0.07625	33	275.3	33.6	32.8
0.08	9.6	0.324	0.08065	33	443.7	42.8	32.4
0.10	12.0	0.328	0.08961	33	618.5	48.8	32.3

$[pn]_t$ = Total concentration of propylenediamine,

$[pn]_f$ = Free legand concentration of propylenediamine,

Series I: log A = 10.30, log B = 15.78, log C = 21.46

Series II: log A = 10.52, log B = 16.00, log C = 21.50

TABLE-3

Cu(II)-PROPYLENEDIAMINE-MALEATE SYSTEM $[Cu^{2-}] = 1 \times 10^{-3}$ M, $\mu = 1.5$ M ($NaNO_3$), pH = 6.43, Temp. = 25 ± 0.1 ºC, $(E_{½})_S = -0.018$ Volts (SCE)

$[pn]_t$ M	$[pn]_f \times 10^{-6}$ M	$-E_{1/2}$ V (SCE)	log I_m/I_c	Slope mv	F_{00} [X,Y] $\times 10^{-8}$	F_{10} [X,Y] $\times 10^{-14}$	F_{20} [X,Y] $\times 10^{-20}$
Series-I $[male^{2-}] = 0.1$ M (Fixed)							
0.01	1.2	0.284	0.0188	30	19.95	5.73	–
0.02	2.4	0.291	0.04249	31	31.1	7.5	12.6
0.03	3.6	0.296	0.04658	31	46.3	9.3	13.2
0.04	4.8	0.300	0.05484	31	64.5	10.7	12.9
0.06	7.2	0.308	0.05484	32	120.3	14.9	14.2
0.08	9.6	0.313	0.05484	33	177.9	17.1	13.0
0.10	12	0.317	0.07625	32	254.6	20.1	13.1
Series-II $[male^{2-}] = 0.2$ M (Fixed)							
0.01	1.2	0.290	0.03049	31	27.9	9.15	–
0.02	2.4	0.297	0.04658	30	50	13.8	16.2
0.03	3.6	0.301	0.06756	32	77.6	16.8	16.9
0.04	4.8	0.307	0.07188	31	115.7	20.6	17.2
0.06	7.2	0.314	0.07188	33	119.6	25.4	14.8
0.08	9.6	0.300	0.08961	32	331.7	32.8	16.3
0.10	12	0.325	0.08961	33	489.6	39.4	16.5

$[pn]_t$ = Total concentration of propylenediamine,

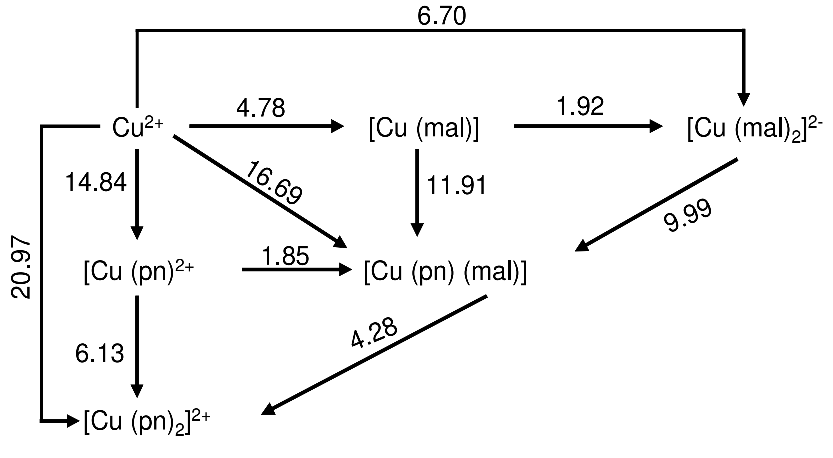
$[pn]_f$ = Free legand Concentration of propylenediamine,

Series I: log A = 10.11, log B = 15.65, log C = 21.12

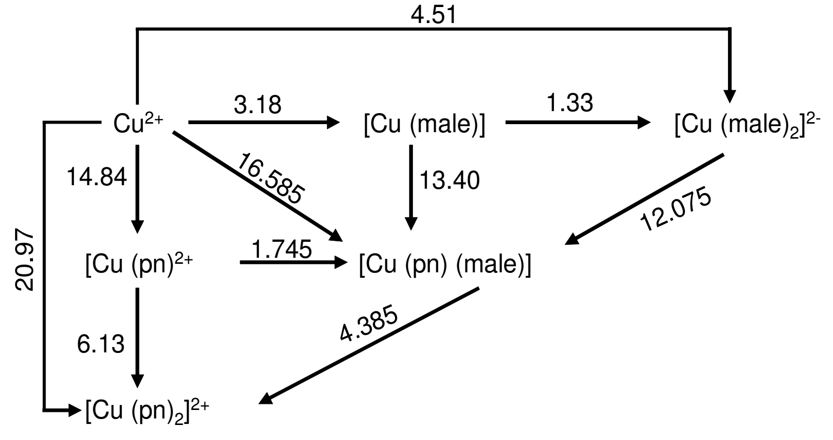
Series II: log A = 10.23, log B = 15.87, log C = 21.20

TABLE-4
STABILITY CONSTANTS OF MIXED LIGAND COMPLEXES OF Cu(II) WITH PROPYLENEDIAMINE AND MALONATE OR MALEATE IONS

Name of system	Composition	$\log \beta_{11}$
Cu(II)-pn-mal^{2-}	[Cu(pn)(mal)]	16.690
Cu(II)-pn-male^{-}	[Cu(pn)(male)]	16.585



Scheme-I: Cu(II)-pn-malonate system



Scheme-II: Cu(II)-pn-maleate system

The equilibrium constants (log values) for the following disproportion reaction:

$$½[Cu(pn)(mal)] \rightleftharpoons [Cu(pn)_2]^{2+} + ½[Cu(mal)_2]^{2-} \qquad (3)$$

$$½[Cu(pn)(male)] \rightleftharpoons [Cu(pn)_2]^{2+} + ½[Cu(male)_2]^{2-} \qquad (4)$$

works out to be -5.71 for reaction 3 and -7.69 for reaction 4. These large negative values favour mixed complexion over simple ones.

The complex [Cu(pn)(mal)] is more stable than the complex [Cu(pn)(male)].

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REFERENCES

1. O.N. Shrivastava and C.M. Gupta, *Analyst*, **97**, 204 (1972).
2. H. Haurr, E.J. Billo and D.W. Margerum, *J. Am. Chem. Soc.*, **93**, 4173 (1971).
3. J.K. Garg, D.S. Jain and P.S. Verms, *J. Electrochem. Soc.*, **32**, 193 (1983).
4. J.K. Garg, *J. Electrochem. Soc.*, **38**, 299 (1989).
5. J.K. Garg, P.S. Verma and D.S. Jain, *Indian J. Chem.*, **21A**, 1142 (1982).
6. H. Sigri, R. Griesser and B. Prijs, *Naturfor, Z. Sel, Terl.*, **27**, 353 (1972).
7. S.C. Khurana, I.J. Nigam, S.P. Saxena and C.M. Gupta, *Aust. J. Chem.*, **28**, 1617 (1975).
8. S.K. Shah and C.M. Gupta, *Chem. Scripta*, **16**, 134 (1980).
9. A. Kumar, P.K.S. Chauhan and R.K. Paliwal, *J. Chemtracks*, **4**, 47 (2002).
10. H.L. Nigam, K.B. Pandeya and V.S. Verma, *J. Indian Chem. Soc.*, **66**, 541 (1989).
11. A. Kumar, P.K.S. Chauhan and R.K. Paliwal, *J. Chemtracks*, **4**, 59 (2002).
12. S. Singh, P.K.S. Chauhan and R.K. Paliwal, *J. Chemtracks*, **7**, 79 (2005).
13. K. Srivastava, M. Kumari, A. Srivastava and J. Prasad, *J. Indian Chem. Soc.*, **84**, 515 (2007).
14. L. Meites, Polarographic Techniques, Inter Science Publ., New York, p. 219 (1965).
15. D.D. Deford and D.N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).
16. W.B. Schaap and D.L. McMaster, *J. Am. Chem. Soc.*, **83**, 4699 (1961).

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