Asian Journal of Chemistry Vol. 17, No. 1 (2005), 355–359

Polarographic Study of Stability Constants of Copper(II) Complexes with β-picoline, Malic and Tartaric Acid

P.K.S. CHAUHAN, AMIT VERMA and R.K. PALIWAL*
Department of Chemistry, Narain College, Shikohabad-205 135 (India)

The mixed ligand complexes of β-picoline (β-pico), malate (mal^{2-}) and tartrate ($tart^{2-}$) with Cu(II) have been studied polarographically at constant ionic strength (μ = 1.5 M ($NaNO_3$) and pH 5.95 at 25 ± 0.1°)C. The reduction of the complexes at d.m.e. is reversible and diffusion-controlled. Two mixed complexes, [Cu(β-pico)(mal)] and [Cu(β-pico)(tart)] are formed. Their stability constants are found to be $\log \beta_{11} = 5.0360$ and $\log \beta_{11} = 4.8932$, respectively at 25°C.

Key Words: Polarographic study, Stability constants, Copper(II) complexes, β-Picoline, Malic and tartaric acid.

INTRODUCTION

Mixed-ligand complexes are important in analytical, biochemical and pharmaceutical fields[1–5]. A large number of such complexes have been studied polarographically during the past decade. Shrivastava and Gupta[6] investigated the complexes of Cu(II) with lactic acid and glycollic acid at d.m.e. in aqueous and non-aqueous media. Garg *et al.*[7–9] have reported polarographic studies of mixed ligand complexes formed by Cu(II) with ethylene diamine/propylene diamine and some dibasic acids, *viz.*, malonic, maleic, succinic, adipic and phthalic acid. Several other workers[10–23] have also studied ternary complexes between Cu(II) and various ligands polarographically. However, there is no work has been reported so far about the polarographic study of mixed ligand complex formation of Cu(II) with β-picoline as primary ligand and hydroxy acids, *viz.*, malic and tartaric acid as secondary ligands. The present communication deals with the studies of mixed-ligand complexes of Cu(II) with β-picoline and hydroxy acids (malic and tartaric acid).

EXPERIMENTAL

All reagents were analytical grade and their solutions were prepared in conductivity water. The ionic strength was maintained constant at μ = 1.5 using $NaNO_3$ as supporting electrolyte. The concentration of Cu(II) was maintained at 1×10^{-3} M. Polarograms were obtained[24] 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°C and pH 5.95. A saturated calomel electrode (S.C.E.) was used as reference electrode. The d.m.e. had the following characteristics (in 0.1 M $NaNO_3$, open circuit): m = 2.129 mg/sec, t = 3.5 sec, $m^{2/3}t^{1/6} = 2.10\ mg^{2/3}sec^{-1/2}$, $h_{corr} = 40$ cm.

RESULTS AND DISCUSSION

(a) Simple System

The simple systems of Cu(II) with β-picoline and Cu(II) with hydroxy acids (malic and tartaric acid) were studied by the method of Deford and Hume[25]. 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 temperature was maintained constant at 25 ± 0.1°C. The values of stability constants of simple complexes have been tabulated in Table-1.

TABLE-1
STABILITY CONSTANTS OF β-PICOLINE, MALATE AND TARTRATE WITH Cu(II)

Contents	$\log \beta_1$	$\log \beta_2$
β-Picoline	3.5440	5.0820
Malate	3.0791	4.5465
Tartrate	2.1139	3.8401

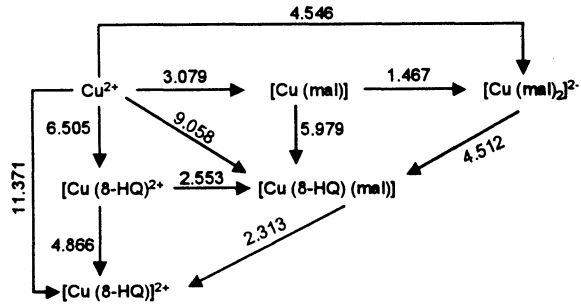
(b) Mixed System

β-picoline concentration was varied from 0.05 to 0.25 M and that of malate and tartrate was kept constant at 0.10 M. The $E_{1/2}$ values were greater compared to those obtained in the absence of malate and tartrate thereby showing the formation of mixed complexes. The system was repeated at another concentration of malate and tartrate (0.20 M).

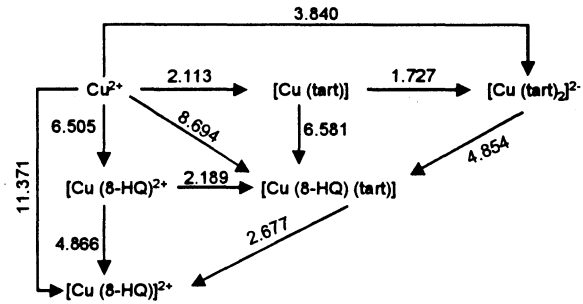
The method of Schaap and McMaster[26] was used to determine the values of the stability constants of mixed complexes. The polarographic characteristics and $F_{ij}[XY]$ functions of mixed complexes of Cu(II) with β-picoline and malate and tartrate at fixed $[mal^{2-}]$ and $[tart^{2-}]$ (0.10 and 0.20 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 Table-4 is formed in each mixed system.

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



Scheme-I



Scheme-II

TABLE-2

Cu(II)–β-PICOLINE-MALATE SYSTEM

$[Cu^{2+}] = 1 \times 10^{-3}$ M, $\mu = 1.5$ M ($NaNO_3$), pH = 5.95,

Temp. = 25 ± 0.1°C, $(E_{1/2})_s$ = +0.016 volts (S.C.E.)

[β-pico]	$-E_{1/2}$ V (S.C.E.)	log I_m/I_c	Slope (mV)	$F_{00}[X, Y] \times 10^{-1}$	$F_{10}[X, Y] \times 10^{-3}$	$F_{20}[X, Y] \times 10^{-5}$
Series-I [mal^{2-}] = 0.10 M (Fixed)						
0.05	0.086	0.09691	30	35.2957	48.8114	0.731
0.10	0.098	0.11539	30	93.7952	82.9052	7.065
0.15	0.107	0.11539	32	189.0882	118.7988	7.103
0.20	0.114	0.11539	31	326.2004	157.6553	7.270
0.25	0.119	0.12493	32	492.2463	192.5425	7.221
Series-II [mal^{2-}] = 0.20 M (Fixed)						
0.05	0.094	0.10605	32	67.2225	74.6250	10.413
0.10	0.107	0.12493	31	193.2878	163.3778	14.081
0.15	0.115	0.13469	31	368.6519	225.8279	13.551
0.20	0.122	0.13469	33	635.9705	303.0302	14.023
0.25	0.127	0.14468	32	960.6927	372.3130	13.990

Series I	log A = 3.0370	log B = 4.0881	log C = 5.8475
Series II	log A = 3.4758	log B = 4.3533	log C = 6.1373

TABLE-3
Cu(II)–β-PICOLINE-TARTRATE SYSTEM

$[Cu^{2+}] = 1 \times 10^{-3}$ M, μ = 1.5 M ($NaNO_3$), pH = 5.95,
Temp. = 25 ± 0.1°C, $(E_{1/2})_s$ = +0.016 volts (S.C.E.)

[β-pico]	$-E_{1/2}$ V (S.C.E.)	log I_m/I_c	Slope (mV)	$F_{00}[X, Y] \times 10^{-1}$	$F_{10}[X, Y] \times 10^{-3}$	$F_{20}[X, Y] \times 10^{-5}$
		Series-I [$tart^{2-}$] = 0.10 M (Fixed)				
0.05	0.074	0.07918	31	13.3050	18.2500	2.358
0.10	0.088	0.07918	30	36.8515	32.6715	2.621
0.15	0.096	0.08795	32	75.3490	47.4460	2.732
0.20	0.102	0.09691	31	122.7515	59.2857	2.641
0.25	0.107	0.10605	31	150.0650	72.3540	2.635
		Series-II [$tart^{2-}$] = 0.20 M (Fixed)				
0.05	0.080	0.08795	30	21.6657	30.5314	2.356
0.10	0.094	0.08795	31	64.4785	58.0785	3.932
0.15	0.102	0.10605	30	125.3626	79.3082	4.037
0.20	0.108	0.11539	32	204.4071	99.0035	4.012
0.25	0.113	0.11539	31	301.7543	118.1417	3.975

Series I	log A = 2.6211	log B = 3.8102	log C = 5.4199
Series II	log A = 2.8061	log B = 3.8102	log C = 5.6031

TABLE-4
STABILITY CONSTANTS OF MIXED LIGAND COMPLEXES
OF Cu(II) WITH β-PICOLINE, MALATE AND TARTRATE

Name of system	Composition	log β_{11}
Cu(II)-β-pico–mal^{2-}	[Cu(β-pico) (mal)]	5.0360
Cu(II)-β-pico–$tart^{2-}$	[Cu(β-pico) (tart)]	4.8932

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

$$½[Cu(\beta\text{-pico})_2]^{2+} + ½[Cu(mal)_2]^{2-} \rightleftharpoons [Cu(\beta\text{-pico})(mal)] \quad (1)$$

$$½[Cu(\beta\text{-pico})_2]^{2+} + ½[Cu(tart)_2]^{2-} \rightleftharpoons [Cu(\beta\text{-pico})(tart)] \quad (2)$$

is given by the relation

$$\log K_M = \log \beta_{11} - ½(\log \beta_{20} + \log \beta_{02})$$

These work out to be +0.222 for reaction (1) and +0.432 for reaction (2). The positive value shows that the mixed complexes [Cu(β-pico)(mal)] and [Cu(β-pico)(mal)] are more stable their simple complexes: $[Cu(\beta\text{-pico})_2]^{2+}$, $[Cu(mal)_2]^{2-}$ and $[Cu(tart)_2]^{2-}$.

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

$$2[Cu(\beta\text{-pico})(mal)] \rightleftharpoons [Cu(\beta\text{-pico})_2]^{2+} + [Cu(mal)_2]^{2-} \quad (3)$$

$$[Cu(\beta\text{-pico})(tart)] \rightleftharpoons [Cu(\beta\text{-pico})_2]^{2+} + \tfrac{1}{2}[Cu(tart)_2]^{2-} \quad (4)$$

work out to be –0.443 for reaction (3) and –0.864 for reaction (4). These negative log values favour mixed complexation over simple ones.

The complex [Cu(β-pico)(mal)] is more stable than the complex [Cu(β-pico)(tart)].

ACKNOWLEDGEMENT

We thank Dr. MC. Yadav, Principal, Narain College, Shikohabad for provision of facilities.

REFERENCES

1. R.N. Patel, H.C. Pandey and K.B. Pandey, *Bull. Electrochem.*, **12**, 612 (1996).
2. B.K. Singh, C.L. Jain and R.S. Sindhu, *Trans. SEAST*, **30**, 04 (1995).
3. R.R. Amaro, M. Sanchez, E. Munoz, J.J. Ruiz and L. Camcho, *J. Electrochem. Soc.*, **143**, 2132(A) (1996).
4. P. Rajeshwari, R. Thamilarasi and S. Rajeshwari, *Trans. SEAST*, **31**, 3 (1996).
5. M. Zelic, *Electroanalysis*, **7**, 4 (1995).
6. O.N. Shrivastava and C.M. Gupta, *Analyst*, **97**, 204 (1972).
7. J.K. Garg, P.S. Verma and D.S. Jain, *Indian J. Chem.*, **21A**, 1142 (1982).
8. J.K. Garg, D.S. Jain and P.S. Verma, *J. Electrochem. Soc. (India)*, **32**, 193 (1983).
9. J.K. Garg, *J. Electrochem. Soc. (India)*, **38**, 299 (1989).
10. H. Haurr, E.J. Billo and D.W. Margerum, *J. Am. Chem. Soc.*, **93**, 4173 (1971).
11. H. Sigri, R. Griesser and B. Prijs, *Naturfor. Z. Sel. Terl.*, **27**, 353 (1972).
12. S.C. Khurana, I.J. Nigam, S.P. Saxena and C.M. Gupta, *Aust. J. Chem.*, **28**, 1617 (1975).
13. S.K. Shah and C.M. Gupta, *Chemica Scripta*, **16**, 134 (1980).
14. S.K. Shah, K.M. Suyan and C.M. Gupta, *Talanta*, **27**, 455 (1980).
15. H.L. Nigam, K.B. Pandeya and V.S. Verma, *J. Indian Chem. Soc.*, **66**, 541 (1989).
16. H.L. Nigam, K.B. Pandeya and R.N. Patel, *J. Indian Chem. Soc.*, **69**, 530 (1992).
17. K.B. Pandeya and R.N. Patel, *J. Indian Chem. Soc.*, **29**, 602 (1990).
18. R.S. Sindhu, S. Tikku and S. Bansal, *J. Indian Chem. Soc.*, **68**, 289 (1991).
19. U. Gupta and A.L. Rao, *J. Indian Chem. Soc.*, **70**, 206 (1993).
20. A. Sharma and M. Singh, *J. Indian Chem. Soc.*, **73**, 423 (1996).
21. B.K. Singh, C.L. Jain and R.S. Sindhu, *J. Indian Chem. Soc.*, **73**, 297 (1996).
22. A.K. Jain and F. Khan, *J. Indian Chem. Soc.*, **75**, 31 (1998).
23. R.K. Lohiya, P.L. Pratihar, R.V. Singh and S.K. Mukherjee, *Orient. J. Chem.*, **17**, 391 (2001).
24. L. Meites, Polarographic Techniques, Interscience Publ., New York, p. 219 (1965).
25. D.D. Deford and D.N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).
26. W.B. Schaap and D.L. McMaster, *J. Am. Chem. Soc.*, **83**, 4699 (1961).

(*Received*: 27 March 2004; *Accepted*: 25 August 2004) AJC-3536