

Polarographic Study of Stability Constants of Cadmium(II) Complexes with β -picoline and Some Hydroxy Acids

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 Cd(II) have been studied polarographically at constant ionic strength ($\mu = 1.5 \text{ M}$, NaNO_3) and pH 5.95 at $25 \pm 0.1^\circ\text{C}$. The reduction of the complexes at d.m.e. is reversible and diffusion-controlled. Three mixed complexes $[\text{Cd}(\text{mal})(\beta\text{-pico})]$, $[\text{Cd}(\text{mal})(\beta\text{-pico})_2]$ and $[\text{Cd}(\text{mal})_2(\beta\text{-pico})]^{2-}$ are formed in Cd(II) β -picoline-malate system with the stability constants $\log \log \beta_{11} = 2.7224$, $\log \beta_{12} = 4.2805$ and $\log \beta_{21} = 3.9661$. Two mixed complexes $[\text{Cd}(\beta\text{-pico})(\text{tart})]$ and $[\text{Cd}(\beta\text{-pico})_2(\text{tart})]$ are formed in Cd- β -picoline-tartrate system and their stability constants are found to be $\log \beta_{11} = 2.1368$ and $\log \beta_{12} = 4.1065$, respectively.

Key Words: Polarographic studies, Stability, Cadmium(II) complexes, β -picoline.

INTRODUCTION

Kim *et al.*¹ have studied the mixed complexes of Cd(II) with histidine and hydroxy ion and determined the stability constants by applying Schaap and McMaster's method. Khurana and Gupta² have studied polarographically the mixed complexes of Cd(II) with oxalate and maleate ions and found that two mixed species are found. Khan *et al.*³⁻⁵ have undertaken the polarographic studies of mixed ligand complexes of Cd(II) with amino acids as primary ligands and carboxylic acids as secondary ligands. Besides this, from the survey of literature⁶⁻¹⁶ it appears that polarographic studies of mixed complexes of Cd(II) with β -picoline, malate and tartrate are still lacking. The present communication deals with the studies of mixed ligand complexes of Cd(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 $\mu = 1.5$ using NaNO_3 as supporting electrolyte. The concentration of Cd(II) was maintained at $1 \times 10^{-3} \text{ M}$. Polarograms were obtained¹⁷ by means of a manual polarograph

(Toshniwal CL 02) in conjunction with Toshniwal polyflex galvanometer (PL 50). All the measurements were made at $25 \pm 0.1^\circ\text{C}$ 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) $m = 2.129 \text{ mg/sec}$, $t = 3.5 \text{ sec}$, $m^{2/3}t^{1/6} = 2.10 \text{ mg}^{2/3}\text{sec}^{-1/2}$, $h_{\text{corr}} = 40 \text{ cm}$.

RESULTS AND DISCUSSION

The reduction of Cd(II) in β -picoline, malate and tartrate was found to be reversible and diffusion controlled. The same was true for the mixed system. The slopes of linear plots of $\log i/i_d - i$ vs. $E_{\text{d.m.e.}}$ were in the range 30–33 mV and the plots of i_d vs. $h_{\text{corr}}^{1/2}$ were linear and passed through the origin. The stability constants of simple complexes of Cd(II) with β -picoline, malate and tartrate were determined separately prior to the study of mixed ligand system. Identical conditions were maintained in both the simple and mixed systems.

(a) Simple System

The simple systems of Cd(II) with β -picoline and Cd(II) with hydroxy acids (malic and tartaric acid) were studied by the method of Deford and Hume¹⁸. 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 Cd(II)

Contents	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
β -Picoline	1.2470	2.2100	3.3110
Malate	1.7923	2.8027	3.3673
Tartrate	1.5947	2.0280	2.8102

(b) Mixed System

β -picoline concentration was varied from 0.10 to 0.60 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 McMaster¹⁹ was used to determine the values of the stability constants of mixed complexes. The polarographic characteristics and $F_{ij}[\text{XY}]$ functions of mixed complexes of Cd(II) with β -picoline and malate at fixed [β -pico] (0.10 and 0.20 M) and Cd(II) with β -picoline and tartrate at fixed [tart^{2-}] (0.10 and 0.20 M) are presented in Tables 2 and 3.

TABLE-2
Cd(II)-MALATE- β -PICOLINE SYSTEM

$[Cd^{2+}] = 1 \times 10^{-3} M$, $\mu = 1.5 M$ (NaNO₃), pH = 5.95,

Temp. = $25 \pm 0.1^\circ C$, $(E_{1/2})_s = +0.582$ volts (S.C.E.)

$[mal^{2-}]$	$-E_{1/2} V$ (S.C.E.)	$\log I_m/I_c$	Slope (mV)	$F_{00}[X, Y]$ $\times 10^{-1}$	$F_{10}[X, Y]$ $\times 10^{-2}$	$F_{20}[X, Y]$ $\times 10^{-3}$	$F_{30}[X, Y]$ $\times 10^{-4}$
Series-I [β-pico] = 0.10 M (Fixed)							
0.1	0.633	0.05223	30	5.9928	4.9428	2.9428	1.14
0.2	0.650	0.05223	30	22.5305	10.7402	4.3701	1.28
0.3	0.662	0.06012	31	58.4305	19.1268	5.7089	1.30
0.4	0.671	0.06012	31	117.7940	29.1860	6.7965	1.24
0.5	0.678	0.07967	32	212.5660	42.3032	8.0606	1.25
0.6	0.684	0.08922	31	346.7631	57.6188	9.2698	1.24
Series-II [β-pico] = 0.20 M (Fixed)							
0.1	0.644	0.05435	31	14.1874	9.9754	2.7799	0.77
0.2	0.657	0.05859	30	39.4414	17.6147	5.2096	1.60
0.3	0.666	0.07033	32	81.6913	25.8264	6.0210	1.40
0.4	0.674	0.08922	31	159.1175	38.7263	7.8827	1.47
0.5	0.681	0.09041	32	275.2507	54.2077	9.4024	1.21
0.6	0.687	0.09433	32	443.2385	73.1710	10.9959	1.49
Series I	$\log A = 1.0211$	$\log B = 2.3010$	$\log C = 3.2552$	$\log D = 4.0934$			
Series II	$\log A = 1.6244$	$\log B = 2.8570$	$\log C = 3.3010$	$\log D = 4.1643$			

TABLE-3
Cd(II)- β -PICOLINE-TARTRATE SYSTEM

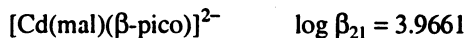
$[Cd^{2+}] = 1 \times 10^{-3} M$, $\mu = 1.5 M$ (NaNO₃), pH = 5.95,

Temp. = $25 \pm 0.1^\circ C$, $(E_{1/2})_s = +0.582$ volts (S.C.E.)

$[\beta$ -pico]	$-E_{1/2} V$ (S.C.E.)	$\log I_m/I_c$	Slope (mV)	$F_{00}[X, Y]$ $\times 10^{-1}$	$F_{10}[X, Y]$ $\times 10^{-2}$	$F_{20}[X, Y]$ $\times 10^{-3}$	$F_{30}[X, Y]$ $\times 10^{-4}$
Series-I [$tart^{2-}$] = 0.10 M (Fixed)							
0.1	0.614	0.05859	30	13.8419	9.2719	4.7459	1.86
0.2	0.628	0.05927	30	41.2590	18.3445	6.9092	2.00
0.3	0.639	0.07410	31	100.5762	32.0020	9.1586	2.09
0.4	0.648	0.08432	31	207.5860	50.7540	11.5570	2.16
0.5	0.655	0.08952	32	362.4261	71.5712	13.4090	2.10
0.6	0.661	0.09478	31	585.4212	96.8085	15.3804	2.08
Series-II [$tart^{2-}$] = 0.20 M (Fixed)							
0.1	0.623	0.06344	31	28.2183	12.4683	6.3033	2.14
0.2	0.635	0.06344	30	71.8636	28.0568	10.9459	3.39
0.3	0.645	0.07833	32	162.0744	48.7748	14.2032	3.34
0.4	0.653	0.08432	31	306.4477	72.6744	16.6773	3.11
0.5	0.660	0.09375	32	540.2652	104.9030	19.7416	3.11
0.6	0.666	0.10430	32	883.3768	144.6044	23.0732	3.15
Series I	$\log A = 0.6599$	$\log B = 1.6557$	$\log C = 2.4592$	$\log D = 3.3222$			
Series II	$\log A = 1.1972$	$\log B = 1.7899$	$\log C = 2.6191$	$\log D = 3.4969$			

The stability constants of the mixed complexes were calculated from the constants⁸ A, B, C and D. Three mixed complexes are formed in each mixed system:

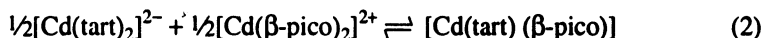
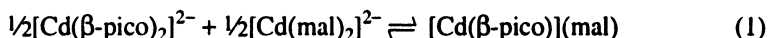
Cd(II)-malate-β-picoline system



Cd(II)-picoline-tartrate system



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



is given by the relation

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

These works out to be +0.215 for reaction (1) and +0.401 for reaction (2). The positive values show that the mixed complexes $[\text{Cd}(\beta\text{-pico})(\text{mal})]$, $[\text{Cd}(\text{tart})(\beta\text{-pico})]$ are more stable than simple complexes: $[\text{Cd}((\beta\text{-pico})_2)]^{2+}$, $[\text{Cd}(\text{mal})_2]^{2-}$ and $[\text{Cd}(\text{mal})_2]^{2-}$.

The mixed complexes exist in solution in the equilibria shown in Tables 5 and 6. The log values of equilibrium constants are also computed for each equilibrium.

TABLE-4
EQUILIBRIA INVOLVED IN Cd(II)-MALATE-β-PICOLINE SYSTEM
AND THEIR EQUILIBRIUM CONSTANT (K) VALUES

	Equilibrium	log K
1.	$\text{Cd}^{2+} + \text{mal}^{2-} + \beta\text{-pico} \rightleftharpoons [\text{Cd}(\text{mal})(\beta\text{-pico})]$	2.722
2.	$\text{Cd}^{2+} + \text{mal}^{2-} + 2\beta\text{-pico} \rightleftharpoons [\text{Cd}(\text{mal})(\beta\text{-pico})_2]$	4.280
3.	$\text{Cd}^{2+} + 2\text{mal}^{2-} + \beta\text{-pico} \rightleftharpoons [\text{Cd}(\text{mal})_2(\beta\text{-pico})]^{2-}$	3.966
4.	$[\text{Cd}(\text{mal})(\beta\text{-pico})] + \beta\text{-pico} \rightleftharpoons [\text{Cd}(\text{mal})(\beta\text{-pico})_2]$	1.558
5.	$[\text{Cd}(\text{mal})(\beta\text{-pico})] + \text{mal}^{2-} \rightleftharpoons [\text{Cd}(\text{mal})_2(\beta\text{-pico})]^{2-}$	1.244
6.	$[\text{Cd}(\text{mal})(\beta\text{-pico})] + \beta\text{-pico} \rightleftharpoons [\text{Cd}(\text{mal})(\beta\text{-pico})_2] + \beta\text{-pico}$	0.969

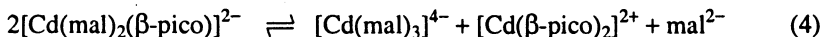
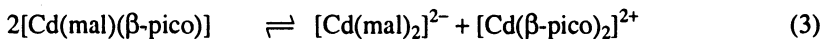
From the above equations it is seen that β-picoline can add readily to $[\text{Cd}(\text{mal})(\beta\text{-pico})]$ than does $[\text{mal}^{2-}]$ (equilibria 4 and 5). But mal^{2-} can replace $[\beta\text{-pico}]$ from complexes $[\text{Cd}(\text{mal})(\beta\text{-pico})]$ and $[\text{Cd}(\text{mal})_2(\beta\text{-pico})]^{2-}$ but not *vice versa* (equilibrium 6). This shows that mal^{2-} is a stronger ligand than β-picoline.

TABLE-5
EQUILIBRIA INVOLVED IN Cd(II)- β -PICOLINE-TARTRATE SYSTEM
AND THEIR EQUILIBRIUM CONSTANT (K) VALUES

	Equilibrium	log K
1.	$\text{Cd}^{2+} + \beta\text{-pico} + \text{tart}^{2-} \rightleftharpoons [\text{Cd}(\beta\text{-pico})(\text{tart})]$	2.520
2.	$\text{Cd}^{2+} + 2\beta\text{-pico} + \text{tart}^{2-} \rightleftharpoons [\text{Cd}(\beta\text{-pico})_2(\text{tart})]$	3.092
3.	$[\text{Cd}(\beta\text{-pico})(\text{tart})] + \beta\text{-pico} \rightleftharpoons [\text{Cd}(\beta\text{-pico})_2(\text{tart})]$	0.572
4.	$[\text{Cd}(\beta\text{-pico})_2(\text{tart})] + \beta\text{-pico} \rightleftharpoons [\text{Cd}(\beta\text{-pico})_3]^{2+} \text{tart}^{2-}$	0.219
5.	$[\text{Cd}(\text{tart})_2]^{2-} + \beta\text{-pico} \rightleftharpoons [\text{Cd}(\beta\text{-pico})(\text{tart})] + \text{tart}^{2-}$	0.492
6.	$[\text{Cd}(\text{tart})_3]^{4-} + 2\beta\text{-pico} \rightleftharpoons [\text{Cd}(\beta\text{-pico})_2(\text{tart})] + 2\text{tart}^{2-}$	0.282

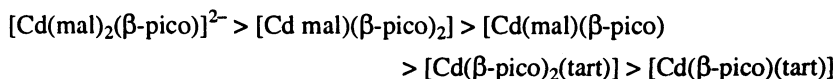
From the above equations it is seen that β -pico can add readily to $[\text{Cd}(\beta\text{-pico})(\text{tart})]$ than does $[\text{tart}^{2-}]$ (equilibria 4 & 5). Further β -pico can replaced $[\text{tart}^{2-}]$ from complexes $[\text{Cd}(\beta\text{-pico})(\text{tart})]^{2-}$ and $[\text{Cd}(\beta\text{-pico})_2(\text{tart})_2]$ but not *vice versa* (equilibrium 6–8) from this. It follows that β -pico is a stronger ligand than tart^{2-} .

The equilibrium constant (log values) for the following disproportion reactions:



work out to be -1.238, -3.140 and -0.802, -2.873 for the disproportionate reactions 3, 4, 5 and 6 respectively. The negative log values for the equilibrium constant show that the formation of mixed complexes is favoured over simple ones.

The stabilities of the mixed complexes follow the order :



ACKNOWLEDGEMENT

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

REFERENCES

1. K. Kim, Y.K. Park, J.D. Suh and C.H. Lee, *Chem. Abstr.*, **80**, 103, 1730 (1974).
2. S.C. Khurana and C.M. Gupta, *J. Inorg. Nucl. Chem.*, **35**, 209 (1973).
3. K. Nema and F. Khan, *J. Indian Chem. Soc.*, **64**, 629 (1987).
4. F. Khan, *J. Indian Chem. Soc.*, **65**, 464 (1988).

5. F. Khan and K. Nema, *J. Indian Chem. Soc.*, **66**, 17 (1989).
6. D.N. Chaturvedi and C.M. Gupta, *J. Inorg. Nucl. Chem.*, **36**, 2155 (1974).
7. S.C. Khurana and C.M. Gupta, *Aust. J. Chem.*, **40**, 2089 (1978).
8. C.P.S. Chandel, C.M. Gupta and N.P. Sachan, *Chemica Scripta*, **20**, 229 (1982).
9. ———, *Chemica Scripta*, **20**, 11 (1982).
10. N. Gupta, C.P.S. Chandel, P.C. Gupta and C.M. Gupta, *Bull. Chem. Soc. (Japan)*, **56**, 3138 (1983).
11. C.M. Gupta, R. Kumari and C.P.S. Chandel, *Indian J. Chem.*, **25A**, 677 (1986).
12. F. Khan and F. Khan, *J. Indian Chem. Soc.*, **74**, 171 (1997).
13. A. Jain and F. Khan, *J. Indian Chem. Soc.*, **75**, 31 (1998).
14. S.K. Singh and C.P.S. Chandel, *Orient. J. Chem.*, **17**, 239 (2001).
15. F. Khan and P.L. Sahu, *J. Indian Chem. Soc.*, **79**, 176 (2002).
16. G. Sharma and C.P.S. Chandel, *Asian J. Chem.*, **14**, 23 (2002).
17. L. Meites, *Polarographic Techniques*, Interscience Publ., New York, p. 219 (1965).
18. D.D. Deford and D.N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).
19. W.B. Schaap and D.L. McMaster, *J. Am. Chem. Soc.*, **83**, 4699 (1961).

(Received: 27 March 2004; Accepted: 25 August 2004)

AJC-3535

7th WORLD CONGRESS OF CHEMICAL ENGINEERING

10-14 JULY 2005

Contact:

Concorde Services Ltd

4B, 50 Speirs Wharf

Glasgow, G4 9TB, UK

Tel: +44 (0) 141 331 0123; Fax: +44 (0) 141 331 0234