Asian Journal of Chemistry Vol. 17, No. 3 (2005), 1423–1428

Polaigraphically Determination of Stability Constants of Mixed Ligand complexes of Cadmium(II) with Pyridine and Some Amino Acids

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The mixed ligand complexes of pyridine and lysine and metheonine with Cd(II) have been studied polarographically at constant ionic strength, $\mu = 1.5$ M ($NaNO_3$) and pH 8.2 at 25.4 ± 0.1°C. The reduction of the complexes at d.m.e. is reversible and diffusion-controlled. Two mixed complexes $[Cd(lys)(pyr)]^+$, and $[Cd(lys)_2(pyr)]$ are formed in Cd(II)—lysine-pyridine system with the stability constants $\log \beta_{11} = 5.230$ and $\log \beta_{21} = 8.602$. Three mixed complexes $[Cd(meth)(pyr)]^+$, $[Cd(meth)(pyr)_2]^+$ and $[Cd(meth)_2(pyr)]$ are formed in Cd(II)-metheonine-pyridine system with the stability constants $\log \beta_{11} = 5.322$, $\log \beta_{12} = 6.518$ and $\log \beta_{21} = 9.113$ respectively.

Key Words: Stability constants, Cadmium(II), Mixed ligand complexes, Pyridine, Lysine, Metheonine, Polarographic.

INTRODUCTION

Khan *et al.*[1] have studied polarographically the mixed ligand complexes of Cd(II) and Zn(II) with amino acids, *viz.*, tyrosine, arginine, metheonine, hydroxy tryptophane, hydroxy proline, proline and histidine as primary ligands and vitamin B_6 as secondary ligands and reported the formation of 1 : 1 : 1, 1 : 1 : 2 and 1 : 2 : 1 complexes. Gupta *et al.*[2–4] have undertaken comprehensive polarographic studies on mixed complexes of Cd(II) with amino acids as primary ligands and pyridoxine (Vitamin B_6) and ascorbic acid as secondary ligand. Besides this on the survey of literature[5–15], it appears that polarographic studies of mixed complexes of Cd(II) with pyridine and lysine and metheonine are still lacking. The present work reported the studies of mixed ligand complexes of Cd(II) with pyridine and lysine and metheonine.

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

1×10^{-3} M. Polarograms were obtained[16] by means of a manual polarograph (Toshniwal CL 02) in conjunction with Toshniwal polyflex galvanometer (PL 50). All the measurements were made at 25.4 ± 0.1°C and pH 8.2. 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): m = 2.219 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

The reduction of Cd(II) in pyridine, lysine and metheonine was found to be reversible and diffusion controlled. The same was true for the mixed system. The slopes of linear plots of log *i/id–i vs.* $E_{d.m.e.}$ were in the range 30–33 mV and the plots of i_d *vs.* $h_{corr}^{1/2}$ were linear and passed through the origin. The stability constants of simple complexes of Cd(II) with pyridine, lysine and metheonine 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 pyridine and Cd(II) with lysine and metheonine were studied by the method of Deford and Hume[17]. The values of stability constants of simple complexes have been tabulated in Table-1.

TABLE-1
STABILITY CONSTANTS OF LYSINE, METHEONINE AND PYRIDINE WITH Cd(II)

Contents	log β_1	log β_2	log β_3	log β_4
Lysine	4.204	7.301	10.113	—
Metheonine	4.447	7.255	10.414	—
Pyridine	1.079	2.070	2.430	2.591

(b) Mixed System

Lysine concentration was varied from 0.02 to 0.12 M, metheonine concentration was varied from 0.005 to 0.030 M and that of pyridine was kept constant at 0.10 M. The $E_{1/2}$ values were greater compared to those obtained in the absence of pyridine thereby showing the formation of mixed complexes. The system was repeated at another concentration of pyridine (0.20 M).

The method of Schaap and McMaster[18] 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 Cd(II) with pyridine and lysine and metheonine at fixed [pyr] (0.10 and 0.20 M) are presented in Tables 2 and 3.

TABLE-2

Cd(II)-LYSINE-PYRIDINE SYSTEM $[Cd^{2+}] = 1 \times 10^{-3}$ M, $\mu = 1.5$ M ($NaNO_3$), pH = 8.2, Temp. = 25.4 ± 0.1°C, $(E_{1/2})_s = -0.592$ volts (S.C.E.)

$[lys]_t$ M	$[lys]_f$ $\times 10^4$ M	$-E_{1/2}$ V (SCE)	log I_m/I_c	Slope mv	F_{00} [X, Y]	F_{10} [X, Y] $\times 10^{-4}$	F_{20} [X, Y] $\times 10^{-7}$	F_{30} [X, Y] $\times 10^{-10}$
Series-I [pyr] = 0.10 M (Fixed)								
0.02	5.6	0.642	0.05293	30	55.10	4.48	2.64	—
0.04	11.2	0.659	0.06105	30	210.55	15.72	11.71	5.09
0.06	16.8	0.670	0.06932	30	504.74	28.25	15.02	5.36
0.08	22.4	0.678	0.06932	32	940.14	40.63	16.79	4.81
0.10	28.0	0.685	0.08635	32	1684.95	59.10	20.03	5.01
0.12	33.6	0.691	0.08635	31	2686.48	79.06	22.63	4.94
Series-II [pyr] = 0.20 M (Fixed)								
0.02	5.6	0.643	0.06105	30	60.68	4.58	2.46	—
0.04	11.2	0.661	0.06105	31	245.98	18.83	13.95	5.75
0.06	16.8	0.672	0.06517	31	589.65	33.01	17.74	6.09
0.08	22.4	0.681	0.06932	32	1187.11	51.43	21.53	6.26
0.10	28.0	0.687	0.09513	32	2008.63	70.48	24.02	5.90
0.12	33.6	0.693	0.09513	33	3202.55	94.27	27.10	5.83

$[lys]_t$: Total concentration of lysine. $[lys]_f$: Free ligand concentration of lysine.

Series I: log A = 1.477 log B = 4.477 log C = 7.778 log D = 10.698

Series II: log A = 1.544 log B = 4.505 log C = 7.875 log D = 10.778

The stability constants of the mixed complexes were calculated from the constants[8] A, B, C and D. Two mixed complexes in Cd(II)-lysine-pyridine system and three mixed complexes in Cd(II)-metheonine-pyridine system as noted below are formed:

Cd(II)-Lysine-pyridine system	Cd(II)-Metheonine-pyridine system
$[Cd(lys)(pyr)]^+$; $\log \beta_{11} = 5.230$	$[Cd(meth)(pyr)]^+$; $\log \beta_{11} = 5.322$
$[Cd(lys)_2(pyr)]$; $\log \beta_{21} = 8.602$	$[Cd(meth)(pyr)_2]^+$; $\log \beta_{12} = 6.518$
	$[Cd(meth)_2(pyr)]$; $\log \beta_{21} = 9.113$

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

$$\tfrac{1}{2}[Cd(lys)_2] + \tfrac{1}{2}[Cd(pyr)_2]^{2+} \rightleftharpoons [Cd(lys)(pyr)]^+ \tag{1}$$

$$\tfrac{1}{2}[Cd(meth)_2] + \tfrac{1}{2}[Cd(pyr)_2]^{2+} \rightleftharpoons [Cd(meth)(pyr)]^+ \tag{2}$$

is given by the relation

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

These work out to be +0.5445 for reaction 1 and +0.6595 for reaction 2. The positive values show that the mixed complexes $[Cd(lys)(pyr)]^+$ and $[Cd(meth)(pyr)]^+$ are more stable than simple complexes: $[Cd(lys)_2]$, $[Cd(meth)_2]$ and $[Cd(pyr)_2]^{2+}$.

TABLE-3

Cd(II)-METHEONINE-PYRIDINE SYSTEM $[Cd^{2+}] = 1 \times 10^{-3}$ M, $\mu = 1.5$ M ($NaNO_3$), pH = 8.2, Temp. = 25.4 ± 0.1°C, $(E_{1/2})_s = -0.592$ volts (SCE)

$[Meth]_t$ M	$[Meth]_f$ $\times 10^4$ M	$-E_{1/2}$ V (SCE)	log I_m/I_c	Slope mv	F_{00} [X, Y]	F_{10} [X, Y] $\times 10^{-4}$	F_{20} [X, Y] $\times 10^{-7}$	F_{30} [X, Y] $\times 10^{-10}$
				Series–I [pyr] = 0.10 M (Fixed)				
0.005	4.0	0.645	0.04103	30	67.70	11.92	9.80	—
0.010	9.0	0.659	0.04103	30	201.07	20.11	13.55	—
0.015	13.0	0.669	0.05293	31	449.68	33.05	19.26	3.28
0.020	18.0	0.677	0.05697	32	845.43	45.85	21.02	3.34
0.025	22.0	0.682	0.06105	32	1258.89	56.31	21.95	3.15
0.030	27.0	0.686	0.06517	33	1734.49	63.49	20.55	2.05
				Series–II [pyr] = 0.20 M (Fixed)				
0.005	4.0	0.647	0.04496	30	79.80	9.95	—	—
0.010	9.0	0.665	0.05293	31	329.49	32.16	13.51	3.90
0.015	13.0	0.672	0.06105	31	578.53	41.42	16.47	4.97
0.020	18.0	0.678	0.06932	32	940.14	50.00	16.66	3.70
0.025	22.0	0.682	0.06932	32	1386.83	61.21	18.73	3.96
0.030	27.0	0.687	0.08203	33	1948.94	70.70	18.77	3.24

$[meth]_t$: Total concentration of metheonine. $[meth]_f$: Free ligand concentration of metheonine.

Series I:	log A = 1.301	log B = 4.903	log C = 8.176	log D = 10.505
Series II:	log A = 1.602	log B = 5.301	log C = 8.000	log D = 10.579

The mixed complexes exist in solution in the equilibria shown in Tables 4 and 5. The log values of equilibrium constants are given for each equilibrium.

TABLE-4

EQUILIBRIA INVOLVED IN Cd(II)-LYSINE-PYRIDINE SYSTEM AND THEIR EQUILIBRIUM CONSTANT (K) VALUES

Equilibrium			log K
1. $Cd^{2+} + lys^{-} + pyr$	$\rightleftharpoons$	$[Cd(lys)(pyr)]^{+}$	5.230
2. $Cd^{2+} + 2lys^{-} + pyr$	$\rightleftharpoons$	$[Cd(lys)_2(pyr)]$	8.602
3. $[Cd(lys)(pyr)]^{+} + lys^{-}$	$\rightleftharpoons$	$[Cd(lys)_2(pyr)]$	3.372
4. $[Cd(lys)_2(pyr)] + lys^{-}$	$\rightleftharpoons$	$[Cd(lys)_3]^{-} + pyr$	1.544
5. $[Cd(lys)]^{1+} + pyr$	$\rightleftharpoons$	$[Cd(lys)(pyr)]^{+}$	1.026
6. $[Cd(lys)_2] + pyr$	$\rightleftharpoons$	$[Cd(lys)_2(pyr)]$	1.301
7. $[Cd(pyr)]^{2+} + lys^{-}$	$\rightleftharpoons$	$[Cd(lys)(pyr)]^{+}$	4.151
8. $[Cd(pyr)_2]^{2+} + lys^{-}$	$\rightleftharpoons$	$[Cd(lys)(pyr)]^{+} + pyr$	3.160
9. $[Cd(pyr)_3]^{2+} + lys^{-}$	$\rightleftharpoons$	$[Cd(lys)(pyr)]^{+} + 2pyr$	2.800

From the above equations, it is seen that lys^- has greater tendency to add to $[Cd(lys)(pyr)]^+$ as compared to pyr (eq. 3). Further, lys^- can replace pyr from the species $[Cd(lys)_2(pyr)]$ but not *vice-versa*. Equilibrium eqs. (4), (8) and (9) also confirm that lys^- is a stronger ligand than pyr.

TABLE-5
EQUILIBRIA INVOLVED IN Cd(II)-METHEONINE-PYRIDINE SYSTEM AND THEIR EQUILIBRIUM CONSTANT (K) VALUES

Equilibrium			log K
1. $Cd^{2+} + meth^- + pyr$	$\rightleftharpoons$	$[Cd(meth)(pyr)]^+$	5.322
2. $Cd^{2+} + meth^- + 2\,pyr$	$\rightleftharpoons$	$[Cd(meth)(pyr)_2]^+$	6.518
3. $Cd^{2+} + 2\,meth^- + pyr$	$\rightleftharpoons$	$[Cd(meth)_2(pyr)]$	9.113
4. $[Cd(meth)(pyr)]^+ + meth^-$	$\rightleftharpoons$	$[Cd(meth)_2(pyr)]$	3.791
5. $[Cd(meth)(pyr)]^+ + pyr$	$\rightleftharpoons$	$[Cd(meth)(pyr)_2]^+$	1.196
6. $[Cd(meth)_2(pyr)] + pyr$	$\rightleftharpoons$	$[Cd(meth)(pyr)_2] + meth^-$	–2.595
7. $[Cd(meth)_2(pyr)] + meth^-$	$\rightleftharpoons$	$[Cd(meth)_3]^- + pyr$	1.301

From the above equations it is seen that $meth^-$ can add readily to $[Cd(meth)(pyr)]^+$ than does pyr (equilibria 4 and 5). Further, $meth^-$ can replace pyr from complexes $[Cd(meth)_2(pyr)]$ but not *vice-versa* (eq. 6 & 7). It appears therefore that $meth^-$ is a stronger ligand than pyr.

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

$$2[Cd(lys)(pyr)]^+ \rightleftharpoons [Cd(lys)_2] + [Cd(pyr)_2]^{2+} \qquad (3)$$

$$2[Cd(lys)_2(pyr)] \rightleftharpoons [Cd(lys)_3]^{1-} + [Cd(pyr)_2]^{2+} + lys^- \qquad (4)$$

$$2[Cd(meth)(pyr)]^+ \rightleftharpoons [Cd(meth)_2] + [Cd(pyr)_2]^{2+} \qquad (5)$$

$$2[Cd(meth)(pyr)_2]^+ \rightleftharpoons [Cd(meth)_2] + [Cd(pyr)_3]^{2+} + pyr \qquad (6)$$

$$2[Cd(meth)_2(pyr)] \rightleftharpoons [Cd(meth)_3]^{1-} + [Cd(pyr)_2]^{2+} + meth^- \qquad (7)$$

works out to be –1.089, –4.988, –1.319, –3.351 and –5.742 for the disproportion reactions (3), (4), (5), (6) and (7) respectively. The large negative log values for the equilibrium constants show that the formation of mixed complexes is strongly favoured over simple ones.

ACKNOWLEDGEMENT

Authors are thankful to Dr. M.C. Yadav, Principal, Narain College, Shikohabad for providing the facilities.

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(*Received*: 24 April 2004; *Accepted:* 1 March 2005) AJC-4117