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STABILITY CONSTANTS OF CADMIUM (II) COMPLEXES WITH ETHYLENEDIAMINE AND SOME CARBOXYLIC ACIDS : A POLAROGRAPHIC STUDY

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ABSTRACT

The mixed ligand complexes of ethylenediamine (en), glutarate (glu^{2-}) and adipate ((adp^{2-}) with Cd (II) have been studied polarographically at constant ionic strength, $\mu = 1.5$ M ($NaNO_3$) and pH 8.2 at 25 ± 0.1°C. The reduction of the complexes at d.m.e is reversible and diffusion–controlled. Three mixed complexes [Cd(en) (glu)], $[Cd(en)(glu_2]^{2-}$ and $[Cd(en)_2(glu)]$ are formed in Cd (II) ethylenediamine–glutarate system with the stability constants log $\beta_{11} = 7.414$, log $\beta_{12} = 8.204$ and log $\beta_{21} = 11.301$. Three mixed complexes [Cd(en) (adp)], $[Cd(en)(adp)_2]^{2-}$ and $[Cd(en)_2(adp)]$, are formed in Cd–ethylenediamine–adipate system and their stability constants are log $\beta_{11} = 7.342$, log $\beta_{12} = 8.079$ and log $\beta_{21} = 11.204$.

Key words : Ethylenediamine, Polarographic, Stability constant

INTRODUCTION

Sundaresan[1] have undertaken polarographic studies on Cd (II)– glycine–methionine complexes. Gupta et al.[2,3] have undertaken comprehensive polagraphic studies on mixed complexes of Cd (II) with amino acids as primary ligands and pyriodoxine (Vitamin B_6) and ascorbic acid as secondary ligands. From survey of literature[5–15], it appears that polarographic studies of mixed complexes of Cd (II) with ethylenediamine and glutarate and adipate are still lacking. Hence the present work has been undertaken. The present communication deals with the studies of mixed ligand complexes of Cd (II) with ethylenediamine and glutarate and adipate.

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 1.0×10^{-3} M. Polarograms were obtained[17] by means of a manual polarograph (Toshniwal CL 02) in conjuction with Toshniwal polyflex galvanometer (PL 50). All the measurement were made at 25 ± 0.1°C and pH 8.2. 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

The reduction of Cd (II) in ethylenediamine, adipate and glutarate 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 id vs $h^{1/2}_{corr}$ were linear and passed through the origin. The stability constants of simple complexes of Cd (II) with ethylenediamine, adipate and glutarate 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 ethylenediamine and Cd (II) with carboxylic acids (glutaric and adipic acid) were studied by the method of Deford and Hume[18]. 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 ± 1°C. The values of stability constants of simple complexes have been tabulated in Table 1.

Table 1. Stability constants of ethylenediamine, glutarate and adipate with Cd (II)

Contents	log β_1	log β_2	log β_3
Ethylenediamine	5.7781	9.2552	12.9703
Glutarate	1.6232	2.3010	3.5078
Adipate	1.4471	2.2041	3.3502

(b) Mixed system

Ethylenediamine concentration was varied from 2.0 M to 10.0 M and that of glutarate and adipate was kept constant at 0.10 M. The $E_{1/2}$ values were greater compared to those obtained in the absence of glutarate and adipate; thereby showing the formation of mixed complexes. The system was repeated at another concentration of glutarate and adipate (0.20 M).

The method of Schaap and McMaster[19] 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 ethylenediamine and glutarate and adipate at fixed [glu^{-2}] and [adp^{-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, C and D. Three mixed complexes as are formed in each mixed system.

Cd (II)– ethylenediamine – glutarate system		Cd (II)–ethylenediamine–adipate system	
[Cd (en) (glu)]	$\log\beta_{11}$ = 7.414	[Cd (en) (adp)]	$\log\beta_{12}$ = 7.342
$[Cd(en)(glu)]^{2-}$	$\log\beta_{12}$ = 8.204	$[Cd(en)(adp)]^{2-}$	$\log\beta_{12}$ = 8.079
$[Cd(en)_2(glu)]$	$\log\beta_{21}$ = 11.301	$[Cd(en)_2(adp)]$	$\log\beta_{21}$ = 11.204

Table 2 : Cd (II) – ethylenediamine – glutarate system $[Cu^{2+}] = 1 \times 10^{-3}$ M, μ = 1.5 M ($NaNO_3$), pH = 8.2, Temp = 25 ± .1°C $(E_{1/2})_s$ = + 0.584 Volts (S.C.E.)

$[en]_t$ x10^3 M	$[en]_f$ x10^4 M	$-E_{1/2}$ V (S.C.E.)	Log I_m/I_c	Slope mv	F_{00} [X, Y] x 10^{-2}	F_{10} [X, Y] x 10^{-5}	F_{20} [X,Y] x 10^{-9}	F_{30} [X,Y] x 10^{-13}
Series – I [Glu^{2-}] = 0.05 M (Fixed)								
2.0	3.0	0.688	0.0449	31	36.57	75.23	17.41	1.00
4.0	6.0	0.703	0.0636	31	122.84	181.40	26.40	2.40
6.0	9.0	0.715	0.0682	32	316.17	335.74	34.74	2.52
8.0	12.0	0.724	0.0820	32	657.96	536.63	42.80	2.56
10.0	15.0	0.730	0.0969	33	1174.65	773.76	50.05	2.53
Series – II [Glu^{2-}] = 0.10 M (Fixed)								
2.0	3.0	0.693	0.0529	31	55.0	130.0	27.33	1.77
4.0	6.0	0.709	0.0682	31	198.12	303.53	42.58	3.43
6.0	9.0	0.720	0.0820	32	481.81	517.56	52.17	3.35
8.0	12.0	0.729	0.0820	32	971.29	796.07	62.33	3.36
10.0	15.0	0.735	0.1153	33	1673.51	1105.00	70.46	3.25

Series I : log A = 3.146 log B = 6.361 log C = 10.079 log D = 13.382
Series II : log A = 3.204 log B = 6.681 log C = 10.342 log D = 13.525

Table 3. Cd (II) – ethylenediamine – adpate system $[Cu^{2+}] = 1 \times 10^{-3}$ M, μ = 1.5 M ($NaNO_3$), pH = 8.2, Temp = 25 ± .1°C $(E_{1/2})_s$ = + 0.584 Volts (S.C.E.)

$[en]_t$ x10^3 M	$[en]_f$ x10^4 M	$-E_{1/2}$ V (S.C.E.)	Log I_m/I_c	Slope mv	F_{00} [X, Y] x 10^{-2}	F_{10} [X, Y] x 10^{-5}	F_{20} [X,Y] x 10^{-9}	F_{30} [X,Y] x 10^{-13}
Series – I [Adp^{2-}] = 0.05 M (Fixed)								
2.0	3.0	0.686	0.0403	30	30.97	64.90	16.63	2.21
4.0	6.0	0.701	0.0529	30	102.56	154.26	23.37	2.22
6.0	9.0	0.713	0.0682	31	270.56	289.51	29.94	2.21
8.0	12.0	0.722	0.0791	31	559.29	457.74	36.47	2.20
10.0	15.0	0.729	0.0969	32	1005.19	663.46	42.89	2.19
Series – II [Adp^{2-}] = 0.10 M (Fixed)								
2.0	3.0	0.691	0.0529	30	47.06	116.86	25.62	3.20
4.0	6.0	0.707	0.0529	30	163.67	252.78	35.46	3.24
6.0	9.0	0.718	0.0791	31	409.56	441.73	44.63	3.18
8.0	12.0	0.727	0.0907	31	847.98	696.65	54.72	3.22
10.0	15.0	0.734	0.1025	32	1503.14	994.09	63.60	3.17

Series I : log A = 3.000 log B = 6.301 log C = 10.000 log D = 13.344
Series II : log A = 3.079 log B = 6.602 log C = 10.204 log D = 13.502

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

$$^{1}/_{2}[Cd(en)_2]^{2+} + {}^{1}/_{2}[Cd(glu)_2]^{2-} \rightleftharpoons [Cd(en)\,(glu)] \quad ...(1)$$

$$^{1}/_{2}[Cd(pn)_2]^{2+} + {}^{1}/_{2}[Cd(adp)_2]^{2-} \rightleftharpoons [Cd(en)\,(adp)] \quad ...(2)$$

is given by the relation

$$\log K_M = \log\beta_{11} - {}^{1}/_{2}\,(\log\beta_{20} + \log\beta_{02})$$

These works out to be + 1.636 for reaction 1 and + 1.613 for reaction 2. The positive value shows that the mixed complexes [Cd(en) (glu)] and [Cd(en) (adp)] are more stable than their simple complexes : $[Cd(en)_2]^{2+}$, $[Cd(glu)_2]^{2+}$ and $[Cd(adp)_2]^{2-}$.

Table 4. Equlibria involved in Cd (II) – ethylenediamine–glutarate system and their equilibrium constant (K) values

	Equilibrium			log K
1.	$Cd^{2+} + en + glu^{2-}$	$\rightleftharpoons$	[Cd(en) (glu]	7.414
2.	$Cd^{2+} + en + 2\,glu^{2-}$	$\rightleftharpoons$	$[Cd(en)\,(glu)_2]^{2-}$	8.204
3.	$Cd^{2+} + 2\,en + glu^{2-}$	$\rightleftharpoons$	$[Cd(en)_2\,(glu)]$	11.301
4.	[Cd (en) (glu)] + en	$\rightleftharpoons$	$[Cd(en)\,(glu)_2]^{2-}$	3.887
5.	$[Cd\,(en)\,(glu)] + glu^{2-}$	$\rightleftharpoons$	$[Cd(en)_2\,(glu)_2]^{2-}$	0.790
6.	$[Cd\,(en)\,(glu)_2]^{2-}$ + en	$\rightleftharpoons$	$[Cd(en)_2\,(glu)] + glu^{2-}$	3.097
7.	$[Cd\,(en)_2\,(glu)]$ + en	$\rightleftharpoons$	$[Cd(en)_3]^{2+}\ glu^{2-}$	1.669
8.	$[Cd\,(en)_2\,(glu)] + glu^{2-}$	$\rightleftharpoons$	$[Cd(en)\,(glu)_2]^{2-}$+en	–3.097
9.	$[Cd\,(en)\,(glu)_2] + glu^{2-}$	$\rightleftharpoons$	$[Cd(en)\,(glu)_3]^{4-}$+en	–4.967

Table 5. Equlibria involved in Cd (II) – ethylenediamine–adipate system and their equilibrium constant (K) values

	Equilibrium			log K
1.	$Cd^{2+} + en + adp^{2-}$	$\rightleftharpoons$	[Cd(en) (adp]	7.342
2.	$Cd^{2+} + en + 2\,adp^{2-}$	$\rightleftharpoons$	$[Cd(en)\,(adp)_2]^{2-}$	8.079
3.	$Cd^{2+} + 2\,en + adp^{2-}$	$\rightleftharpoons$	$[Cd(en)_2\,(adp)]$	11.204
4.	[Cd (en) (adp)] + en	$\rightleftharpoons$	$[Cd(en)\,(adp)_2]^{2-}$	3.862

	Equilibrium			log K
5.	$[Cd (en) (adp)] + adp^{2-}$	$\rightleftharpoons$	$[Cd(en)_2 (adp)_2]^{2-}$	0.737
6.	$[Cd (en) (adp)_2]^{2-} + en$	$\rightleftharpoons$	$[Cd(en)_2 (adp)] + adp^{2-}$	3.125
7.	$[Cd (en)_2 (adp)] + en$	$\rightleftharpoons$	$[Cd(en)_3]^{2+} adp^{2-}$	1.766
8.	$[Cd (en)_2 (adp)] + adp^{2-}$	$\rightleftharpoons$	$[Cd(en) (adp)_2]^{2-} + en$	–3.125
9.	$[Cd (en) (glu)_2] + adp^{2-}$	$\rightleftharpoons$	$[Cd(en) (adp)_3]^{4-} + en$	–4.729

From the equilibrium constant values, tendency of a ligand to add a complex and to substitute another ligand may be compared. It is seen that en can add to [Cd (en) (glu) [Cd(en) (adp)] readily. (Table 3; equilibria 4–5 and Table 5; equilibria 4–5). Further ethylendiamine can replace glu^{2-} from $[Cd(en) (glu)_2]^{-2}$ and $[Cd(en)_2 (glu)]$ but not the vice–versa (Table 4; equlibria 6–9) and en can also replace adp^{2-} from the complexes $[Cd (en) (adp)_2]^{2-}$ and $[Cd (en)_2 (adp)]$ but not the vice–versa (Table 5; equilibria 6–9). The equilibrium constant (log values) for the following disproportion reactions:

$$2 [Cd(en) (glu)] \rightleftharpoons [Cd(en)_2]^{2+} + [Cd(glu)]^{2-} \quad ...(3)$$

$$2 [Cd(en) (glu)_2]^{2-} \rightleftharpoons [Cd(en)_2]^{2+} + [Cd(glu)]^{4-} + glu^{2-} \quad ...(4)$$

$$2 [Cd(en)_2 (glu)] \rightleftharpoons [Cd(en)_3]^{2+} + [Cd(glu)_2]^{2-} + en \quad ...(5)$$

$$2 [Cd(en) (adp)] \rightleftharpoons [Cd(en)_2]^{2+} + [Cd(adp)]^{2-} \quad ...(6)$$

$$2 [Cd(en) (adp)_2]^{2-} \rightleftharpoons [Cd(en)_2]^{2+} + [Cd(adp)_3]^{4-} + glu^{2-} \quad ...(7)$$

$$2 [Cd(en)_2 (adp)] \rightleftharpoons [Cd(en)_3]^{2+} + [Cd(adp)_2]^{2-} + en \quad ...(8)$$

works out to be –3.272, –3.646, –7.331, –3.235, –3.553 and –7234 for the disproportion reactions 3, 4, 5, 6, 7 and 8, respectively. The large negative log values for the equilibrium constant show that the formation of mixed complexes is strongly favoured over simple ones.

The stabilities of the mixed complexes follow the order:

$[Cd (en)_2 (glu)] > [Cd (en) (glu)_2]^{2-} > [Cd (en) (glu)]$

$[Cd (en)_2 (adp)] > [Cd (en) (adp)_2]^{2-} > [Cd (en) (adp)]$

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