Mixed Chelates of Cadmium(II) with *N*-(2-Hydroxyethyl)ethylenediamine and Some Amino Acids

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An extended method of Schaap and McMasters[1] has been applied for the study of mixed-ligand complexes of Cadmium(II) with *N*-(2-hydroxyethyl) ethylenediamine (heda) and some amino acids polarographically at DME. The reduction of mixed-ligand complex at DME has been found to be reversible, and diffusion controlled at temp (30±0.5)°C and μ=1.0 M†† (KNO_3). The formation of MXY, MXY_2, and MX_2Y has been used to discuss the non-existence of MX_3 complexes, where X has been used for heda and Y for amino acids. The values of stability constants β_{01}, β_{02}, β_{03}, β_{11}, β_{12}, and β_{21} are 3.90, 6.80, 8.94, 8.85, 11.00, and 12.13 for Cd–heda–isoleucinate system, 4.30, 7.70, 9.80, 9.36, 11.75, and 12.42 for Cd–heda–glycinate system, 3.95, 6.81, 8.90, 8.35, 10.99, and 12.12 for Cd–heda–valinate system, 4.10, 7.10, 9.08, 9.02, 11.20, and 12.18 for Cd–heda–serinate system, 4.48, 8.02, 10.33, 9.55, 12.00, and 12.59 for Cd–heda–glutamate system, 4.24, 7.54, 9.54, 9.26, 11.62, and 12.33 for Cd–heda–alaninate system and 4.06, 7.06, 9.02, 9.00, 11.16, and 12.20 for Cd–heda–threoninate system respectively.

For the determination of mixed-ligand complexes where third complex does not exist in any one out of the simple systems studied, an extention has been made in the method of Schaap and McMasters.

In this communication the extended method of Schaap and McMasters has been used to discuss the mixed-ligand complex formation of cadmium(II) with *N*-(2-hydroxyethyl)ethylenediamine(heda) and isoleucinate, glycinate, valinate, serinate, glutamate, alaninate, and threoninate. The weeker ligand (amino acids) forms three complexes (MY, MY_2, and MY_3) while strong ligand (heda) does not form MX_3 complex.

A survey of literature reveals that the stability constants of the above type mixed-ligand complexes have not been evaluated to date, except our earlier studies.[3]

Theory

For a complexation reaction,

$$M + {}_iX + {}_jY \rightleftharpoons MX_iY_j.$$

Where i, j are stoichiometry numbers, X and Y are two different ligands and charges have been ignored for simplicity.

The overall stability constant β_{ij} for the above reaction is given by

$$\beta_{ij} = \frac{MX_iY_j}{M[X]^i[Y]^j}.$$

According to the method of Schaap and McMasters the formation function $F_{00}[X, Y]$ may be expressed by

$$\begin{aligned} F_{00}[X, Y] = {} & \{\beta_{00}+\beta_{01}[Y]+\beta_{02}[Y]^2+\beta_{03}[Y]^3\}[X]^0 \\ & + \{\beta_{10}+\beta_{11}[Y]+\beta_{12}[Y]^2\}[X] \\ & + \{\beta_{20}+\beta_{21}[Y]\}[X]^2 \\ & + \{\beta_{30}\}[X]^3, \end{aligned} \quad (1)$$

which may, for simplicity, be written as

$$F_{00}[X, Y] = A + B[X] + C[X]^2 + D[X]^3. \quad (2)$$

Where A, B, C, and D are constant for a given value of [Y], and have values as defined by equiv (1).

The plot of $F_{00}[X, Y]$ *vs.* [X] when extrapolated to [X]=0 on the $F_{00}[X, Y]$ axis, will give the value of the constant A which should essentially be equal to the value of $F_0[Y]$ for the simple M–Y system, as calculated by the method of DeFord and Hume. The constant B can be found similarly from the F_{10} [X, Y] function, defined as

$$\begin{aligned} F_{10}[X,Y] &= \frac{F_{00}[X, Y]-A}{[X]} \\ &= B + C[X] + D[X]^2, \end{aligned} \quad (3)$$

by obtaining the intercept from the plot of $F_{10}[X, Y]$ *vs.* [X]. Similarly, plots of $F_{20}[X, Y]$ and $F_{30}[X, Y]$ *vs.* [X] will give intercepts on $F_{20}[X, Y]$ and $F_{30}[X, Y]$ at [X]=0, as C and D respectively. The value of D should be equal (within experimental errors) to the overall stability constant of the MX_3 complex when calculated from the simple M–X system.

From the knowledge of values of B and C at two different concentrations of Y, the values of stability constants of mixed-ligand complexes MXY, MXY_2 and MX_2Y can be evaluated.

Experimental

Chemicals. *N*-(2-hydroxyethyl)ethylenediamine (heda) was obtained from Fluka A.G. (Switzerland) and serine from Merck and other amino acids from S.D.'s Chemical Co., while potassium nitrate was used as supporting electrolyte and gelatin as maxima suppressor.

Apparatus. Manual polarograph with capillary characteristics $m^{2/3}t^{1/6}=1.96\ mg^{2/3}s^{-1/2}$ in open circuit was used. Elico., Digital pH meter model Ll-120 was used to determine the pH of the solutions. The experimental technique was same as described earlier.[4]

Results

Binary Systems. The dissociation constants for *N*-(2-hydroxyethyl)ethylenediamine and amino acids were calculated by the method of Albert and Sergeant[5] which agreed well with literature.[6–8] (Table 1). The stepwise formation constants of the complexes of Cd(II) with amino acids were determined separately before

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†† 1 M=1 mol dm^{-3}.

TABLE 1. pK VALUES OF THE LIGANDS

Ligand	pK_2^H
Heda	9.80±0.01
Isoleucine	9.74±0.01
Glycine	9.62±0.02
Valine	9.50±0.02
Serine	9.10±0.02
Glutamic acid	9.40±0.02
Alanine	9.70±0.02
Threonine	9.12±0.02

TABLE 2. FORMATION CONSTANTS FOR BINARY COMPLEXES

Cadmium complex	Formation constants (log)	Cadmium complex	Formation constants (log)
Cd(heda)	5.39	Cd(serinate)	4.10
$Cd(heda)_2$	9.80	$Cd(serinate)_2$	7.10
Cd(isoleucinate)	3.90	$Cd(serinate)_3$	9.08
$Cd(isoleucinate)_2$	6.80	Cd(glutamate)	4.48
$Cd(isoleucinate)_3$	8.94	$Cd(glutamate)_2$	8.02
Cd(glucinate)	4.30	$Cd(glutamate)_3$	10.33
$Cd(glycinate)_2$	7.70	Cd(alaninate)	4.24
$Cd(glycinate)_3$	9.80	$Cd(alaninate)_2$	7.54
Cd(valinate)	3.95	$Cd(alaninate)_3$	9.54
$Cd(valinate)_2$	6.81	Cd(threoninate)	4.06
$Cd(valinate)_3$	8.90	$Cd(threoninate)_2$	7.06
		$Cd(threoninate)_3$	9.02

the study of the mixed-ligand system, by the method of DeFord and Hume.[2] The conditions used corresponded as closely as possible to those for the mixed systems *i.e.* ionic strength was 1.0 M (KNO_3) and temp. (303±1)K. The formation constants which are in good agreement with literature,[9–13] have been tabulated in Table 2.

Ternary Systems. The cadmium–heda–amino acid systems were studied by keeping the concentration of the weaker ligand (amino acids) constant at two different values while varying the concentration of heda in each case, the total cadmium concentration was kept at 5×10^{-4} M.

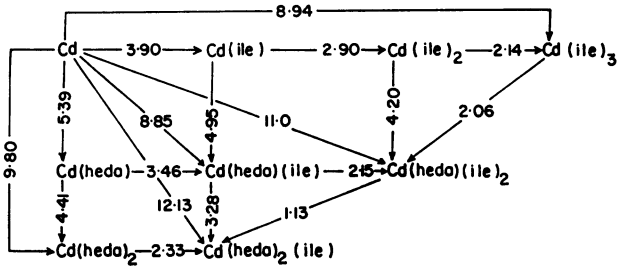
Free ligand concentration for each system has been calculated with the help of pH of the solution, pK values and amount of the ligand.

In all cases a single well-defined wave was obtained for which the plots of $-E_{de}$ *vs.* log $i/(i_d-i)$ gave a slope of (30±2) mV, indicating that the reduction is reversible and involves the transfer of two electrons. The reduction is diffusion controlled as evident by the direct proportionality of the limiting current to the square root of the effective height of mercury column.

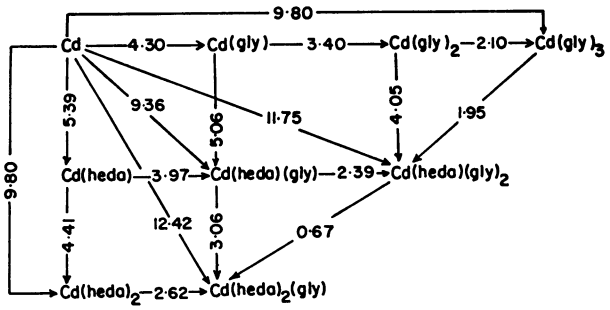
By increasing the heda concentration, the half wave potential shifts towards more negative side and this shift is greater in the presence of the weaker ligands (amino acids) than in its absence. It signifies the formation of mixed-ligand complexes. The F_{1o} function was evaluated by extending the method of Schaap and McMasters and A, B, and C were calculated by Leden's–graphical extrapolation method.[16] Stability constants

TABLE 3. STABILITY CONSTANTS OF MIXED-LIGAND COMPLEXES

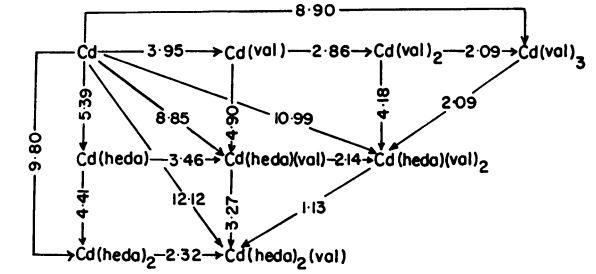
System	log β_{11}	log β_{12}	log β_{21}
Cd-heda-isoleucinate	8.85	11.00	12.13
Cd-heda-glycinate	9.36	11.75	12.42
Cd-heda-valinate	8.85	10.99	12.12
Cd-heda-serinate	9.02	11.20	12.18
Cd-heda-glutamate	9.55	12.00	12.59
Cd-heda-alaninate	9.26	11.62	12.33
Cd-heda-threoninate	9.00	11.16	12.20



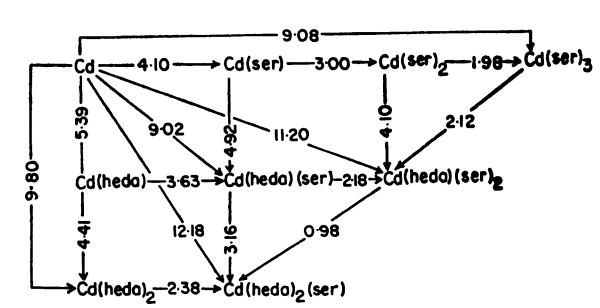
Scheme 1. Cadmium–heda–isoleucinate system.



Scheme 2. Cadmium–heda–glycinate system.



Scheme 3. Cadmium–heda–valinate system.



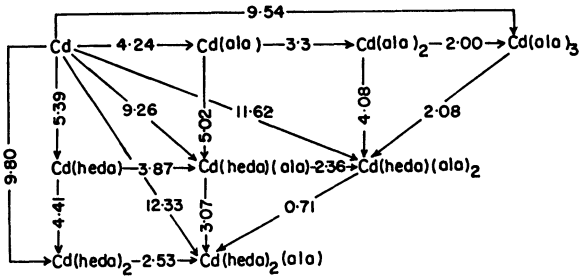
Scheme 4. Cadmium–heda–serinate system.

of mixed-ligand complexes have been presented in Table 3 and summarised in Schemes 1—7.

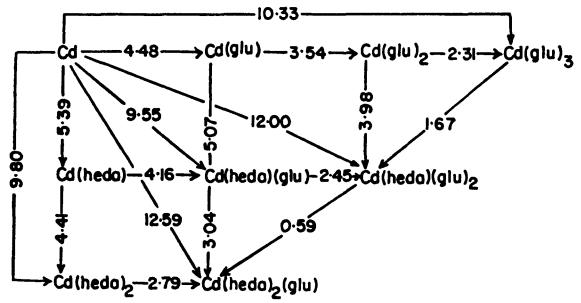
Discussion

The values of F_{20} for Cd–heda–isoleucinate are constant as 6.30×10^{10} and 2.80×10^{11} at 0.04 and 0.2 M of isoleucinate respectively (Tables 4 and 5). But these values differ appreciably with each other. Similar results have also been observed in Cd–heda–glycinate, Cd–heda–valinate, Cd–heda–serinate, Cd–heda–glutamate, Cd–heda–alaninate, and Cd–heda–threoninate. This proves the formation of maximum number of complexes, simple and mixed in each mixed-ligand system and these complexes contain more than one mixed-ligand species. It may be concluded that the formation of MXY, MXY_2 and MX_2Y mixed-ligand complexes is taking place in the solution.

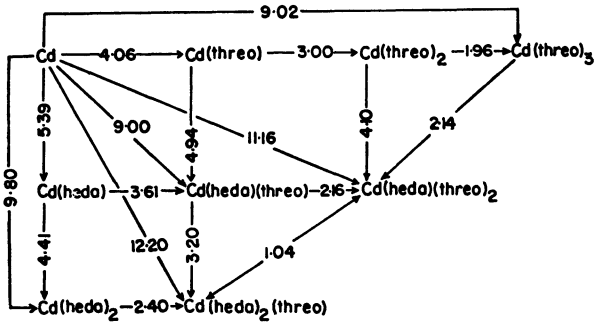
With the help of Schemes 1—7 too, the formation of MXY, MXY_2, and MX_2Y may be explained. For the addition of heda to Cd(heda), Cd(ile), Cd(gly),



Scheme 6. Cadmium–heda–alaninate system.



Scheme 5. Cadmium–heda–glutamate system.



Scheme 7. Cadmium–heda–threoninate system.

Table 4. Data and results for cadmium–heda–isoleucinate system, (ile) = 0.04 M, $E_{1/2}$(M) = −0.580 V *vs.* SCE

$10^4\times$[X]/M	$\Delta E_{1/2}$/V	$\log\frac{I_M}{I_C}$	$F_{00}\times10^{-5}$	$F_{10}\times10^{-8}$	$F_{20}\times10^{-10}$	F_{00}(calcd)$\times10^{-5}$	ΔE/%*
0.52	0.145	0.0093	0.68	0.38	—	0.67	−1.47
2.68	0.152	0.0286	1.22	2.09	7.46	1.21	−0.82
8.14	0.162	0.0386	2.68	2.48	7.25	2.60	−2.99
24.22	0.177	0.0437	8.56	3.26	5.66	8.80	+2.80
46.10	0.189	0.0488	21.72	4.57	5.81	22.27	+2.53
102.46	0.207	0.0488	86.24	8.35	6.30	83.75	−2.89
148.36	0.215	0.0540	161.08	10.81	6.01	162.30	+0.76
218.30	0.224	0.0593	324.92	14.85	5.94	331.18	+1.93
290.69	0.231	0.0646	562.30	19.32	6.00	568.52	+1.11

$A=6.6\times10^4$ (calcd), $B=1.89\times10^8$, $C=(6.30\pm1.16)\times10^{10}$.

Table 5. Data and results for Cd–heda–isoleucinate system, (ile) = 0.2 M, $E_1/_2$(M) = −0.580 V *vs.* SCE

$10^4\times$[M]/M	$\Delta E_{1/2}$/V	$\log\frac{I_M}{IC}$	$F_{00}\times10^{-6}$	$F_{10}\times10^{-9}$	$F_{20}\times10^{-11}$	F_{00}(calcd)$\times10^{-6}$	ΔF/%*
10.24	0.211	0.0374	11.41	4.10	—	11.73	+2.80
34.72	0.221	0.0440	24.93	5.10	2.76	24.92	−0.04
66.18	0.229	0.0508	46.73	5.97	2.77	46.74	+0.02
152.46	0.243	0.0574	138.68	8.62	2.94	134.71	−2.86
198.66	0.247	0.0642	191.38	9.27	2.58	198.78	+3.87
274.40	0.254	0.0713	332.57	11.86	2.81	329.38	−0.96
344.26	0.259	0.0778	495.14	14.17	2.91	478.02	−3.46

$A=7.21\times10^6$ (calcd), $B=4.14\times10^9$, $C=(2.80\pm0.22)\times10^{11}$

* $\Delta F(\%)=\frac{100}{F_{00}(\text{exptl})}[F_{00}(\text{calcd})-F_{00}(\text{exptl})]$.

Cd(val), Cd(ser), Cd(glu), Cd(ala), and Cd(thr), the log values of stability constants are 4.41, 4.95, 5.06, 4.90, 4.92, 5.07, 5.02, and 4.94 respectively. These values indicate that it is easier for heda to add Cd (amino acids) than to Cd(heda) and also that the addition of heda is slightly favoured as the stability of the Cd(amino acids) decreases. The log K values for the addition of, isoleucinate- to Cd(ile) and Cd (heda) are 2.90 and 3.46, glycinate to Cd(gly) and Cd(heda) are 3.40 and 3.97, valinate to Cd(val) and Cd(heda) are 2.86 and 3.46, serinate to Cd(ser) and Cd(heda) are 3.00 and 3.63, glutamate to Cd(glu) and Cd(heda) are 3.54 and 4.16; alaninate to Cd(ala) and Cd(heda) are 3.30 and 3.87 and threoninate to Cd(thr) and Cd(heda) are 3.00 and 3.61, indicating that the mixed-ligand complexation is favoured.

The logarithms of stability constants for the addition of isoleucinate to $Cd(heda)_2$, Cd(heda) (ile), and $Cd(ile)_2$ are 2.33, 2.15, and 2.14 respectively and show that the mixed-ligand complex formation is preferred. The other systems follow suit.

The case of mixed-ligand complex formation by the addition of amino acids to $Cd(heda)_2$ and Cd(heda) (amino acids) may easily be confirmed on the basis of statistical considerations,[14] only when the values of stability constant of $Cd(heda)_3$ complex is known. In our experimental conditions such complex has not been identified but for the understanding view point such value may be evaluated by using equations 4—6 as proposed by Watters and Dewitt:[15]

$$\beta_{11} = 2 \times 3 \times \beta_{30}^{1/3} \times \beta_{03}^{1/3}, \quad (4)$$

$$\beta_{12} = 3 \times \beta_{30}^{1/3} \times \beta_{03}^{2/3}, \quad (5)$$

$$\beta_{21} = 3 \times \beta_{30}^{2/3} \times \beta_{03}^{1/3}. \quad (6)$$

These above equations are valid strictly when mixed-ligand complexation is characterised by the statistical factor. The values of stability-constants of $Cd(heda)_3$ complex so obtained from each system are given in Table 6.

Since all these β_{30} values are much higher than the stability constants of $Cd(heda)_2$, $Cd(heda)_3$ complex must exist at maximum heda concentration. This shows that the formation of $Cd(heda)_3$ complex is favoured by statistical factors whereas it does not exist in the simple system. The formation of $Cd(heda)_3$ may be opposed by some factors like the bulky nature of heda molecule.

By calculating the disproportionation constant K^D for the equilibria,

$$2Cd(heda)(\text{amino acids}) \rightleftharpoons Cd(\text{amino acids})_2 + Cd(heda)_2,$$

the tendency of the formation of 1:1:1 mixed ligand complex should be easily expressed. For statistical reasons the value of log K^D is −0.6 but the observed values are −1.10, −1.22, −1.11, −1.18, −1.28, −1.22, and −1.14 for Cd–heda–ile, Cd–heda–gly, Cd–heda–val., Cd–heda–ser., Cd–heda–glu., Cd–heda–ala and Cd–heda–thr, respectively. More negative values of log K^D for each equilibrium show that mixed-ligand complex formation is effected by some other factors.

TABLE 6. STABILITY CONSTANTS OF $Cd(heda)_3$ BY USING WATTERS AND DEWITTS EQUATIONS

System	Using equation 4	Using equation 5	Using equation 6
Cd-heda-isoleucinate	15.58	13.69	13.01
Cd-heda-glycinate	15.94	14.23	13.01
Cd-heda-valinate	15.31	13.75	12.99
Cd-heda-serinate	15.64	14.02	13.01
Cd-heda-glutamate	16.00	13.90	13.01
Cd-heda-alaninate	15.91	14.35	13.01
Cd-heda-threoninate	15.64	14.02	13.07

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