

Study of mixed complexes by polarography : cadmium-glycine-methionine and cadmium-glycine-ethylenediamine complexes

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Abstract. The mixed complexes of cadmium with glycine and methionine and glycine and ethylenediamine have been studied by polarography and the stability constants of the various species formed have been evaluated.

Keywords. Mixed complexes ; cadmium ; glycine ; methionine ; ethylenediamine ; polarography.

1. Introduction

Though Schaap and McMasters (1961) pioneered the extension of the polarographic method of DeFord and Hume (1951) to the study of mixed complexes, not much work has since been reported in the literature. This paper presents a polarographic study of the mixed complexes of cadmium with glycine-methionine and glycine-ethylenediamine.

2. Experimental

Glycine (E Merck, pro analysi) and DL-methionine (E Merck, LR) were used without purification. Ethylenediamine (E Merck, LR) was standardised against hydrochloric acid using methyl orange as the indicator. A stock solution of cadmium was prepared from cadmium sulphate (E Merck, GR) and standardised with EDTA. Potassium nitrate, used as the supporting electrolyte, was of BDH AnalaR grade. The solutions were made in double distilled water and pH was measured with a Philips pH-meter (PP-9040). Polarograms were taken on a manual set-up using a H-cell with an agar plug and a saturated calomel electrode (SCE) served as the reference electrode. Currents are reported after correcting for the residual currents. Correction for the IR drop in the potentials was not necessary.

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3. Results and discussion

3.1. Cadmium-glycine-methionine complexes

'Simple' complexes of cadmium with glycine and with methionine were studied separately in 1.0 M potassium nitrate at different pH. The electrode reaction was reversible in both the cases. The glycinate [G] and the methioninate [Me] concentrations were calculated from the pH of the solution and the pK_a of the ligands determined as 9.76 for glycine and 9.10 for methionine. The half-wave potentials were measured as a function of $\log [G]$ or $\log [Me]$ from which the stability constants were calculated as $\log \beta_3 = 9.40$ for cadmium-glycine and $\log \beta_1 = 3.80$, $\log \beta_2 = 6.35$ and $\log \beta_3 = 8.19$ for cadmium-methionine systems by the methods of Lingane (1941) and DeFord and Hume (1951) respectively

In the investigation of cadmium-glycine-methionine system three series of measurements were made under the same experimental conditions as for the 'simple' systems, keeping [Me] constant and varying [G]. The polarograms were well defined and the reduction was reversible. The half-wave potentials (table 1) were used to calculate a function, F_{00} , using the relationship (Schaap and McMasters 1961)

$$F_{00}(\text{Me}, \text{G}) = \text{antilog} [0.4343 nF/RT \{E_{1/2(a)} - E_{1/2(b)}\} + \log \{i_{d(a)}/i_{d(b)}\}] \quad (1)$$

where the symbols have the usual meaning. This may be written, at constant methioninate concentration, as

$$F_{00}(\text{Me}, \text{G}) = A + B[G] + C[G]^2 + D[G]^3 \quad (2)$$

where

$$\left. \begin{aligned} A &= [1 + \beta_{\text{Me}_2\text{G}_0} [\text{Me}] + \beta_{\text{Me}_3\text{G}_0} [\text{Me}]^2 + \beta_{\text{Me}_4\text{G}_0} [\text{Me}]^3] \\ &= [1 + \beta_{10} [\text{Me}] + \beta_{20} [\text{Me}]^2 + \beta_{30} [\text{Me}]^3], \\ B &= [\beta_{\text{Me}_2\text{G}_1} + \beta_{\text{Me}_3\text{G}_1} [\text{Me}] + \beta_{\text{Me}_4\text{G}_1} [\text{Me}]^2] \\ &= [\beta_{01} + \beta_{11} [\text{Me}] + \beta_{21} [\text{Me}]^2], \\ C &= [\beta_{\text{Me}_2\text{G}_2} + \beta_{\text{Me}_3\text{G}_2} [\text{Me}]] \\ &= [\beta_{02} + \beta_{12} [\text{Me}]] \text{ and} \\ D &= \beta_{\text{Me}_2\text{G}_3} = \beta_{03}. \end{aligned} \right\} \quad (3)$$

$\beta_{\text{Me}_n\text{G}_m}$ refer to the stability constants of the mixed complex species $\text{Cd Me}_n\text{G}_m$. The constants A , B , C and D , evaluated by a graphical procedure, are reported in table 1.

The values of A agreed with the calculated values based on the stability constants obtained from the 'simple' system. β_{11} and β_{21} were calculated from the values of B using (3) as 1.0×10^8 and 1.26×10^9 respectively. Similarly β_{02} and β_{12} were determined from C as 3.98×10^7 and 3.16×10^9 respectively. The average value of D corresponds to β_{03} and agreed with that obtained from cadmium-glycine system.

The relative stability of a mixed complex over the parent binary complex and the compatibility between the ligands, indicated by the "mixing constant" k_M

Table 1. Cadmium-methionine-glycine system : Half-wave potential data
 $Cd = 3.8 \times 10^{-4} M$; $\mu = 1.0 (KNO_3)$; $pH = 9.50$; $m^{2/3} t^{1/6} = 1.84 \text{ mg}^{2/3} \text{ sec}^{-1/2}$; $E_{1/2(s)} = -0.580 \text{ V vs SCE}$; $i_{d(s)} = 2.35 \mu A$; $i_{d(s) \text{ mean}} = 2.00 \mu A$.

$[G] \times 10^3$ [M]	$E_{1/2}$ - V vs SCE	$F_{00} \times 10^{-4}$	$F_{10} \times 10^{-6}$	$F_{20} \times 10^{-8}$
$[Me] = 3.58 \times 10^{-2} M$				
1.42	0.701	1.25	1.74	0.66
2.84	0.705	1.69	2.43	2.75
5.67	0.710	2.49	2.62	1.71
9.93	0.717	4.25	3.27	1.63
14.19	0.725	7.84	4.82	2.24
21.29	0.733	13.94	6.08	2.08
28.37	0.738	21.24	7.13	1.93
42.57	0.743	31.15	7.08	1.28
56.74	0.759	106.1	18.53	2.97
$A = 1.00 \times 10^4$; $B = 1.65 \times 10^6$; $C = 1.55 \times 10^8$; $D = 2.30 \times 10^9$.				
$[Me] = 7.15 \times 10^{-2} M$				
1.42	0.725	7.74	5.25	..
2.84	0.727	9.03	7.14	3.32
5.67	0.729	11.36	7.68	2.61
9.93	0.735	17.31	10.38	4.21
14.19	0.738	20.97	9.84	2.57
21.29	0.745	37.25	14.21	3.76
28.37	0.749	50.60	15.37	3.23
42.57	0.759	108.9	23.93	4.16
56.74	0.764	159.7	26.91	3.65
$A = 7.00 \times 10^4$; $B = 6.20 \times 10^6$; $C = 2.75 \times 10^8$; $D = 2.20 \times 10^9$.				
$[Me] = 0.107 M$				
1.42	0.739	22.93	10.07	..
2.84	0.739	22.93	5.04	..
5.67	0.743	31.16	17.04	3.93
9.93	0.746	39.12	17.83	3.05
14.19	0.749	47.48	18.31	2.47
21.29	0.754	72.37	23.89	4.27
28.37	0.760	110.3	31.30	5.82
42.57	0.765	168.1	34.44	4.61
56.74	0.772	287.4	46.86	5.65
$A = 2.15 \times 10^5$; $B = 1.48 \times 10^7$; $C = 3.75 \times 10^8$; $D = 2.70 \times 10^9$.				

and the enhanced (or sometimes decreased) stability due to factors other than statistical, given by the "stabilisation constant" k_s , are calculated from the expressions (Marcus and Eliezer 1962)

$$k_{M(x,y)} = \beta_{xy} \cdot \beta_{m,0}^{-x/m} \cdot \beta_{0,m}^{-y/m}, \quad (x + y = m), \quad (4)$$

and $\log k_s = \log k_M - \log (m! / x! y!). \quad (5)$

The values of k_M and k_s for this system, calculated in this manner, are given in table 2.

3.2. Cadmium-glycine-ethylenediamine complexes

A preliminary investigation of cadmium-ethylenediamine complexes in 1.0 M potassium nitrate indicated reversible reduction. The dissociation constant, pK_2 of ethylenediamine was determined as 10.10 and the stability constant β_3 was calculated from the half-wave potential data as $10^{11.98}$. In the study of cadmium-glycine-ethylenediamine system, three sets of data were obtained at three concentrations of glycine, varying that of ethylenediamine. The reduction was reversible and the half-wave potential data (not presented here for the sake of brevity) were solved for the stability constants of the various complex species as discussed earlier. These values as well as $\log k_M$ and $\log k_s$ are given in table 2.

Table 2. Stability constants and $\log k_M$ and $\log k_s$ values.

Complex species	log β		log k_M	log k_s
	Present work	Literature values	Present work	
Cd(Me)	3.80	3.81
Cd(Me) ₂	6.35	6.24
Cd(Me) ₃	8.19	8.32
Cd(G)	..	4.54
Cd(G) ₂	7.60	8.08
Cd(G) ₃	9.40	9.78
Cd(Me)G	6.00	..	-0.98	-1.28
Cd(Me) ₂ G	9.10	..	+0.51	+0.03
Cd(Me)G ₂	9.50	..	+0.59	+0.02
Cd(En)	..	5.60
Cd(En) ₂	..	10.63
Cd(En) ₃	11.98	12.10
Cd(En)G	9.11	..	-0.01	-0.31
Cd(En)G ₂	11.23	..	+0.97	+0.50
Cd(En) ₂ G	12.02	..	+0.90	+0.42

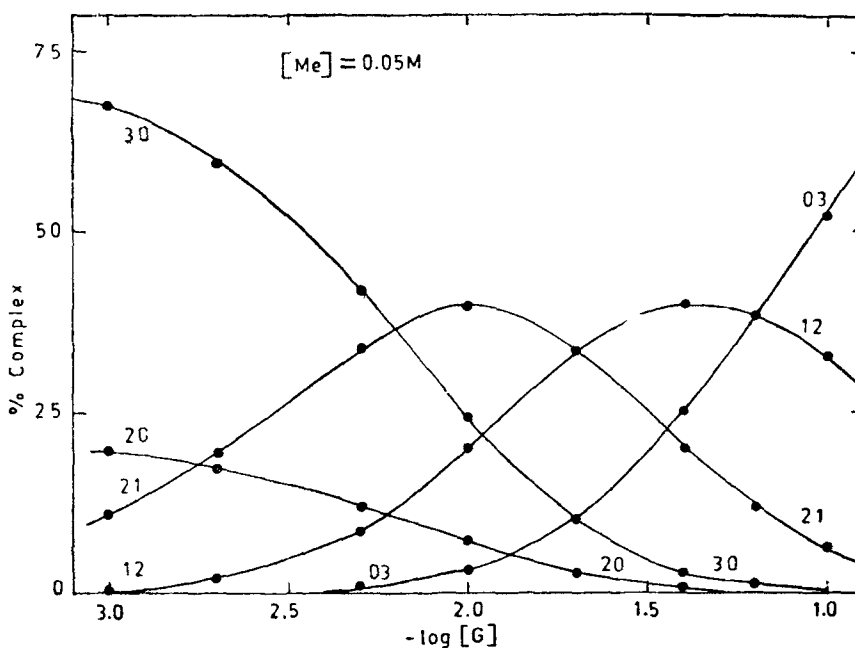


Figure 1. Distribution of cadmium as complexes.

Table 3. Complex equilibria and equilibrium constants.

Equilibria	log K
$\text{Cd} + \text{Me} + \text{G} \rightleftharpoons \text{Cd}(\text{Me})(\text{G})$	6.00
$\text{Cd} + 2\text{Me} + \text{G} \rightleftharpoons \text{Cd}(\text{Me})_2(\text{G})$	9.10
$\text{Cd} + \text{Me} + 2\text{G} \rightleftharpoons \text{Cd}(\text{Me})(\text{G})_2$	9.50
$\text{Cd}(\text{Me})(\text{G}) + \text{G} \rightleftharpoons \text{Cd}(\text{Me})(\text{G})_2$	3.50
$\text{Cd}(\text{Me})(\text{G}) + \text{Me} \rightleftharpoons \text{Cd}(\text{Me})_2(\text{G})$	3.10
$\text{Cd}(\text{Me})_2(\text{G}) + \text{G} \rightleftharpoons \text{Cd}(\text{Me})(\text{G})_2 + \text{Me}$	0.40
$\text{Cd}(\text{G})_2 + \text{Me} \rightleftharpoons \text{Cd}(\text{Me})(\text{G})_2$	1.90
$\text{Cd}(\text{Me}) + \text{G} \rightleftharpoons \text{Cd}(\text{Me})(\text{G})$	2.20
$\text{Cd}(\text{Me})_2 + \text{G} \rightleftharpoons \text{Cd}(\text{Me})(\text{G}) + \text{Me}$	-0.35
$\text{Cd}(\text{Me})_3 + \text{G} \rightleftharpoons \text{Cd}(\text{Me})_2(\text{G}) + \text{Me}$	0.91
$\text{Cd}(\text{Me})(\text{G})_2 + \text{G} \rightleftharpoons \text{Cd}(\text{G})_3 + \text{Me}$	-0.10
$\text{Cd} + \text{En} + \text{G} \rightleftharpoons \text{Cd}(\text{En})(\text{G})$	9.11
$\text{Cd} + \text{En} + 2\text{G} \rightleftharpoons \text{Cd}(\text{En})(\text{G})_2$	11.23
$\text{Cd} + 2\text{En} + \text{G} \rightleftharpoons \text{Cd}(\text{En})_2(\text{G})$	12.02
$\text{Cd}(\text{En})(\text{G}) + \text{En} \rightleftharpoons \text{Cd}(\text{En})_2(\text{G})$	2.91
$\text{Cd}(\text{En})(\text{G}) + \text{G} \rightleftharpoons \text{Cd}(\text{En})(\text{G})_2$	2.12
$\text{Cd}(\text{En})(\text{G})_2 + \text{En} \rightleftharpoons \text{Cd}(\text{En})_2(\text{G}) + \text{G}$	0.79
$\text{Cd}(\text{G})_2 + \text{En} \rightleftharpoons \text{Cd}(\text{En})(\text{G}) + \text{G}$	1.51
$\text{Cd}(\text{G})_3 + \text{En} \rightleftharpoons \text{Cd}(\text{En})(\text{G})_2 + \text{G}$	1.83
$\text{Cd}(\text{En})_2(\text{G}) + \text{En} \rightleftharpoons \text{Cd}(\text{En})_3 + \text{G}$	-0.04

It is seen from table 2 that $\log k_M$ for the 1, 2 and 2, 1 complexes of both the systems are positive indicating the compatibility between the ligands. Glycine is more compatible with ethylenediamine probably because the chelating power of ethylenediamine is more due to the presence of two nitrogen donors. The co-ordination unsaturated 1, 1 is 'not important' in both the systems as inferred from the negative values of $\log k_s$ and $\log k_M$. It is, therefore, apparent that the species present in solution in the concentration ranges studied are mostly 20, 30, 21, 12 and 03 complexes. The distribution of cadmium as these complex species at $[Me] = 0.05$ M is depicted in figure 1 as a function of glycinate concentration as an example. The equilibria between the different complex species are given in table 3 from which the facility with which a ligand adds on to or substitutes another ligand may be deduced.

References

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