

ELECTROCHEMICAL INVESTIGATION OF TERNARY COMPLEXES OF Cd(II) WITH SOME AMINO ACIDS (α -ALANINE AND β -ALANINE) AND CITRATE ANIONS

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The ternary complexes of Cd(II) with citrate anions as a primary ligand and amino acids (α -alanine and β -alanine) as a secondary ligand have been investigated using differential pulse polarography. Formation of three mixed complexes, [Cd(amino acid)(citrate)], [Cd(amino acid)(citrate)₂] and [Cd(amino acid)₂(citrate)] is observed in each case. The stability constants and the mixing constants of the ternary system have been calculated, as well as the stabilization constants. The electrochemical reduction was reversible and diffusion controlled. The various equilibria involved in the ternary systems are also given.

Mixed ligand complexes are generally formed when metal ion is present in a mixture of two or more ligands in solution. The DeFord-Hume method¹ for simple complexes was extended to study the formation constants of mixed-ligand complexes by Schaap and McMasters², which has been extensively used by several workers³⁻⁶.

The toxic effects of cadmium in the form of Cd²⁺ are well established and documented⁷. It has been found to induce various pathological diseases⁷⁻⁹. It is also known, that most of the Cd²⁺ in biological systems is not in the form of free Cd²⁺ ions, but it is complexed by the abundance of biological ligands therein¹⁰. Thus, the complexation of cadmium(II) ions with biological ligands is of great concern for mankind.

In continuation of our studies on the ternary systems¹¹ using modern electro-analytical techniques, we report here the results of the mixed complexation of cadmium(II) with citrate as a primary ligand and α - and β -alanines as secondary ligands.

EXPERIMENTAL

Polarograms were obtained using Metrohm polarographic analysis instrument (626 Polarecord), which was connected with 663 VA stand. The Ag/AgCl reference electrode (3M KCl) was used throughout the measurements.

In fast polarography a drop time of 1.0 s and a scan rate of 5 mV/s, and in differential pulse polarography (DPP) 50 mV pulse amplitude were used.

All the measurements were made at 25°C, and ionic strength was kept constant at 1.0 mol · dm⁻³ with NaNO₃ as supporting electrolyte. The pH of all the experimental solutions was maintained constant at 8.0 with the help of HNO₃/NaOH solutions. The concentration of Cd²⁺ ions was 1 · 10⁻⁴ mol dm⁻³.

The amino acids used were BDH reagents. All other chemicals used were of a.r. grade.

RESULTS AND DISCUSSION

The polarographic reduction of Cd(II) in the presence of α-alanine, β-alanine and citrate separately was found to be reversible with two electrons and diffusion controlled process. Also, the same was true in the case of mixed-ligand systems. In DC sampled polarography (fast mode), the plots of log [*i*/(*i*_d - *i*)] vs *E* were linear with a slope of 30 ± 2 mV, and in DPP, the half-width of the peak was 62 ± 2 mV. These values are in good agreement with those calculated by Dillard and Hanck¹² using digital simulation. The results indicate the reversibility of the reduction for both simple and mixed systems. On the other hand, the plots of *i*_d vs *h*^{1/2} were linear and passed through the origin (using DC Sargent-Welch polarograph Model 3001).

For the simple systems, Cd(α-alanine), Cd(β-alanine) and Cd(citrate), the composition and the stability constants for each system were studied separately. The Cd²⁺ ions concentration was kept constant at 1 · 10⁻⁴ mol dm⁻³ using NaNO₃ as supporting electrolyte (ionic strength of 1.0 mol dm⁻³) and pH 8. The free ligand concentration of the amino acids was calculated from the reported value¹³ of p*K*₂ (α-alanine = 9.70, β-alanine = 10.09). The stability constants *B*_{*i*} of these systems were determined using DeFord-Hume¹ expression modified by Heath and Hefter¹⁴ for DPP. This expression may be written as follows:

$$\log F_0(X) = \log \sum_i B_i [X]^i = \left(\frac{0.434nF}{RT} \Delta E_p + \log \frac{(I_p)_s}{(I_p)_c} \right), \quad (1)$$

where [*X*] is the ligand concentration and other symbols have their usual significance. The obtained values of *B*_{*i*} are given in Table I.

In case of ternary systems the concentration of α-alanine and β-alanine varied, while the concentration of citrate (cit) anions was kept constant at (0.10 and 0.20 mol · dm⁻³) because at these concentrations, [Cd(cit)]⁻ and [Cd(cit)₂]⁻⁴ complexes, were found to be predominant, respectively. The Schaap and McMasters² expression modified by Killa et al.¹¹ for DPP was applied to calculate the stability constants of mixed-ligand complexes from the shift in the peak potential (Δ*E*_{*p*}). This expression may be written as follows:

$$\log F_{00}(XY) = \left(\frac{0.434nF}{RT} \Delta E_p + \log \frac{(I_p)_s}{(I_p)_c} \right), \quad (2)$$

where the F_{00} function

$$F_{00}(XY) = A + B[X] + C[X]^2 + D[X]^3$$

with

$$A = B_{01}[Y] + B_{02}[Y]^2 + B_{03}[Y]^3$$

$$B = B_{10} + B_{11}[Y] + B_{12}[Y]^2$$

$$C = B_{20} + B_{21}[Y]$$

$$D = B_{30}$$

Here $[X]$ and $[Y]$ refer to α -alanine or β -alanine and citrate ligands, respectively. The extrapolation method² was used to calculate A , B , C and D which are given in Table II.

In the stability constants B_{ij} the first subscript refers to the number of α -alanine or β -alanine molecules while the second number refers to the citrate ligands. With respect to previous notation, $B_{i0} \equiv B_i$ and $B_{0i} \equiv B_j$. Once the $F_{00}(XY)$ function is obtained by using Eq. (2), the functions F_{10} , F_{20} and F_{30} defined as

$$F_{10} = \frac{F_{00} - A}{[X]}, \quad F_{20} = \frac{F_{10} - B}{[X]}, \quad F_{30} = \frac{F_{20} - C}{[X]}$$

can be evaluated. By their plotting vs $[X]$, the values of B , C and D respectively, could be calculated, cf. Table II. The results point to the formation of three mixed

TABLE I

The composition and stability constants B_i of the binary systems, at 25°C, $\mu = 1.0 \text{ mol dm}^{-3}$ (NaNO_3) and pH 8.0

System	Complex species	$\log B_i$
Cd(α -alanine)	$[\text{Cd}(\alpha\text{-ala})]^+$	4.71
	$[\text{Cd}(\alpha\text{-ala})_2]$	7.32
	$[\text{Cd}(\alpha\text{-ala})_3]^-$	9.65
Cd(β -alanine)	$[\text{Cd}(\beta\text{-ala})]^+$	3.60
	$[\text{Cd}(\beta\text{-ala})_2]$	5.80
	$[\text{Cd}(\beta\text{-ala})_3]^-$	7.05
Cd(citrate)	$[\text{Cd}(\text{cit})]^-$	2.92
	$[\text{Cd}(\text{cit})_2]^{-4}$	4.20
	$[\text{Cd}(\text{cit})_3]^{-7}$	4.65

species in Cd(α -ala-cit) and Cd(β -ala-cit) systems. The obtained values (observed) together with the statistically calculated values using Watters and De Witt expression¹⁵ are given in Table III.

From the two values of C , the mixed-ligand stability constants B_{21} were calculated for both α -alanine and β -alanine. The average values for $\log B_{21}$ are given in Table III. At the same time, the two values of $\log D$ from both series are 9.31 and 9.52 (average = 9.42 ± 0.11) in case of Cd(α -ala-cit) system, which agree with the experimentally determined value $\log B_{30}$ (9.65). Similarly, the $\log D$ values of Cd(β -ala-cit) system were 6.78, 6.94 (average = 6.86 ± 0.08) which are in agreement with $\log B_{30}$ (7.05). The statistically calculated values are slightly lower than the observed values. This behaviour may be attributed to the electrostatic and steric factors as concluded by Hughes et al.¹⁶.

TABLE II
Mixed ligand stability constant parameters at 25°C, $\mu = 1.0 \text{ mol dm}^{-3}$ (NaNO₃) and pH 8.0

System	[cit] mol dm ⁻³	log A ^a	log B	log C	log D
Cd(α -ala-cit)	0.10	2.45	5.46	7.65	9.31
	0.20	3.06	5.84	8.10	9.52
Cd(β -ala-cit)	0.10	2.45	4.62	6.05	6.78
	0.20	3.06	5.03	6.36	6.44

^a Calculated.

TABLE III
Mixed ligand stability constants B_{ij} at 25°C

System		log B ₁₁	log B ₁₂ (average)	log B ₂₁
Cd(α -ala-cit)	obs. ^a	6.16	6.95	8.55
	sta. ^b	5.88	6.79	8.45
Cd(β -ala-cit)	obs. ^a	5.37	6.15	6.91
	sta. ^b	5.12	5.92	6.72

^a Obs. observed values; ^b sta. statistically calculated values.

For the reactions

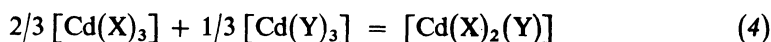
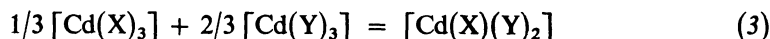
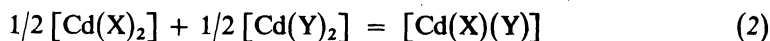


TABLE IV

The values of the mixing constants ($\log K_M$) and stabilization constants ($\log K_s$) of the ternary complexes

System	$\log K_{M_{11}}$	$\log K_{M_{12}}$	$\log K_{M_{21}}$	$\log K_{s_{11}}$	$\log K_{s_{12}}$	$\log K_{s_{21}}$
Cd(α -ala-cit)	+0.40	+0.95	+0.85	+0.099	0.65	0.55
Cd(β -ala-cit)	+0.37	+1.05	+0.84	+0.069	0.75	0.54

TABLE V

Equilibria of the ternary complexes with α -alanine and citrate and values of equilibrium constants K

No.	Equilibria ^a	$\log K$
1.	$\text{Cd} + \alpha\text{-ala} + (\text{cit}) \rightleftharpoons [\text{Cd}(\alpha\text{-ala})(\text{cit})]$	6.16
2.	$\text{Cd} + \alpha\text{-ala} + 2(\text{cit}) \rightleftharpoons [\text{Cd}(\alpha\text{-ala})(\text{cit})_2]$	6.95
3.	$\text{Cd} + 2(\alpha\text{-ala}) + (\text{cit}) \rightleftharpoons [\text{Cd}(\alpha\text{-ala})_2(\text{cit})]$	8.55
4.	$[\text{Cd}(\alpha\text{-ala})(\text{cit})] + \alpha\text{-ala} \rightleftharpoons [\text{Cd}(\alpha\text{-ala})_2(\text{cit})]$	2.39
5.	$[\text{Cd}(\alpha\text{-ala})(\text{cit})] + (\text{cit}) \rightleftharpoons [\text{Cd}(\alpha\text{-ala})(\text{cit})_2]$	0.79
6.	$[\text{Cd}(\alpha\text{-ala})] + \alpha\text{-ala} \rightleftharpoons [\text{Cd}(\alpha\text{-ala})_2]$	2.61
7.	$[\text{Cd}(\text{cit})] + \alpha\text{-ala} \rightleftharpoons [\text{Cd}(\alpha\text{-ala})(\text{cit})]$	3.24
8.	$[\text{Cd}(\alpha\text{-ala})] + (\text{cit}) \rightleftharpoons [\text{Cd}(\alpha\text{-ala})(\text{cit})]$	1.45
9.	$[\text{Cd}(\alpha\text{-ala})] + 2(\text{cit}) \rightleftharpoons [\text{Cd}(\alpha\text{-ala})(\text{cit})_2]$	2.24
10.	$[\text{Cd}(\text{cit})] + 2(\alpha\text{-ala}) \rightleftharpoons [\text{Cd}(\alpha\text{-ala})_2(\text{cit})]$	5.63
11.	$[\text{Cd}(\text{cit})_2] + \alpha\text{-ala} \rightleftharpoons [\text{Cd}(\alpha\text{-ala})(\text{cit})_2]$	2.75
12.	$[\text{Cd}(\alpha\text{-ala})(\text{cit})_2] + \alpha\text{-ala} \rightleftharpoons [\text{Cd}(\alpha\text{-ala})_2(\text{cit})] + (\text{cit})$	1.60
13.	$[\text{Cd}(\text{cit})_2] + 2(\alpha\text{-ala}) \rightleftharpoons [\text{Cd}(\alpha\text{-ala})_2(\text{cit})] + (\text{cit})$	4.35
14.	$[\text{Cd}(\text{cit})_3] + (\alpha\text{-ala}) \rightleftharpoons [\text{Cd}(\alpha\text{-ala})(\text{cit})_2] + (\text{cit})$	2.30

^a The charges are neglected for simplicity.

where X means α -alanine or β -alanine and Y means citrate anions, the mixing constants K_M (ref.¹⁷) are respectively expressed as follows:

$$\log K_{M_{11}} = \log B_{11} - 1/2 (\log B_{20} + \log B_{02}) \quad (5)$$

$$\log K_{M_{12}} = \log B_{12} - (1/3 \log B_{30} + 2/3 \log B_{03}) \quad (6)$$

$$\log K_{M_{21}} = \log B_{21} - (2/3 \log B_{30} + 1/3 \log B_{03}) \quad (7)$$

and the stabilization constants K_s are given by the following relation¹⁸:

$$\log K_s = (\log K_M - \log 2). \quad (8)$$

The values of $\log K_M$ and $\log K_s$ for the mixed complexes are shown in Table IV. The positive values of mixing and stabilization constants show that the mixed complexes are more stable than the simple complexes.

The disproportionation constants ($\log K_{dis}$) for the reaction



TABLE VI

Equilibria of the ternary complexes with β -alanine and citrate and values of equilibrium constants K

No.	Equilibria ^a	$\log K$
1.	$\text{Cd} + (\beta\text{-ala}) + (\text{cit}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})(\text{cit})]$	5.37
2.	$\text{Cd} + (\beta\text{-ala}) + 2(\text{cit}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})(\text{cit})_2]$	6.16
3.	$\text{Cd} + 2(\beta\text{-ala}) + (\text{cit}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})_2(\text{cit})]$	6.81
4.	$[\text{Cd}(\beta\text{-ala})(\text{cit})] + (\beta\text{-ala}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})_2(\text{cit})]$	1.44
5.	$[\text{Cd}(\beta\text{-ala})(\text{cit})] + (\text{cit}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})(\text{cit})_2]$	0.78
6.	$[\text{Cd}(\beta\text{-ala})] + (\beta\text{-ala}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})_2]$	2.20
7.	$[\text{Cd}(\text{cit})] + (\beta\text{-ala}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})(\text{cit})]$	2.45
8.	$[\text{Cd}(\beta\text{-ala})] + (\text{cit}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})(\text{cit})]$	1.77
9.	$[\text{Cd}(\beta\text{-ala})] + 2(\text{cit}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})(\text{cit})_2]$	2.55
10.	$[\text{Cd}(\text{cit})] + 2(\beta\text{-ala}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})_2(\text{cit})]$	3.89
11.	$[\text{Cd}(\text{cit})_2] + (\beta\text{-ala}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})(\text{cit})_2]$	1.95
12.	$[\text{Cd}(\beta\text{-ala})(\text{cit})_2] + (\beta\text{-ala}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})_2(\text{cit})] + (\text{cit})$	2.61
13.	$[\text{Cd}(\text{cit})_2] + 2(\beta\text{-ala}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})_2(\text{cit})] + (\text{cit})$	1.50
14.	$[\text{Cd}(\text{cit})_3] + (\beta\text{-ala}) \rightleftharpoons [\text{Cd}(\beta\text{-ala})(\text{cit})_2] + (\text{cit})$	2.20

^a The charges are neglected for simplicity.

are given by

$$\log K_{\text{dis}} = \log K_{\text{Cd}(\text{X})_2} + \log K_{\text{Cd}(\text{Y})_2} - 2 \log K_{\text{Cd}(\text{XY})}$$

If the disproportionation is purely statistical¹⁹ in nature, the $\log K_{\text{dis}}$ should be -0.60 . The observed values of citrate complexes with α -alanine and β -alanine were -0.80 and -0.74 , respectively, showing that the first are less prone to disproportionation because the $\text{Cd}(\beta\text{-ala})_2$ complex is less stable than the $\text{Cd}(\alpha\text{-ala})_2$ complex, which is due to the increasing bulkness of the alkyl group and the expected behaviour of the amino acids. The negative values of $\log K_{\text{dis}}$ reveal the stability of mixed species.

The equilibria between various species formed in solution in the two ternary systems, $\text{Cd}(\alpha\text{-ala-cit})$ and $\text{Cd}(\beta\text{-ala-cit})$ are characterized in Tables V and VI, respectively, by the equilibrium constant for each reaction. It was found that the addition of α -alanine or β -alanine to $[\text{Cd}(\text{cit})]^-$ proceeds easier than to $[\text{Cd}(\alpha\text{-ala}/\beta\text{-ala})]^+$ (equilibria 6 and 7), i.e. the formation of ternary complexes is more favoured than that of binary complexes. The equilibria 7 to 11 also favour mixed complexation over the simple complexes. The α -alanine or β -alanine can replace $(\text{cit})^{3-}$ anions (equilibria 12 to 14), while there is no tendency to replace α -alanine or β -alanine. Also, the α -alanine or β -alanine can join $[\text{Cd}(\alpha\text{-alanine or } \beta\text{-alanine})(\text{cit})]^{2-}$ more easily than citrate (equilibria 4 and 5). This indicates that the citrate is much weaker ligand than α -alanine or β -alanine.

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