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Polarographic Study of Mixed-Ligand Complexes of Cadmium(II) with Ascorbic Acid & Some Amino Acids

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The polarographic reduction of cadmium(II) in the presence of ascorbic acid and some amino acids (glutamic acid, aspartic acid, serine, threonine and tryptophan) has been found to involve a two-electron, reversible and diffusion-controlled step. The stability constants for the mixed chelates have been computed. It is shown that steric and electrostatic effects are important apart from statistical considerations.

Polarographic studies on the complexes of cadmium with ascorbic acid, glutamic acid, aspartic acid, serine, threonine and tryptophan are reported in the literature[1,2], but the mixed ligand complexes of Cd(II) with ascorbic acid and the above five amino acids have not been studied. Hence the title study was undertaken.

Polarograms were recorded on a manual polarograph using a saturated calomel electrode as the reference electrode. The capillary had the following characteristics: $m = 1.96$ mgs^{-1}, $t = 4.00$ sec drop^{-1} and $h_{corr} = 40.0$ cm.

All the chemicals used were of AR grade, and their stock solutions were prepared in conductivity water. Potassium nitrate was used as a supporting electrolyte to maintain the ionic strength constant at 1.0 *M*. *p*H of the test solution was maintained at 8.5 ± 0.1 with an Elico Digital *p*H meter (model LI-120). The temperature was kept constant at 303 ± 1 K. The experimental technique was the same as described earlier[3].

Simple (binary) system

The stability constants of Cd(II) with ascorbic acid and amino acids (glutamic, aspartic, serine, threonine and tryptophan) were first determined by the method of DeFord and Hume[4]. The results are in good agreement with the reported values in the literature[1,2] and are summarised in Table 1.

Mixed (ternary) systems

The concentration of the weaker ligand (ascorbic acid) was kept constant while that of the amino acid was varied. The two fixed concentrations (0.04 *M* and 0.2 *M*) of ascorbate ions were so chosen that at the lower value 1:1 species and at the higher value 1:2 species predominated in the simple system. In all the systems, solutions containing 5×10^{-4} *M* Cd^{2+}, 0.04 *M* ascorbic acid and requisite amount of 2.5 *M* KNO_3 (to maintain $\mu = 1.0$ *M*) were polarographed at varying concentrations of amino acids. The pK_a values of the glutamic acid, aspartic acid, threonine and tryptophan were found to be 9.42, 9.61, 9.10 and 9.65 respectively by the Albert and Serjeant's method[5]. Free ligand concentration for each system was calculated using *p*H of the solution, *pK* value and amount of the ligand.

In each case, a single well-defined wave was obtained. The plots of E_{de} vs, $\log i/(i_d - i)$ were linear with a slope of 30 ± 2 mV, showing that the two-electron reduction was reversible. The direct

Table 1—Stability Constants of Simple and Mixed Complexes

Complex species	Stability constants
[Cd(asc)]	log β_{01} 1.40
$[Cd(asc)_2]^{2-}$	log β_{02} 1.85
$[Cd(asc)_3]^{4-}$	log β_{03} 2.24
$[Cd(glu)]^{+}$	log β_1 4.30
$[Cd(glu)_2]$	log β_2 7.40
$[Cd(glu)_3]^{-}$	log β_3 10.10
$[Cd(asp)]^{+}$	log β_1 4.10
$[Cd(asp)_2]$	log β_2 7.20
$[Cd(asp)_3]^{-}$	log β_3 9.40
$[Cd(ser)]^{+}$	log β_1 4.00
$[Cd(ser)_2]$	log β_2 7.10
$[Cd(ser)_3]^{-}$	log β_3 9.30
$[Cd(threo)]^{+}$	log β_1 4.00
$[Cd(threo)_2]$	log β_2 6.70
$[Cd(threc)_3]^{-}$	log β_3 9.10
$[Cd(trypto)]^{+}$	log β_1 4.40
$[Cd(trypto)_2]$	log β_2 7.40
$[Cd(trypto)_3]^{-}$	log β_3 10.50
$[Cd(glu)(asc)]^{-}$	log β_{11} 5.20 (4.89*)
$[Cd(glu)(asc)_2]^{3-}$	log β_{12} 5.41 (5.34*)
$[Cd(glu)_2(asc)]^{2-}$	log β_{21} 7.98 (7.96*)
$[Cd(asp)(asc)]^{-}$	log β_{11} 5.00 (4.66*)
$[Cd(asp)(asc)_2]^{3-}$	log β_{12} 5.19 (5.10*)
$[Cd(asp)_2(asc)]^{2-}$	log β_{21} 7.52 (7.49*)
$[Cd(ser)(asc)]^{-}$	log β_{11} 4.99 (4.63*)
$[Cd(ser)(asc)_2]^{3-}$	log β_{12} 5.20 (5.07*)
$[Cd(ser)_2(asc)]^{2-}$	log β_{21} 7.52 (7.42*)
$[Cd(threo)(asc)]^{-}$	log β_{11} 4.80 (4.49*)
$[Cd(threo)(asc)_2]^{3-}$	log β_{12} 5.11 (5.00*)
$[Cd(threo)_2(asc)]^{2-}$	log β_{21} 7.35 (7.29*)
$[Cd(trypto)(asc)]^{-}$	log β_{11} 5.18 (5.02*)
$[Cd(trypto)(asc)_2]^{3-}$	log β_{12} 5.59 (5.47*)
$[Cd(trypto)_2(asc)]^{2-}$	log β_{21} 8.25 (8.22*)

*Statistical values calculated according to ref. 7.

proportionality of the diffusion current to the effective height of the mercury column indicated that the reduction was entirely diffusion controlled. The same results were obtained when [ascorbic acid] was kept constant at 0.2 *M*.

The overall stability constants, $\log \beta_{11}$, $\log \beta_{12}$ and $\log \beta_{21}$, were calculated by the method of Schaap and McMasters[6] and are given in Table 1.

The values of equilibrium constants (K) for various complex equilibria have been calculated. The tendency to add ascorbate by [Cd(ascorbate)] and [Cd(amino acids)] can be compared. The $\log K$ values are (0.45, 0.90), (0.45, 0.90), (0.45, 0.99), (0.45, 0.80) and (0.45, 0.78) for cadmium-ascorbate-glutamate, cadmium-ascorbate-aspartate, cadmium-ascorbate-serinate, cadmium-ascorbate-threoninate and cadmium-ascorbate-tryptophanate systems, respectively. The greater part of the difference in $\log K$ values must be attributed to entropy and electrostatic effects which would favour the formation of charged complex. The tendency of [Cd(ascorbate)] and [Cd(amino acids)] to add amino acids can also be compared. The $\log K$ values are (3.80, 3.10), (3.60, 3.10), (3.59, 3.10), (3.40, 2.70) and (3.78, 3.00) for cadmium-ascorbate-glutamate, cadmium-ascorbate-aspartate, cadmium-ascorbate-serinate, cadmium-ascorbate-threoninate and cadmium-ascorbate-tryptophanate systems, respectively. These data show that formation of the mixed complex is favoured by an amount corresponding to that predicted by the statistical considerations. The $\log K$ values for the addition of amino acids to [Cd(ascorbate)$_2$], [Cd(ascorbate) (amino acids)] and [Cd(amino acids)$_2$] are (3.56, 2.78 and 2.70) (3.34, 2.53 and 2.20), (3.35, 2.53 and 2.20), (3.26, 2.55 and 2.40) and (3.74, 3.07 and 3.10) for cadmium-ascorbate-glutamate, cadmium-ascorbate-aspartate, cadmium-ascorbate-serinate, cadmium-ascorbate-threoninate and cadmium-ascorbate-tryptophanate systems, respectively. These values show that the addition of an amino acid to [Cd(ascorbate)$_2$] is preferred in comparison to its addition to [Cd(ascorbate) (amino acids)] and [Cd(amino acids)$_2$]. In a similar way the $\log K$ values for the addition of ascorbate to [Cd(ascorbate)$_2$] and [Cd(ascorbate) (amino acids)] and [Cd(amino acids)$_2$ are (0.39, 0.21 and 0.58) (0.39, 0.19 and 0.32) (0.39, 0.21 and 0.42) (0.39, 0.31 and 0.65) and (0.39, 0.41 and 0.85) for all the systems, respectively, indicating that the addition of ascorbate ion to [Cd(amino acids)$_2$] is preferred as compared to its addition to [Cd(ascorbate) (amino acids)] and [Cd(ascorbate)$_2$]. The low $\log K$ values in the case of addition of ascorbate ion to [Cd(ascorbate) (amino acids)] and [Cd(ascorbate)$_2$] may be due to repulsion of the like charges in ascorbate.

The formation of mixed-ligand complexes may easily be confirmed on the basis of statistical considerations using Eqs (1)-(3) as proposed by Watters and Dewitt[7],

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

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

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

The values of stability constants so obtained from the above equations are given in parentheses along with the experimental values (Table 1).

For comparing the stabilities of simple and mixed complexes, it is convenient to measure the mixing constants

$$K_M = \beta_{11} / \sqrt{(\beta_{02}\beta_{20})}$$

and stabilization constants,

$$\log K_s = \log K_M - \log 2.$$

The $\log K_M$ values are 0.575, 0.475, 0.515, 0.525 and 0.555 and the $\log K_s$ values are 0.274, 0.150, 0.214, 0.224 and 0.254 for cadmium-ascorbate-glutamate, cadmium-ascorbate-aspartate, cadmium-ascorbate-serinate, cadmium-ascorbate-threoninate and cadmium-ascorbate-tryptophanate systems, respectively. The positive values of mixing constants and stabilization constants show that the ternary complexes are more stable than the binary complexes.

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