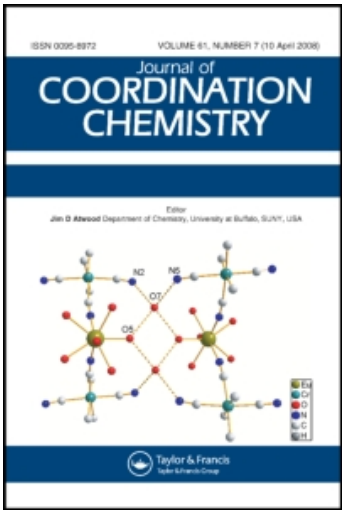


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# Complex Formation Between Cadmium(II) and Aspartate and Glutamate

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# COMPLEX FORMATION BETWEEN CADMIUM(II) AND ASPARTATE AND GLUTAMATE

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The behaviour of aspartate and glutamate as ligands towards cadmium(II) has been studied at 25°C in 1.00 M $NaClO_4$ by measuring the electromotive force of galvanic cells containing cadmium amalgam and glass electrodes. The experimental data of the cadmium(II)–aspartate system can be explained by assuming the existence of the species CdL. $CdHL^+$, $CdH_2L^{2+}$, $CdL_2^{2-}$, $CdH_2L_2$, $CdH_4L_2^{2+}$, $CdL_3^{4-}$, $CdHL_3^{3-}$ and $CdH_2L_3^{2-}$, while the data obtained for the cadmium(II)-glutamate system can be accounted for by CdL, $CdHL^+$, $CdH_2L^{2+}$, $CdL_2^{2-}$, $CdHL_2^-$, $CdH_2L_2$, $CdH_4L_2^{2+}$, $CdL_3^{4-}$, $CdHL_3^{3-}$ and $CdH_3L_3^-$, where in all cases L indicates the ligand. The stability constants have been determined. The protonation constants of glutamate were determined under the same experimental conditions, by using a $H_2$ electrode. Good agreement between experimental and calculated values supports the validity of the model.

**Keywords:** Cadmium(II), aspartic acid, glutamic acid, complexes, stability constants

## INTRODUCTION

The presence of heavy metals in soil, plants, waters, food and in living organisms represents a widely studied subject from different points of view. Cadmium is one of the most toxic cations. The yield and uptake of cadmium, lead and zinc by wheat grown in a soil polluted with heavy metals,[1] cadmium-induced ovarian toxicity in some animals[2] and the effect of cadmium-metallothionein on renal organic ion transport[3] have been recently studied, as examples. Other authors[4,5] considered the toxicity of cadmium in the marine enviroment to be strongly dependent on the equilibria in which cadmium(II) participates; that is a function of the organic and inorganic ligands present in the natural medium. Thus they studied cadmium(II) complexes of aminoacids in seawater conditions. By taking into account that aminoacids are present in living organisms, it is most probable that they contribute to the transport of cations like cadmium(II) as complexes under suitable conditions. To explain and to study this behaviour it is necessary to know the equilibria occurring between cadmium(II) and aminoacids.

We have studied the equilibria existing between cadmium(II) and glycine[6] and serine[7]. In this paper, complex formation between cadmium(II) and aspartate and glutamate, respectively, is investigated.

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A survey of the literature[8-10] reveals only a few reports on this subject. Only the formation of CdL and $CdL_2$ is proposed to explain experimental data relative to the cadmium(II)–aspartate system. Equilibria occurring between gluatamate and cadmium(II) have been even less studied. By means of polarography and potentiometry using a glass electrode, the presence of CdL and $CdL_2$ was found.[4] Only recently the presence of CdL, $CdL_2$ and $CdL_3$ was proposed and the relative stability constants reported.[11]

We decided to investigate the cadmium(II)–aspartate and cadmium(II)–glutamate systems over a wide range of reagent concentrations, because all previous studies were performed over a limited range and because by similarly studying complex formation between cadmium(II) and glycine and serine, we found formation of $CdL_3$ and of protonated species as well. As both aspartic and glutamic acids are terdentate ligands, they have the potential of a number of modes of attachment to cadmium(II) because of the presence of the carboxylic group in the side chain. This increases the possibility of formation of protonated species as well. For this purpose it was decided to study both systems in constant ionic medium[12] (1.00 M $NaClO_4$) by e.m.f. measurements of cells containing glass and cadmium amalgam electrodes at 25°C. It was necessary to determine the protonation constants of glutamate these not being known under the selected experimental conditions.



## EXPERIMENTAL

### *Methods*

All test solutions (S) were prepared by adding an excess of $NaClO_4$ with respect to the reagents, as according to Biedermann and Sillèn,[12] and thus their general composition was the following: $B$ M in Cd(II); $H$ M in $H^+$; $A$ M in L; (1-2 $B$-$H$) M in $Na^+$; 1.00 M in $ClO_4^-$, where $B$ and $A$ indicate the total concentration of cadmium(II) and the ligand (aspartate or glutamate), respectively, and $H$ represents the analytical excess of hydrogen ions. As the ionic medium concentration was high with respect to that of the reagents, activity coefficients could be considered to remain constant[12] and activities could be replaced by concentrations in all calculations. At 25.00 ± 0.05°C, the e.m.f. of the galvanic cells (*I*) and (*II*)

$$(-)\,\mathrm{Cd(Hg)/Solution\ S/R.E.}\,(+) \qquad (I)$$

$$(-)\,\mathrm{R.E./Solution\ S/G.E.}\,(+) \qquad (II)$$

was measured. Cd(Hg), R.E. and G.E. represent the cadmium amalgam, reference and glass electrodes, respectively. At 25°C and in mV units, the e.m.f. of cells (*I*) and (*II*) can be expressed as a function of $b$ (free concentration of cadmium(II) and $h$ (free concentration of $H^+$) as follows:

$$E_{\mathrm{I}} = E^{\circ}_{\mathrm{I}} - 29.58 \log b - E_{\mathrm{j}}$$

$$E_{\mathrm{II}} = E^{\circ}_{\mathrm{II}} + 59.16 \log h + E_{\mathrm{j}}$$

$E^{\circ}_{\mathrm{I}}$ and $E^{\circ}_{\mathrm{II}}$ are two constants determined in the first part of each measurement in the absence of the ligands, where $B = b$ and $H = h$. $E_{\mathrm{j}}$ represents the liquid junction

potential which, under the selected experimental conditions, is equal to $-62$ h. For each measurement $B$ and $H$ were kept constant, while $A$ and consequently $-\log h$ increased gradually. Titrations were interrupted at $-\log h \leqslant 9$. The values of $b$ and $h$ for each experimental point were obtained by a procedure similar to that described previously.[13]

*Materials and analysis*

Cadmium(II) perchlorate, perchloric acid, sodium hydroxide, sodium perchlorate and cadmium amalgam (~0.01% weight) were prepared and analysed as described.[14] Diluted amalgam gave stable $E_1$ values to $B = 5 \times 10^{-5}$ M and $H =$ 0.100 M. L-Aspartic and L-glutamic acids (C Erba RP, p.a. reagents) were recrystallized twice from doubly-distilled water and then dried at 110°C. Samples of recrystallized and dried acids were analysed by thermogravimetric analysis. All test solutions were freed from $O_2$ by bubbling purified $N_2$ through them,[14] and the apparatus used was similar to that described earlier.[14]



## RESULTS AND DISCUSSION

Several series of e.m.f. measurements have been carried out at different $H$(0.025; 0.035; 0.050; 0.070 and 0.100 M) and $B$ (0.06; 0.12; 0.50; 1.00; 2.00 $\times 10^{-3}$ M). We could calculate the function $\eta$ ( $= \log (B/b)$), because the e.m.f. measurements of cell ($I$) gave $b$ and $B$ was known analytically. Most of the obtained $\eta$ values are plotted in Figures 1 and 2 for aspartate and glutamate, respectively, as a function of $-\log h$. It can be seen that points at the same $H$, but at different $B$ fall on the same curve. Thus $\eta$ is not a function of $B$ and therefore polynuclear species can be neglected. According to this evidence the complexes formed can be indicated as $MH_pL_r$, with the relative stability constant $\beta_{1,p,r}$, where $p \geq 0$ and $r \geq 1$. To find the prevailing values of $p$ and $r$ and the corresponding values of $\beta_{1,p,r}$, it was necessary to know the free concentration of the ligand, $a$.

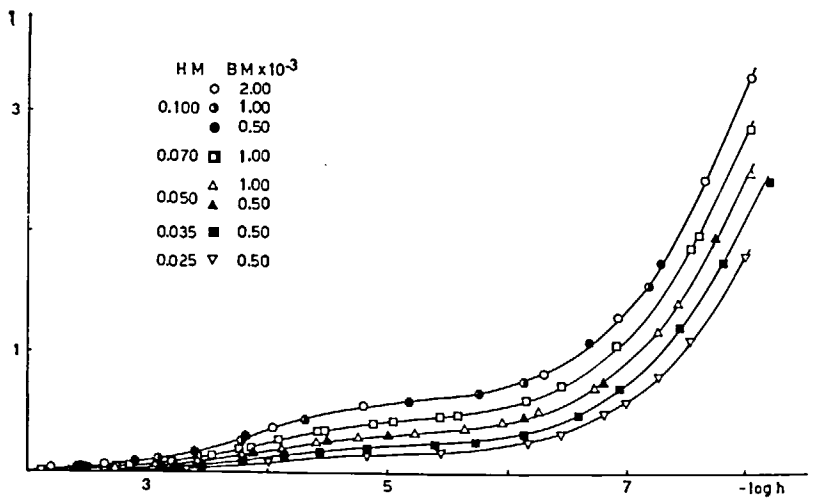


FIGURE 1 Most of the experimental data for the cadmium(II)–aspartate system in the form $\eta(-\log h)_{B,H}$. Curves are calculated by using the values of Table I.

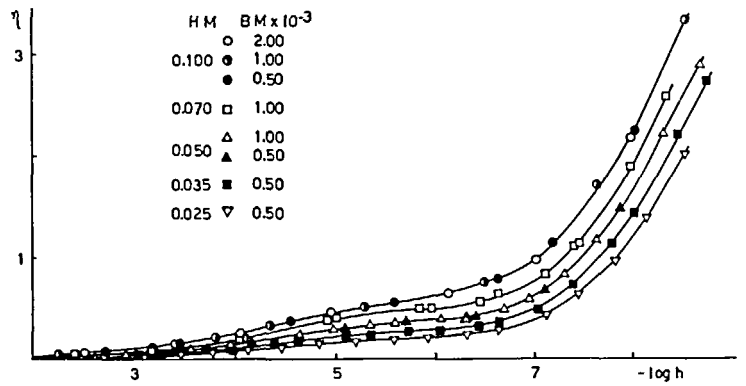


FIGURE 2 Most of the experimental data for the cadmium(II)-glutamate system in the form $\eta(-\log h)_{B,H}$. Curves are calculated by using the values of Table II.



For each point, the $a$ value could be calculated from the mass balance of $H$, by taking into account the mass action low.

$$H = h + k_1 ha + 2k_1k_2h^2a + 3\,k_1k_2k_3h^3a + \Sigma_p\Sigma_r p\beta_{1,p,r}bh^pa^r \qquad (1)$$

In (*1*) and in the following ones, hydrolytic species of cadmium(II) were neglected on the basis of hydrolysis constants found by Biedermann and Ciavatta[15] and of the values of $b$ and $h$ obtained from $E_I$ and $E_{II}$. The terms $k_1$, $k_2$ and $k_3$ are the protonation constants of aspartate and glutamate. The $k_n$ values for aspartate were determined in another work[16] under the same experimental conditions and then we found $\log k_1 = 9.625 \pm 0.01$; $\log k_1k_2 = 13.31 \pm 0.02$; $\log k_1k_2k_3 = 15.42 \pm 0.03$. The protonation constants of glutamate were determined as below described. Both for aspartate and glutamate, first approximate values of $a$ could be calculated from (*1*), by neglecting its last term, because for all points $B \leqslant 0.02\,H$. The loss of accuracy was not relevant, because first approximation and refined values of $\log a$ agreed within $\pm 0.02$. By knowing $a$, the dependence of $\eta$ on $a$ could be studied. Figures 3 and 4 show plots $\eta$ *versus* $a$ for some points in the case of aspartate and glutamate, respectively. Both figures show that $\eta$ is an increasing function of $H$, because points obtained at different $H$ fall on different curves, thus $p \geq 0$. To find the prevailing values of $p$ and $r$ of the species $MH_pL_r$ and the corresponding $\beta_{1,p,r}$ values, different approaches, similar to those described in previous papers,[7] were carried out.

At first, species prevailing in the range $4 \leqslant -\log h \leqslant 7.5$ were found with their stability constants, and by subtracting their contributions from $B$ at higher $-\log h$, other species were found. It was interesting to find the presence of the species $CdH_2L$ and $CdH_4L_2$ and to calculate their stability constants for aspartate and for glutamate. By means of such a procedure the experimental data could be accounted for of presence of the species CdL, $CdHL^+$, $CdH_2L^{2+}$, $CdL_2^{2-}$, $CdHL_2^-$, $CdH_2L_2$, $CdH_4L_2^{2+}$, $CdL_3^{4-}$, $CdHL^{3-}$, and $CdH_2L_3^{2-}$ for aspartate and CdL, $CdHL^+$, $CdH_2L^{2+}$, $CdL_2^{2-}$, $CdHL_2^-$, $CdH_2L_2$, $CdH_4L_2^{2+}$, $CdL_3^{4-}$, $CdHL_3^{3-}$, and $CdH_3L_3^-$ for glutamate. The values obtained for the stability constants of the species found were considered first approximation data. The improvement of $\beta_{1,p,r}$ values was carried out by means of an iterative procedure of successive approxima-

tions. In the meantime, refined values of $a$ were also calculated by introducing the values of found $\beta_{1,p,r}$ in (*1*). First approximation and refined values of log $a$ differ by 0.03 or less.

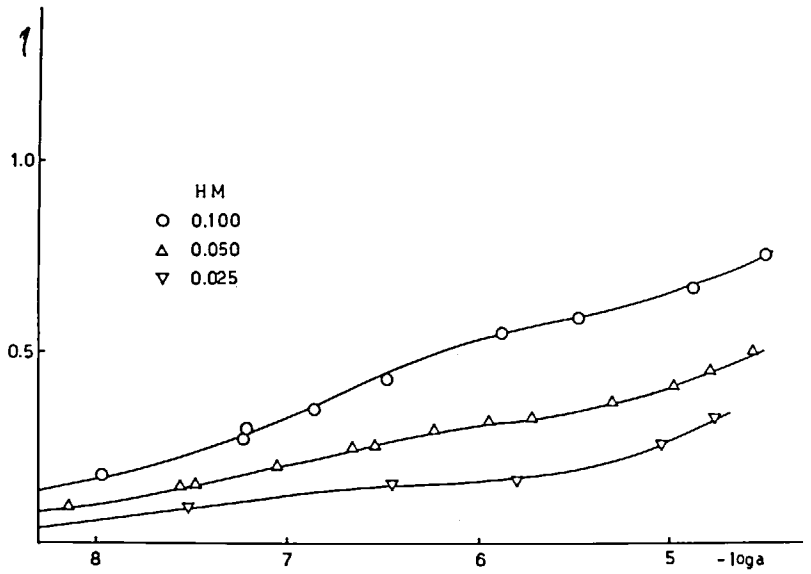


FIGURE 3 Some experimental data obtained for the cadmium(II)–aspartate system at different $H$ values, reported in the form $\eta(-\log a)_{B,H}$. Curves are calculated by using the values of Table I.

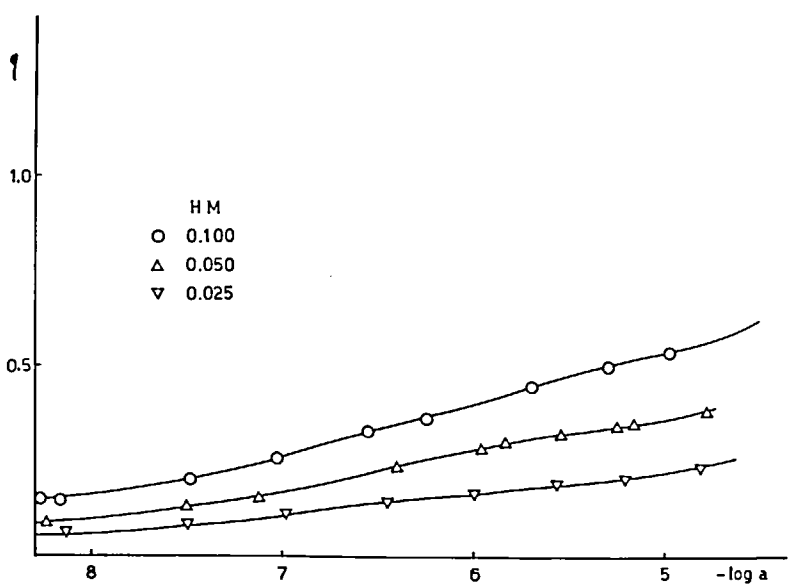


FIGURE 4 Some experimental data obtained for the cadmium(II)-glutamate system at different $H$ values, reported in the form $\eta(-\log a)_{B,H}$. Curves are calculated by using the values of Table II.

TABLE I

The system cadmium(II)–aspartate; values of log $\beta_{1,p,r}$.

| Species | Proposed value |
|---|---|
| CdL | 4.54 ± 0.02 |
| CdHL | 10.80 ± 0.02 |
| $CdH_2L$ | 13.70 ± 0.05 |
| $CdL_2$ | 7.85 ± 0.04 |
| $CdHL_2$ | 14.71 ± 0.04 |
| $CdH_2L_2$ | 21.45 ± 0.03 |
| $CdH_4L_2$ | 28.0 ± 0.1 |
| $CdL_3$ | 11.00 ± 0.05 |
| $CdHL_3$ | 18.04 ± 0.04 |
| $CdH_2L_3$ | 25.15 ± 0.05 |

TABLE II

The system cadmium(II)–glutamate; values of log $\beta_{1,p,r}$.

| Species | Proposed value |
|---|---|
| CdL | 4.02 ± 0.03 |
| CdHL | 10.85 ± 0.02 |
| $CdH_2L$ | 14.40 ± 0.05 |
| $CdL_2$ | 6.97 ± 0.04 |
| $CdHL_2$ | 13.59 ± 0.04 |
| $CdH_2L_2$ | 20.27 ± 0.03 |
| $CdH_4L_2$ | 28.83 ± 0.10 |
| $CdL_3$ | 8.83 ± 0.05 |
| $CdHL_3$ | 17.14 ± 0.04 |
| $CdH_2L_3$ | 31.62 ± 0.05 |



To prove the accuracy of the procedure and to verify that the experimental data were well explained by the proposed species with their appropriate stability constants, the experimental data $b$, $h$, $B$, $H$ together with $k_1$, $k_2$ and $k_3$ were introduced in a computer program, ECORM.[18] By means of this treatment we have derived the refined $\beta_{1,p,r}$ values collected in Tables I and II for aspartate and glutamate, respectively. They agree well with those found by means of the procedures described above.

The protonation constants of glutamate ($L^{2-}$) relative to the equilibria

$$nH^+ + L^{2-} \leftrightarrow H_nL^{+n-2}$$

are defined by the relationship

$$[H_nL] = k_n\, h[H_{n-1}L] \qquad \text{(charges omitted)}$$

where n can be 1, 2 or 3. To determine the values of $k_n$, the e.m.f. of the galvanic cell (*III*)

$$(-)Pt,H_2/\text{Solution T}/\text{R.E}(+) \qquad (III)$$

was measured at 25°C and in 1.00 M $NaClO_4$, as a function of $H$ ($0 \leqslant H \leqslant 0.1$ M) and $A$ ($5 \times 10^{-3} \leqslant A \leqslant 0.02$ M). The values $\log k_1 = 9.52 \pm 0.01$; $\log k_1k_2 = 13.69 \pm 0.02$; $\log k_1k_2k_3 = 16.00 \pm 0.03$ were obtained, where the limits of error correspond to the maximum shift possible between the normalized curve[19] and experimental points for which agreement was still acceptable.

The main results of this work represent the prevailing equilibria between cadmium(II) and aspartate or glutamate at 25°C and in 1.00 M $NaClO_4$ over a wide range of concentration of reagents. This investigation has shown the presence of mixed complexes, some protonated, the presence of $CdL_3$ and the absence of polynuclear species in all cases. In the case of aspartate, Simões Gonçalves and Correia Dos Santos[5] tried to consider the existence of $CdL_3$ or of CdL(OH) to explain their experimental data, but both species were rejected because they did not improve results statistically. According to the same authors, glutamic acid gave similar species so that for this ligand the complex $CdL_3$ was also rejected. Such results depend on the limited ratio studied (1 : 1 or similar) between cation and aspartate or glutamate.



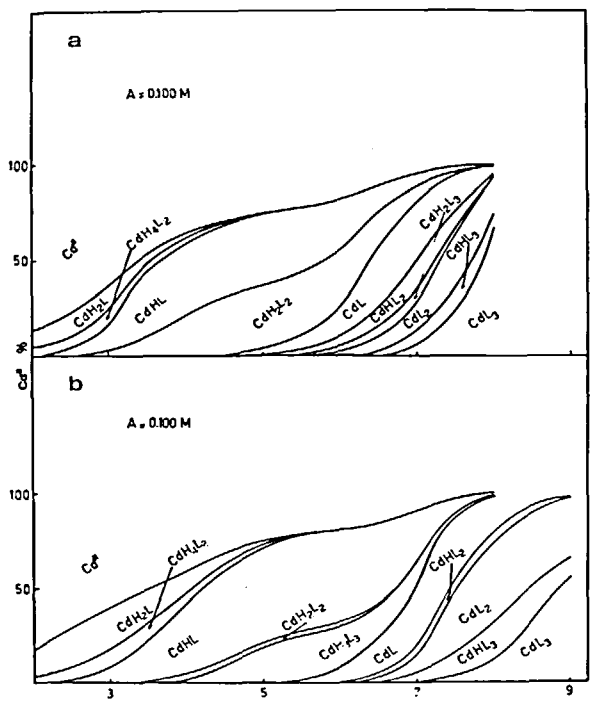


FIGURE 5 Distribution of complexes depending on $-\log h$, at $A = 0.100$ M for the systems cadmium(II)-aspartate (a) and cadmium(II)-glutamate (b). Curves are calculated for $B = 0.5 \times 10^{-3}$ M. Curves calculated for all values of $B$ coincide.

The values of the equilibrium constants found in this work for the complexes CdL and $CdL_2$ are not comparable with corresponding values in the literature, because of the very different experimental conditions used. The values of Table I and Table II were used to calculate the distribution curves of the found complexes as a function of $-\log h$, for cadmium(II)-aspartate and for cadmium(II)-glutamate, respectively, as shown in Figure 5. As expected, at low $-\log h$, the species with high $p/r$ ratio prevail.

In the range $2 \leqslant -\log h \leqslant 3$, the species $CdH_2L$ reaches in both cases a maximum ($\sim 15\%$ for aspartate and $\sim 20\%$ for glutamate). The amount of $CdH_4L_2$ is 5–10% in both cases and it decreases with decreasing $A$. It is remarkable that for aspartate the highest quantities of CdL and $CdL_2$ are $\sim 30\%$ and $\sim 25\%$, respectively, of the total cadmium(II), whereas at $-\log h \sim 8$, 65% of the cadmium(II) is present as $CdL_3$. For glutamate, the highest quantities of CdL, $CdL_2$ and $CdL_3$ are little different. The first reaches $\sim 30\%$, the second $\sim 35\%$, while the last reaches a maximum at $-\log h \sim 9$ ($\sim 50\%$).

On the other hand, $CdH_pL$ and $CdH_{p'}L_2$ are present in significant quantity over the whole $-\log h$ range investigated. In the case of aspartate, CdHL and $CdH_2L_2$ represent some 75% of the total cadmium(II) at $-\log h \sim 5$ and $\sim 60\%$ of total cadmium(II) at $-\log h \sim 6$. At $-\log h \sim 7$, $CdHL_3$ ($\sim 3\%$), $CdHL_2$ ($\sim 10\%$), $CdH_2L_2$ ($\sim 7\%$) and CdHL ($\sim 5\%$) are also present. In the case of glutamate, $CdH_2L_2$ is present in very small amounts ($\sim 3\%$), but CdHL, $CdH_3L_3$ and $CdHL_3$ predominate over a wide $-\log h$ range. The longer side chain of glutamate and, as a consequence, the more probable protonation of the carboxylic group remote from the amine group can explain these results. Protonated species exist in the case of glutamate at higher $-\log h$ than aspartate. The complex CdHL reaches the *ca* 50% of total cadmium(II) at $-\log h \sim 6$, $CdH_3L_3$ is about 20% at the same $-\log h$, and $CdHL_3$ is still present ($\sim 20\%$) at $-\log h = 8$

TABLE III

Comparison between glycinate, serinate, aspartate and glutamate as ligands towards cadmium(II). Values of $\log \beta_{1,p,r}$ are listed.[a]

| Species | Glycinate | Serinate | Aspartate | Glutamate |
|---|---|---|---|---|
| CdL | 4.36 | 4.33 | 4.54 | 4.02 |
| CdHL | 10.52 | 10.45 | 10.88 | 10.85 |
| $CdH_2L$ | | | 13.70 | 14.40 |
| $CdL_2$ | 7.99 | 8.19 | 7.85 | 6.97 |
| $CdHL_2$ | | | 14.71 | 13.59 |
| $CdH_2L_2$ | | 20.56 | 21.45 | 20.27 |
| $CdH_4L_2$ | | | 28.0 | 28.83 |
| $CdL_3$ | 10.13 | 10.6 | 11.0 | 8.83 |
| $CdHL_3$ | | 18.2 | 18.04 | 17.14 |
| $CdH_2L_3$ | | 24.77 | 25.15 | |
| $CdH_3L_3$ | | | | 31.62 |

[a] Equilibria for cadmium(II)–serinate were studied in 3.00 M $NaClO_4$.

The amounts of the species with high $r$ decreases with decreasing $A$, as expected. From a comparison of the $\log \beta_{1,p,r}$ values obtained for aspartate and glutamate, it can be concluded that the former behaves as a stronger ligand than the latter towards cadmium(II). This consideration is more evident for the complexes formed without proton participation. The species $CdL_3$ is much more stable in the case of aspartate than in the case of glutamate. A greater chelating effect can be attributed to aspartate to justify the higher stability of its complexes with respect to those formed by glutamate. In Table III the behaviour of aspartate and glutamate towards cadmium(II) is compared with that of glycinate and serinate. All four ligands are able to form CdL, $CdL_2$ and $CdL_3$. In addition, glycinate forms only one protonated species

(CdHL), while serinate forms CdHL, $CdH_2L_2$, $CdHL_3$ and $CdH_2L_3$. Aspartate and glutamate are able to form even more protonated complexes, because of the additional carboxylic group present in the side chain. The values of the stability constants obtained for aspartate, glycinate and serinate are very similar, while those of glutamate are generally smaller. Probably the presence of the $-OH$ group in serinate and the different length of the side chain of the four ligands play important roles in the formation of complexes with cadmium(II). It seems reasonable to suppose that the long chain of glutamate involves steric difficulties in introducing three ligands per cadmium(II). This hypothesis agrees with the increasing difference between stability constants on going from CdL to $CdL_3$.

The higher stability of $CdL_3$ found for aspartate and serinate with respect to glycinate can be explained by supposing that the presence of $-OH$ (serinate) and $-COO^-$ (aspartate) can contribute to an increase of stability of the corresponding complexes. Finally, it is evident that only aspartate and glutamate can form $CdH_2L$ and $CdH_4L_2$. The formation of species such as $CdH_{p''}L_3$ with $p'' > 3$ could be possible, but they must exist at high $H$ and $A$. Unfortunately, the slight solubility of both aspartic and glutamic acids did not allow us to test solutions where the presence of such species could be appreciable.



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