# STUDY OF THE MIXED COORDINATED SYSTEMS Cu(II)–VALINATE ION–GLYCINATE ION AND Cu(II)–VALINATE ION–LEUCINATE ION

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The mixed ligand ternary systems Cu(II)–valinate ion–glycinate ion and Cu(II)–valinate ion–leucinate ion have been studied polarographically at 25 ± 0.1 °C and at ionic strength 1.0 mol $l^{-1}$, adjusted with sodium perchlorate. The formation of the mixed complexes [Cu(Val$^-$)(Gly$^-$)] and [Cu(Val$^-$)(Leu$^-$)] have been verified, with stability constans $\beta_{11} = (4.6 \pm 0.2) \cdot 10^{15}$ and $\beta_{11} = (7.2 \pm 0.3) \cdot 10^{15}$, respectively.

One of the most interesting procedures currently followed to investigate the structures and functions of complex macromolecules is to examine simpler molecules that present similar properties to those characteristics of the macromolecules. As the model compounds are normally easier to study, the information gained can be extrapolated to the macromolecules.

Freeman[1] has shown the usefulness of the information obtained from a study of some simple complexes in understanding the structure of the active site of carboxypeptidase.

Likewise, diverse observations have led to the study of the formation of metal-ion complexes of low molecular weight since this is the way in which the metal ions are mobilized during prolonged periods of total parenteral nutrition. The reliability of the stability constants values of simple and mixed complexes with amino acids is important, since they represent the main form of administration in the nutritive mixture or the form of excretion. Thus, the reinvestigation of the coordinated system Zn(II)–cysteinate–hystidinate[2] has led to a reduction of the initial estimation of the daily dosage of zinc from 38 mg to 32 mg in some nutritive mixtures studied.

The system Cu(II)–valinate ion–glycinate ion has received certain attention[3-6], and diverse methods have been applied in its study. A great part of the evident dispersion of the results obtained, $\beta_{11} = (1.15 - 10) \cdot 10^{15}$, perhaps can be attributed to this fact.

No data for the Cu(II)–valinate ion–leucinate ion system were found in literature.

## TIIEORETICAL

As the cupric ion forms with the ligands L-valinate ($Val^-$), glycinate ($Gly^-$) and L-leucinate ($Leu^-$) ions (as the symbols Val, Gly, Leu are reserved for unionized amino acids, charges are included into the abbreviation) the parent complexes with one or two ligands, it can be expected that the Schaap and McMasters' $F_{00}$ function[7] presents the following development:

$$F_{00} = \{1 + \beta_{01}[Y^-] + \beta_{02}[Y^-]^2\} + \{\beta_{10} + \beta_{11}[Y^-]\}[X^-] + \{\beta_{20}\}[X^-]^2 . \qquad (1)$$

If the ligand $Y^-$ concentration is maintained constant, the terms in brackets are also constants and the $F_{00}$ and $F_{10}$ are:

$$F_{00} = A + B[X^-] + C[X^-]^2, \qquad (2)$$

$$F_{10} = (F_{00} - A) / [X^-] = B + C[X^-]. \qquad (3)$$

Thus, the $C$ values will coincide with $\beta_{20}$, and those for $B$ will result in the stability constant $\beta_{11}$ determination, if $\beta_{10}$ is known.

## EXPERIMENTAL

Each of the $i$–$E$ curves was plotted with a Metrohm E506 polarograph with an E505 polarographic stand, equipped with thermostated cell (25 ± 0.1 °C).

Metrohm EA285 platinum electrode, Ingold 303 NS saturated calomel reference electrode and DME ($\tau$ = 3 s) were used. Ionic strength was adjusted to 1.0 mol $l^{-1}$ by the addition of sodium perchlorate.

Cupric perchlorate was prepared from cupric oxide and perchloric acid (both Merck). Glycine (Merck), and L-valine and L-leucine (Sigma). Chemically treated mercury was distilled three times under reduced pressure before use. All the reagents used were of a.r. grade.

## RESULTS AND DISCUSSION

The experiments were carried out maintaining constant the total concentration of one amino acid, and the pH by the addition of diluted NaOH or $HClO_4$ solution. Suitable volume corrections were made for every solution.

The dissociation constants of the amino acids, and the stability constants of the parent complexes obtained under the same experimental conditions are shown in Table I.

The polarograms show good symmetry and regular outline. The plots of log $[(\bar{i}_d - \bar{i})/\bar{i}]$ vs $-E$ indicate that in the presence of ligands discharge takes place in a two-electron and reversible process, allowing direct determination of reversible half-wave potentials, $E_{1/2}^r$ .

TABLE I
Dissociation constants of the amino acids and stability constants of the parent complexes with Cu(II)

| Amino acid | $K_{a1}$ | $K_{a2}$ | Ref. | $\beta_{10}$ | $\beta_{20}$ | Ref. |
|---|---|---|---|---|---|---|
| Gly | $10^{-2.36}$ | $10^{-9.56}$ | 8 | $1.8 . 10^{8}$ | $1.7 . 10^{15}$ | 11 |
| Val | $10^{-2.35}$ | $10^{-9.62}$ | 9 | $1.2 . 10^{8}$ | $1.8 . 10^{15}$ | 12 |
| Leu | $10^{-2.37}$ | $10^{-9.62}$ | 10 | $1.8 . 10^{8}$ | $3.6 . 10^{15}$ | 12 |

*Coordinated System Cu(II)–L-Valinate Ion–Glycinate Ion*

The polarograms were recorded under the following conditions: $c(Cu(ClO_4)_2) = 1 . 10^{-5}$ mol $l^{-1}$, at pH 2.9 in the abscence of ligands, and at pH 9.18 in the presence of ligands.

The total amino acid concentrations $c$ (Y) or $c$ (X) and the concentrations of their anoinic forms ($[Y^-]$ or $[X^-]$) during the experiments are:

| Set | Y | X | $c$ (Y), mol $l^{-1}$ | $[Y^-]$, mol $l^{-1}$ | $c$ (X), mol $l^{-1}$ | $[X^-]$, mol $l^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | Val | Gly | 0.02 | $5.262 . 10^{-3}$ | $(1.98 - 7.41) . 10^{-2}$ | $(0.586 - 2.16) . 10^{-2}$ |
| 2 | Gly | Val | 0.02 | $5.813 . 10^{-3}$ | $(2.47 - 6.41) . 10^{-2}$ | $(0.657 - 1.75) . 10^{-2}$ |

Figure 1 presents the plots of $F_{00}$ and $F_{10}$ functions vs concentration of the ligand indicated. The linearity of the dependence of $F_{10}$ function on $Gly^-$ concentration confirms the validity of the expression (*3*). The values obtained for $B$ and $C$ are:

| Set | $B . 10^{-13}$ | $C . 10^{-15}$ |
|---|---|---|
| 1 | 2.388 ± 0.088 | 1.49 ± 0.060 |
| 2 | 2.743 ± 0.122 | 2.32 ± 0.094 |

The $C$ values are in acceptable agreement with those obtained for the corresponding stability constants of the parent complexes $[Cu(Gly^-)_2]$ and $[Cu(Val^-)_2]$.

Substitution in the $B$ definition equation (*1*) leads to $\beta_{11} = (4.54 \pm 0.17) . 10^{15}$ and $\beta_{11} = (4.72 \pm 0.21) . 10^{15}$ which enable to propose the following average value for the stability constant of the complex $[Cu(Val^-)(Gly^-)]$: $\beta_{11} = (4.6 \pm 0.2) . 10^{15}$. This value is in

agreement with those of Petit-Ramel and Pâris[3,4], and with that obtained theoretically from the Watters' equation[13]:

$$\beta_{11} = 2\,\beta_{20}^{1/2}\,\beta_{02}^{1/2} = 2\,(1.8 \cdot 10^{15})^{1/2}\,(1.7 \cdot 10^{15})^{1/2} = 3.5 \cdot 10^{15}\,.$$

*Coordinated System Cu(II)–L-Valinate Ion–L-Leucinate Ion*

The experimental conditions were: $c(Cu(ClO_4)_2) = 1.5 \cdot 10^{-5}$ mol $l^{-1}$, at pH 3.5 in the absence of ligands, and at pH 8.82 and 8.87 in the presence of ligands. The total concentrations of the amino acids were $c(Val^-) = 0.015$ mol $l^{-1}$, $c(Leu^-) = (0.994 - 6.43) \cdot 10^{-2}$ mol $l^{-1}$, and the concentrations of their anionic forms were as follows:

| Set | pH | [Val$^-$], mol $l^{-1}$ | [Leu$^-$], mol $l^{-1}$ |
|---|---|---|---|
| 1 | 8.82 | $2.036 \cdot 10^{-3}$ | $(1.360 - 8.798) \cdot 10^{-3}$ |
| 2 | 8.87 | $2.247 \cdot 10^{-3}$ | $(1.486 - 9.709) \cdot 10^{-3}$ |

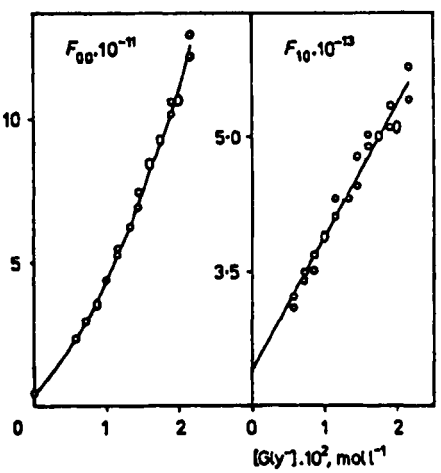


FIG. 1
Plot of the functions $F_{00}$ and $F_{10}$ vs [Gly$^-$]

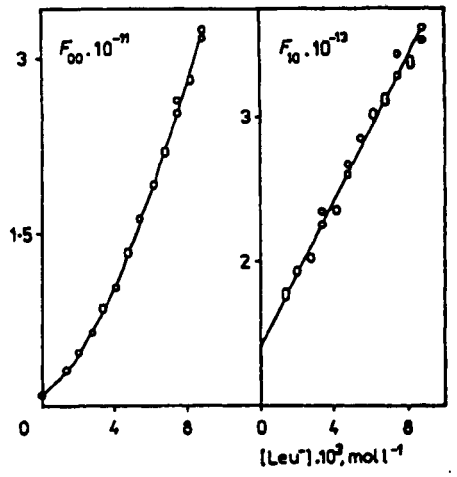


FIG. 2
Plot of the functions $F_{00}$ and $F_{10}$ vs [Leu$^-$]

Linearity of the plot of $F_{10}$ function vs L-leucinate ion concentration (Fig. 2) confirms the validity of the expression (3). From this plot the following data are obtained

| Set | $B \cdot 10^{-13}$ | $C \cdot 10^{-15}$ |
|---|---|---|
| 1 | 1.418 ± 0.032 | 2.50 ± 0.058 |
| 2 | 1.683 ± 0.054 | 2.40 ± 0.087 |

The $C$ value is also in acceptable agreement with the stability constant of the $[Cu(Leu^-)_2]$ complex.

As shown above, from the $B$ definition equation $\beta_{11} = (6.96 \pm 0.16) \cdot 10^{15}$ and $\beta_{11} = (7.49 \pm 0.24) \cdot 10^{15}$ result enabling to propose the following value for the stability constant of the complex $[Cu(Val^-)(Leu^-)]$: $\beta_{11} = (7.2 \pm 0.3) \cdot 10^{15}$. This value is in agreement with that found theoretically by applying the Watters' equation:

$$\beta_{11} = 2\,\beta_{20}^{1/2}\,\beta_{02}^{1/2} = 2\,(1.8 \cdot 10^{15})^{1/2}\,(3.6 \cdot 10^{15})^{1/2} = 5.1 \cdot 10^{15}\,.$$

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REFERENCES

1. Freeman H. C. in: *Inorganic Biochemistry* (G. E. Eichhorn, Ed.), p. 121. Elsevier, Amsterdam 1973.
2. Alemdaroglu T., Berthon G.: Bioelectrochem. Bioenerg. *8*, 49 (1981).
3. Petit-Ramel M. M., Pďris M. R.: Bull. Soc. Chim. Fr. *1968*, 2791.
4. Petit-Ramel M. M., Pďris M. R.: Bull. Soc. Chim. Fr. *1969*, 3070.
5. Lim M. C.: *Thesis*. The State University of New York at Buffalo, Buffalo, New York 1970.
6. Po I. T., Nancollas G. H.: Inorg. Chem. *11*, 2414 (1972).
7. Schaap W. B., McMasters D. L.: J. Am. Chem. Soc. *83*, 4699 (1961).
8. Molina M., Melios C. V., Jafelicci M. jr., Luchiari L. C.: Eclet. Quim. *2*, 103 (1977).
9. Ramel M. M., Pďris M. R.: Bull. Soc. Chim. Fr. *1967*, 1359.
10. Perrin D. D.: J. Chem. Soc. *1958*, 3120 and 3125.
11. Rodríguez Placeres J. C., Sanz Alaejos M. T., García Montelongo F. J.: An. Quím., B *81*, 348 (1985).
12. Sanz Alaejos M. T.: *Thesis*. University of La Laguna, Tenerife 1987.
13. Watters J. I., Dewitt R.: J. Am. Chem. Soc. *82*, 1333 (1960).

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