

Chemistry

POLAROGRAPHIC STUDY OF MIXED LIGAND COMPLEXES
In(III)-L-GLUTAMATE-L-LEUCINATE SYSTEM

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The simple and mixed-ligand complexes of L-glutamic acid and L-leucine with In(III) have been investigated by polarographic technique. The cathodic reduction of simple and mixed complexes involves three-electrons, reversible and diffusion controlled step and two complex species are formed both with L-glutamic acid and L-leucine. The overall formation constants are : $\log \beta_1 = 8.60$ and $\log \beta_2 = 17.86$ with L-glutamic acid and $\log \beta_1 = 7.40$ and $\log \beta_2 = 15.50$ with L-leucine at 30 °C. The logarithmic value of overall stability constant of mixed-ligand complex In(L-glutamate) (L-leucinate) is 17.32. High positive value of mixing constant K_m reveals that the mixed complex is more stable than the parent binary complexes.

INTRODUCTION

RECENTLY, Potentiometry has been used to study the complexes of In(III) with amino acids (Khan *et al.*, 1976; Kojima *et al.*, 1976; Sarin & Munshi, 1973; and Tiwari & Srivastava, 1973). Polarographic study of complexes of In(III) with amino acids has also been made (Kapoor & Jai Kishan, 1977; and Rangrajan *et al.*, 1977). No study has been reported on the complexation reaction of In(III) with L-glutamic acid and on the formation of mixed complexes of In(III) with amino acids. Polarographic investigation of simple and mixed complexes of In(III) with L-glutamic acid and L-leucine are being reported here.

MATERIALS AND METHODS

All chemicals used were of A. R. grade. Indium nitrate (Schuchardt Munchen, Germany) solution was prepared in 0.3M perchloric acid medium and was standardised against EDTA using PAN indicator (Welcher, 1958). The L-glutamic acid was a BDH (England) product and L-leucine was obtained from Centron Research Lab.

The pH of the solution was maintained by using CO₂-free sodium hydroxide and dilute perchloric acid solution. The ionic strength of all the experimental solutions was kept constant at 0.1 by adding appropriate amounts of sodium perchlorate.

Polarograms were obtained with a manual Toshniwal polarograph in conjunction with a PYE (Cambridge, England) galvanometer. The measurements were made at 30 ± 0.1 °C using Ultra thermostat (Type E-149, Hungary). The pH values of test solutions were measured with the help of a NIG 333 digital pH meter. All the test solutions were degassed with pure nitrogen.

The dropping mercury electrode used in this work had the following characteristics at -0.8 V vs. S. C. E. in 0.1M sodium perchlorate solution at 38.5 cm effective mercury height :

$$m = 2.54 \text{ mg/sec.}; t = 3.21 \text{ seconds.}$$

The use of buffers was avoided because of their tendency to form complexes. They would thus have competed with other ligands during mixed complex formation studies.

The solution of L-glutamic acid was prepared in dilute perchloric acid because of its low solubility in water. Therefore, the studies at pH 3.5 were made with $1.2 \times 10^{-4}M$ In(III) only.

RESULTS AND DISCUSSION

Polarograms of solutions containing In(III) and requisite amount of sodium perchlorate (to maintain ionic strength) were recorded with varying concentrations of ligand. The concentrations of the metal ion used with L-glutamic acid and L-leucine were $1.2 \times 10^{-4}M$ and $2 \times 10^{-4}M$ respectively. The respective maximum concentrations of L-glutamic acid and L-leucine were 600 and 800 times the concentration of metal ion. The pH maintained was 3.50 ± 0.01 at ionic strength of 0.1.

In(III) gives reversible, three-electron reduction wave at pH 3.0–3.2 with a half-wave potential of -0.512 V vs. S. C. E. It can be seen from Fig. 1 that the half-wave potential shifted to more negative values as the concentration of each ligand ion was increased which indicated that In(III) formed complexes with L-glutamic acid as well as with L-leucine.

The free concentration of L-glutamate and L-leucinate ions were calculated from the pK values at 30° . The reported pK and $-\Delta H$ values of glutamic acid

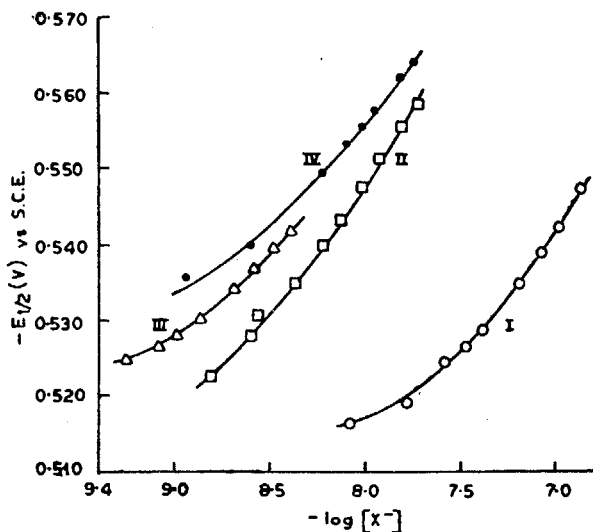


FIG. 1. Plots of $-E_{1/2}$ vs. S.C.E.

- I $-\log$ [leucinate];
- II $-\log$ [glutamate];
- III $-\log$ [glutamate] at [leucinate] = $1.39 \times 10^{-8} M$; and
- IV $-\log$ [glutamate] at [leucinate] = $4.01 \times 10^{-8} M$.

TABLE I
pK and $-\Delta H$ values of glutamic acid and leucine

| Compound | <i>pK</i> | <i>pK</i> at 25° | <i>pK</i> at 30° | $-\Delta H$ (Kcal/mole) |
|---------------|--|---------------------|---------------------|----------------------------|
| Glutamic acid | —COO ⁻ (<i>pK</i> ₁) | 2.12* | 2.11 | 0.8* |
| | —COO ⁻ (<i>pK</i> ₂) | 4.11 | 4.10 | 0.8 |
| | —NH ₂ (<i>pK</i> ₃) | 9.51 | 9.39 | 9.7 |
| Leucine | —COO ⁻ (<i>pK</i> ₁) | 2.46** | 2.46 | — |
| | —NH ₂ (<i>pK</i> ₂) | 9.67 | 9.54 | 10.9@ |

*After Nagypal *et al.* (1974).

**After Snyder and Agelici (1973).

@After Christensen *et al.* (1969).

(Nagypal *et al.*, 1974) and leucine (Christensen *et al.*, 1969; and Snyder & Angelici, 1973) at 25° are given in the Table I.

The *pK* values at 30° have been calculated from the relations:

$$\log \frac{K_{T_2}}{K_{T_1}} = pK_{T_1} - pK_{T_2} = \frac{-\Delta H}{4.576} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \dots(1)$$

The values thus obtained at 30° are also shown in the Table I. The change in *pK*₁ value due to change in temperature in the case of glutamic acid was negligible. Hence the value of *pK*₁ for leucine at 25° was used as such for calculations.

The plots of $-E$ vs. $\log \frac{i}{i_a - i}$ gave slope values of 21 ± 1 mV in all cases, in accordance with a reversible three-electron reduction. The plots of i_a vs. \sqrt{h} (corrected) gave straight lines passing through the origin, which showed that reduction waves were diffusion controlled.

Smooth curves (Fig. 1) were obtained when $-E_{1/2}$ were plotted against $-\log [X^-]$ which indicated the presence of more than one complex species in solution. Hence the DeFord and Hume method (1951) was applied to determine $F_j(X)$ functions (Figs. 2 & 3).

The following values of overall stability constants were obtained:

In(III)-L-Glutamate System :

$$\log \beta_1 = 8.60 \text{ and } \log \beta_2 = 17.86$$

In(III)-L-Leucinate System :

$$\log \beta_1 = 7.42 \text{ and } \log \beta_2 = 15.50$$

The values of stability constants for the system *In(III)-L-leucinate* agree fairly with the reported values at 24° (Khan *et al.*, 1976).

The higher values of stability constants for *In(III)-glutamate* system may be due to the tridentate nature of glutamic acid. Tridentate function of glutamic acid has been reported with Ni(II), Cd(II) and Cu(II) (Sarma, 1956) and with Co(III) (Chang *et al.*, 1960)

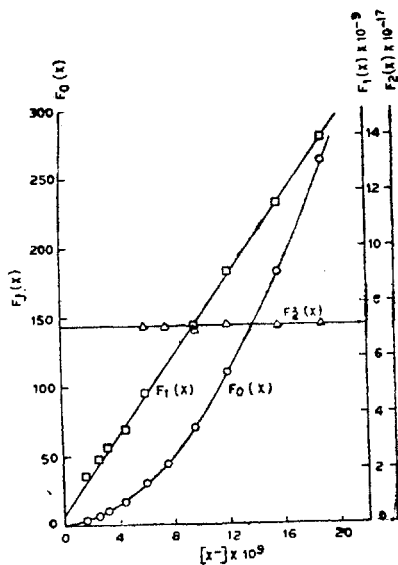


FIG. 2.

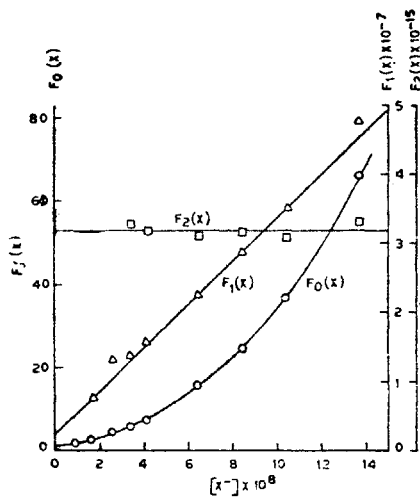


FIG. 3.

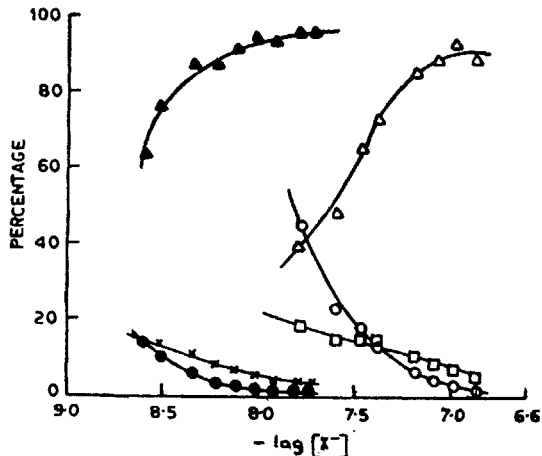
FIG. 2. Plots of $F_j(X)$ vs. [glutamate] FIG. 3. Plots of $F_j(X)$ vs. [leucinate]

FIG. 4. Plots of percentage of species vs. $-\log [X^-]$ (O), (\square) and (\triangle) represent species In^{3+} , $[\text{In}(\text{leu})_2]^{2+}$ and $[\text{In}(\text{leu})_2]^+$ vs. $-\log$ [leucinate], respectively and (\bullet), (\times) and (\blacktriangle) represent species In^{2+} , $[\text{In}(\text{glu})]^{2+}$ and $[\text{In}(\text{glu})_2]^-$ vs. $-\log$ [glutamate], respectively.

Distributions of complex species as a function of ligand concentration have been shown in the Fig. 4.

Mixed *In(III)*-*L*-glutamate-*L*-Leucinate System

Current-potential curves were obtained for solutions containing 1.2×10^{-4} *In(III)*, fixed concentration of leucinate ion and requisite amount of sodium perchlorate (to maintain $\mu = 0.1$) with different concentrations of glutamate ions

3.16 and 3.50. The at pH value of fixed concentrations of L-leucinate ion chosen at pH 3.16 and 3.50 were $1.39 \times 10^{-8}M$ and $4.01 \times 10^{-8}M$ respectively.

On increasing the concentration of glutamate ion, the half-wave potential shifted towards more negative potential at each fixed concentration of leucinate ion (Fig. 1). This shift was greater in comparison to simple In(III)-glutamate system. The results thus indicated mixed-complex formation. In the mixed system also reversible three-electron (slope 21 ± 1 mV), diffusion controlled reduction waves were obtained.

The plots (Fig. 1) of $-E_{1/2}$ vs $-\log [\text{glu}]$ at both fixed leucinate ion concentration ($1.39 \times 10^{-8}M$ and $4.01 \times 10^{-8}M$) were smooth curves, which showed the presence of more than one complex. The stability constants were evaluated using the Schaap and McMasters (1961) method. According to them, the function $F_{00}(X, Y)$ can be obtained from the relation:

$$F_{00}(\text{glu}, \text{leu}) = \text{antilog} \left[0.4343 \frac{nF}{RT} \left\{ (E_{1/2})_s - (E_{1/2})_c \right\} + \log \frac{I_s}{I_c} \right] \quad \dots(2)$$

The $F_{00}(\text{glu}, \text{leu})$ function can be expanded in the form $F_{00}(\text{glu}, \text{leu}) = \{\beta_{00} + \beta_{01} [\text{Leu}] + \beta_{02} [\text{Leu}]^2$

$$+ \{\beta_{10} + \beta_{11} [\text{Leu}]\} [\text{glu}] + \beta_{20} [\text{glu}]^2 \\ = A + B [\text{glu}] + C [\text{glu}]^2 \quad \dots(3)$$

where the quantities A , B and C are defined by eqn. (3) and are constant at each fixed value of $[\text{leu}]$.

The functions F_{10} and F_{20} are obtained from the relations:

$$F_{10} = \frac{F_{00} - A}{[\text{glu}]} \quad \dots (4) \quad \text{and} \quad F_{20} = \frac{F_{10} - B}{[\text{glu}]} \quad \dots(5)$$

The value of A was calculated from the previously determined stability constants of In(III)-leucinate species using eqn. (3). The intercepts at $[\text{glutamate}] = 0$ of the plots of F_{10} and F_{20} vs. $[\text{glutamate}]$ gave the respective values of B and C .

Following values of A , B , C and β_{11} were thus obtained:

(i) $[\text{Leucinate}] = 1.39 \times 10^{-8}M$ (Fig. 5)

$A = 1.96$ (calculated); $B = 3.6 \times 10^9$, $C = 1.29 \times 10^{18}$
($\log C = 18.11$)₂ and $\beta_{11} = 2.30 \times 10^{17}$ ($\log \beta_{11} = 17.36$)

(ii) $[\text{Leucinate}] = 4.01 \times 10^{-8}M$ (Fig. 6)

$A = 7.14$ (calculated), $B = 7.8 \times 10^9$, $C = 9.83 \times 10^{17}$

$\log C = 17.99$) and $\beta_{11} = 1.85 \times 10^{17}$ ($\log \beta_{11} = 17.27$)

Average $\log \beta_{11} = 17.32$ and $\log C = 18.06$

The stability constant β_{11} of mixed complex $[\text{In}(\text{glu})(\text{leu})]$ was calculated from the values of B .

Both the $\log C$ values given above agree fairly with the \log stability constant of the species $[\text{In}(\text{glutamate})_2]^-$.

Comparison of Stability of Mixed Complex with Binary Complexes

The stability of the mixed-ligand complex can be compared with binary complexes through the following relations:

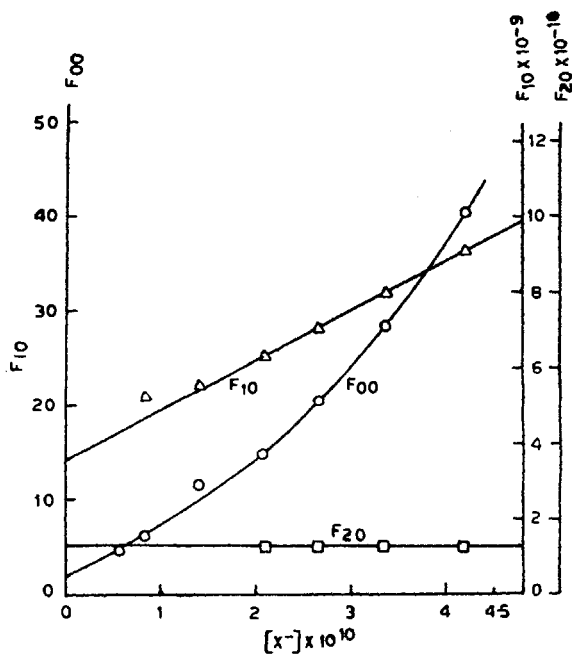


FIG. 5. Plots of F_{10} vs. [glutamate] at [leucinate] = $1.39 \times 10^{-8} \text{ M}$

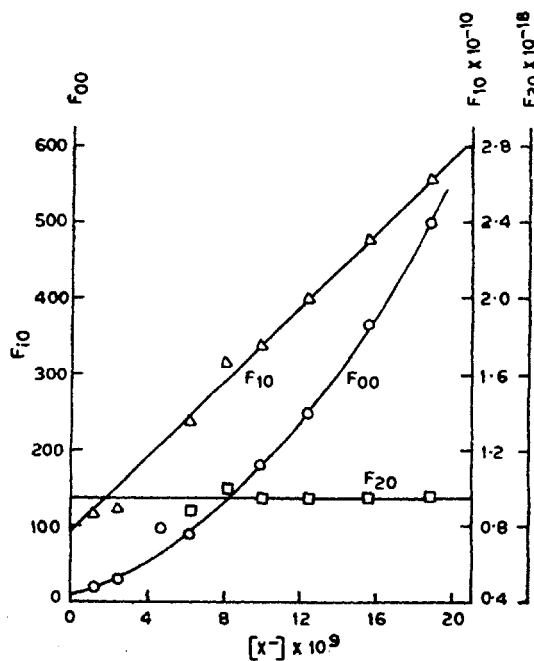


FIG. 6. Plots of F_{10} vs. [glutamate] at [leucinate] = $4.01 \times 10^{-5} \text{ M}$

$$\Delta \log K = \log \beta_{11} - \log \beta_{01} - \log \beta_{10} \quad \dots(6)$$

and

$$\log K_m = \log \beta_{11} - \frac{1}{2} \log \beta_{02} - \frac{1}{2} \log \beta_{20} \quad \dots(7)$$

The statistical values of $\Delta \log K$ and $\log K_m$ are -0.4 (Mitchell & Sigel, 1978) and 0.3 (Ting & Nancollas, 1972), respectively. The experimental values of $\Delta \log K$ and $\log K_m$ for the mixed complex $\text{In}(\text{glu})(\text{leu})$ are 1.32 and 0.64 (0.54 , when average value of $\log C$ is used in place of $\log \beta_{20}$) respectively. Higher than statistical value of $\log k_m$ has also been observed for $\text{Cu}(\text{II})$ -amino acids (Gergely *et al.*, 1975; and Nagypal *et al.*, 1974) and $\text{Ni}(\text{II})$ -amino acids (Blackburn & Jones, 1973) systems.

The high values of $\Delta \log K$ and $\log K_m$ show that the mixed ligand complex is more stable than the simple binary complexes. The high stability of the mixed ligand complex $\text{In}(\text{glu})(\text{leu})$ can be explained on statistical factors, simultaneous π -bonding between $\text{In}(\text{III})$ and glutamate and leucinate due to back donation of electrons from completely filled orbitals of $\text{In}(\text{III})$ ion and neutralisation of $+3$ charge of indium by tridentate glutamate having charge of -2 and bidentate leucinate having charge of -1 . During the study of the neutral mixed ligand complexes of $\text{In}(\text{III})$ with glutamate and methioninate or prolininate, we have also obtained values of $\log K_m$ and $\Delta \log K$ of the same order (*Unpublished data*).

It has been concluded by many workers (Bennett, 1957; Condikey, 1969; Griesser & Sigel, 1970; Marcus & Eliezer, 1969; Schaap & McMasters, 1961; and Sigel *et al.*, 1971) that when the formation of a mixed complex involves neutralisation of charge, i.e., when the mixed species is neutral while the binary species are charged, the extra stabilization is considerably larger than when no such neutralisation occurs. In addition to coulombic effects (enthalpy), such a neutralisation of charge would be expected to be accompanied by a positive entropy change due to a decreased orientation of the solvent molecules (desolvation of the charged species). Hence, neutralisation of charge may be considered an important factor in the enhanced stability of the mixed ligand complex $\text{In}(\text{glu})(\text{leu})$.

Gergely *et al.* (1975) and Ramamoorthi & Manning (1973) have observed that there is a small but essentially larger stabilization when one of the ligands contain two and the other three donor groups. This suggestion may also attribute to the stability of the mixed complex $\text{In}(\text{glu})(\text{leu})$.

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