# Polarographic study of the Composition and Stability Constants of Indium (III) and Lead (II) complexes with DL-Ornithine Hydrochloride

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THE complexation of Pb (II) and In (III) with DL-Ornithine hydrochloride have been studied polarographically at 30°C and 40°C using DeFord and Hume method. The reduction at the dropping mercury electrode has been found to be reversible and diffusion controlled. Tha plots of potential vs. concentration data at ionic strength $\mu = 0.1$M reveal the formation of 3 complexes in case of Pb(II). The stability constants of metal complexes have been calculated at 30°C and 40°C. The overall changes in thermodynamic fuctions $\Delta G$, $\Delta H$ and $\Delta S$ at 30°C are also reported.

IN view of the wide recognition of aminoacids in biological, pharmaceutical and industrial fields, the electrochemical behaviour of some important aminoacids has been reported earlier[1-6]. This paper deals with the polarographic determination of the composition and stability constants of In(III) and Pb (II) complexes with DL-Ornithine hydrochloride at 30°C and 40°C.

## EXPERIMENTAL

DL-Ornithine hydrochloride was supplied by BDH Chemicals Ltd. Poole, England and all other chemicals used were of AnalaR grade.

In (III) and Pb (II) concentration was 1mM in presence of 0.1M $NaClO_4$ and 0.002 per cent Triton-X-100. The concentration of ligand was varied from 0.02 to 0.10M in In(III) and 0.02 to 0.12M in case of Pb (II) respectively.

Toshniwal polarograph in conjunction with a thermostated H-cell was used for recording the current-voltage curves. The capillary used had the following characteristics in 0 1M $NaClO_4$ :

m = 2.953 mgm/sec, t = 3.5 sec/drop, h = 45 cm and −0.4 Volt vs. SCE.

## RESULTS AND DISCUSSIONS

The current voltage curves of In (III) and Pb (II) in the presence of different concentrations of DL-Ornithine hydrochloride are plotted at 30°C and 40°C. In each case, a single well defined cathodic wave appeared. All the plots of log $[i/(i_d - i)]$ vs. $-E_{d.e.}$ yielded straight lines and the slopes agreed with the reversibllity of the reduction. The plots $i_d$ VS $\sqrt{h}_{eff}$ was found to be linear, indicating the diffusion controlled nature of the reduction. The cathodic shift of $E_{1/2}$ coupled with decrease in diffusion current on increasing DL-Ornithine hydrochloride concentration shows the complex formation in both cases.

The curvature obtained in the plot of $-E_{1/2}$ vs. $-\log C_x$ showed the successive complex formation and hence the method of DeFord and Hume[7,8] was adopted for deriving various functions $F_j(X)$. From the experimental data (Tables I & II) the complexity functions $F_j(X)$ is set up ; The graphical extrapolation (Figs 1 to 4) reduces the polynomial equation to $\eta$—equations from which the corresponding $\beta_n$ are obtained.

log $\beta_n$ values for the complexes of Pb (II) with DL-Ornithine HCl

At 30°C log $\beta_1 = 3.0$, log $\beta_2 = 4.74$,
log $\beta_3 = 6.362$ and log $\beta_4 = 7.568$

At 40°C log $\beta_1 = 3.0$, log $\beta_2 = 4.602$,
log $\beta_3 = 6\ 204$ and log $\beta_4 = 7.568$

In case of complexes of In (III) with DL-Ornithine hydrochloride log $\beta_n$ values obtained by DeFord Hume method[7,8] were further confirmed by Mihailov's calculation method[9] by calculating Mihailov's constants a and A.

log $\beta_n$ values for the complexes of In (III) with DL-Ornithine hydrochloride :—

TABLE 1

*Half wave potentials, diffusion currents and the values of various functions $F_i(X)$ at 30°C and 40°C for complexes of In (III) with DL-Ornithine hydrochloride*

| Sl. No. | $C_x$ | —log $C_x$ | $i_d$ | | $-E_{1/2}$ | | $F_o(X)$ | | $F_1(X) \times 10^2$ | | $F_2(X) \times 10^3$ | | $F_3(X) \times 10^4$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 30°C | 40°C | 30°C | 40°C | 30°C | 40°C | 30°C | 40°C | 30°C | 40°C | 30°C | 40°C |
| 1. | 0.00 | — | 3.9 | 4.5 | 0.590 | 0.590 | — | — | — | — | — | — | — | — |
| 2. | 0.02 | 1.6989 | 3.58 | 4.1 | 0.602 | 0.600 | 4.337 | 3.344 | 1.668 | 1.172 | 5.34 | 4.86 | 15.70 | 12.3 |
| 3. | 0.04 | 1.3979 | 3.22 | 3.95 | 0.613 | 0.612 | 17.108 | 13.216 | 4.027 | 3.054 | 8.567 | 7.135 | 15.92 | 11.84 |
| 4. | 0.06 | 1.2218 | 3.32 | 3.90 | 0.622 | 0.621 | 43.765 | 36.487 | 7.627 | 5.914 | 11.71 | 9.524 | 15.85 | 11.87 |
| 5. | 0.08 | 1.0969 | 3.44 | 3.90 | 0.629 | 0.628 | 101.043 | 79.589 | 12.50 | 9.823 | 14.88 | 12.03 | 15.03 | 12.04 |
| 6. | 0.10 | 1.0000 | 3.30 | 3.85 | 0.634 | 0.633 | 187.3 | 145.65 | 18.63 | 14.465 | 18.03 | 14.26 | 15.83 | 11.86 |

TABLE II

*Half wave potentials, diffusion currents and the values of various functions $F_i(X)$ at 30°C and 40°C for the complexes of Pb (II) with DL-Ornithine hydrochloride*

| Sl. No. | $C_x$ | —log $C_x$ | $i_d$ | | $-E_{1/2}$ | | $F_o(X)$ | | $F_1(X) \times 10^3$ | | $F_2(X) \times 10^4$ | | $F_3(X) \times 10^5$ | | $F_4(X) \times 10^6$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 30°C | 40°C | 30°C | 40°C | 30°C | 40°C | 30°C | 40°C | 30°C | 40°C | 30°C | 40°C | 30°C | 30°C |
| 1. | 0.00 | — | 4.35 | 6.1 | 0.720 | 0.720 | — | — | — | — | — | — | — | — | — | — |
| 2. | 0.02 | 1.6989 | 4.10 | 5.20 | 0.774 | 0.772 | 66.94 | 55.81 | 3.297 | 2.74 | 11.49 | 8.70 | 29.92 | 23.50 | 34.62 | 37.50 |
| 3. | 0.04 | 1.3979 | 3.80 | 4.30 | 0.795 | 0.792 | 361.99 | 298.15 | 9.025 | 7.43 | 20.06 | 16.07 | 36.40 | 30,17 | 33.51 | 35.43 |
| 4. | 0.06 | 1.2218 | 3.60 | 4.10 | 0.810 | 0.808 | 1208.33 | 1026.25 | 20.12 | 17.08 | 31.87 | 26.81 | 43.95 | 38.01 | 34.91 | 36.69 |
| 5. | 0.08 | 1.0969 | 3.60 | 4.10 | 0.822 | 0.821 | 3035.19 | 3695.32 | 37.93 | 33.67 | 46.16 | 40.84 | 50.82 | 46.06 | 34.78 | 37.57 |
| 6. | 0.12 | 0.9208 | 3.60 | 4.10 | 0.840 | 0.840 | 12083.8 | 11053.85 | 100.69 | 92.11 | 83.07 | 75.92 | 66.64 | 59.93 | 34.70 | 36.61 |

| Method | 30°C | | | 40°C | | |
|---|---|---|---|---|---|---|
| | $\log \beta_1$ | $\log \beta_2$ | $\log \beta_3$ | $\log \beta_1$ | $\log \beta_2$ | $\log \beta_3$ |
| 1. DeFord & Hume | 1.778 | 3.342 | 5.199 | 1.301 | 3.380 | 5.072 |
| 2. Mihai'ov | 1.604 | 3.481 | 5.184 | 1.398 | 3.335 | 5.082 |

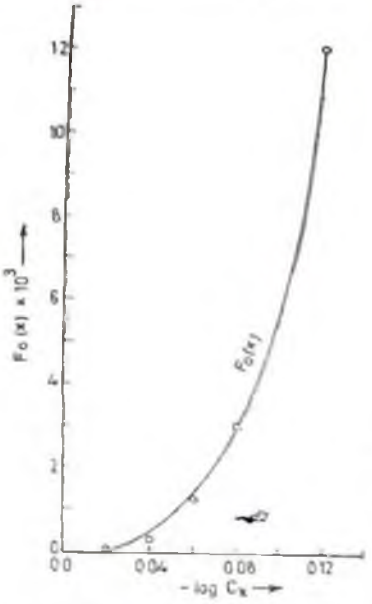



Fig 1: $F_0(x)$ for Pb (II) in DL-Ornithine hydrochloride at 30° C

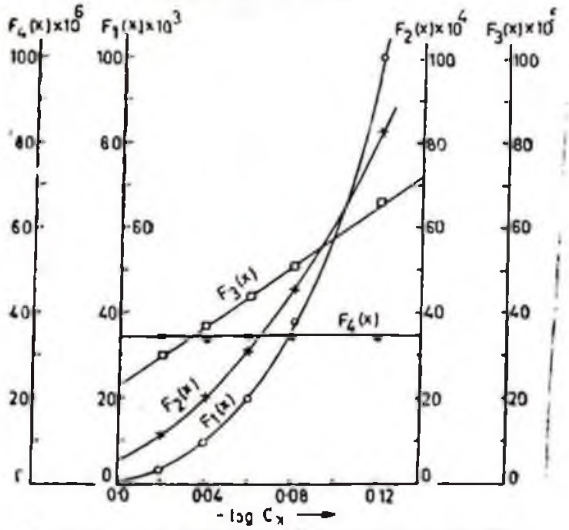



Fig 2: Values of $F_1(x)$, $F_2(x)$, $F_3(x)$ and $F_4(x)$ for Pb (II) in DL-Ornithine HCl at 30°C

## THERMODYNAMIC FUNCTIONS

The values of changes in free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$) accompanying complexation reactions have been determined at 30°C by usual methods and summarised in Table III.

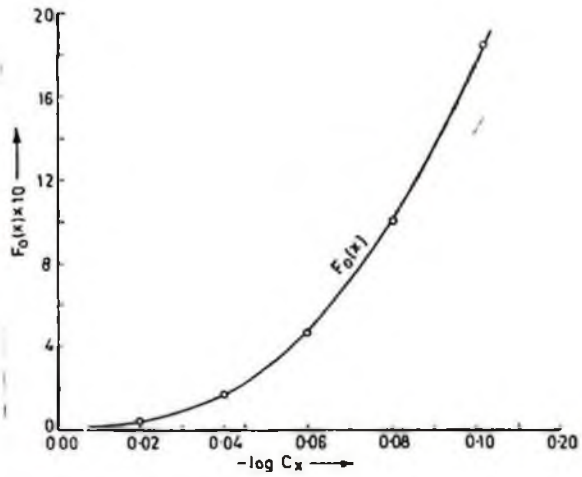



Fig.3 Value of $F_0(x)$ for In (III) in DL-Ornithine hydrocloride at 30° C

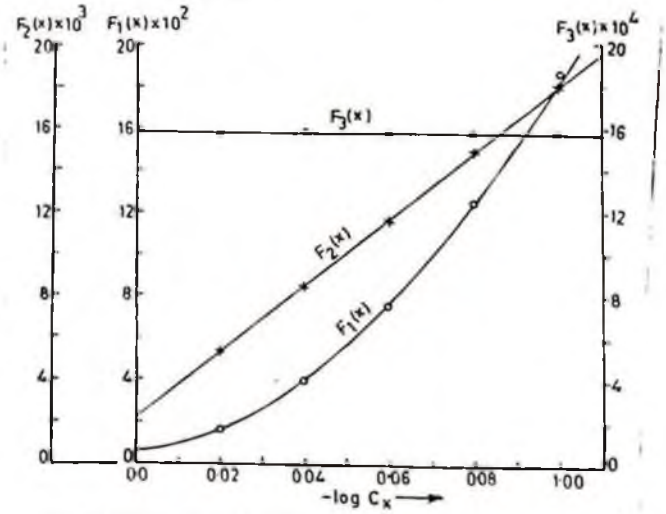



Fig 4: Values of $F_1(x)$, $F_2(x)$ and $F_3(x)$ for In (III) in DL-Ornithine HCl at 30°C

TABLE III

*Thermodynamic functions for complexes of In (III) and Pb (II) with DL-Ornithine hydrochloride at 30°C*

| Name of metal ion | Corresponding to $\beta_1$ | | | Corresponding to $\beta_2$ | | | Corresponding to $\beta_3$ | | | Corresponding to $\beta_4$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\Delta G$ kcal/ mole | $\Delta H$ kcal/ mole | $\Delta S$ cals/ mole/deg | $\Delta G$ kcal/ mole | $\Delta H$ kcal mole | $\Delta S$ cals/ mole/deg | $\Delta G$ kcal/ mole | $\Delta H$ kcal/ mole | $\Delta S$ cal/ mole/deg. | $\Delta G$ kcal/ mole | $\Delta H$ kcal/ mole | $\Delta S$ cal/ mole/deg |
| In (III) | −2.44 | −20.53 | −5.97 | −4.59 | 1.63 | 20.53 | −7.15 | −5.46 | 5.48 | — | — | — |
| Pb(II) | −4.12 | 0 | 13.61 | −6.52 | −5.95 | 1.87 | −8.75 | −6.78 | 6 48 | −10 36 | 1.31 | 38.51 |

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