POLAROGRAPHIC STUDY OF EUROPIUM(III)–L-PROLINE COMPLEXES

By S. Lal*

The electro-reduction of europium(III) at the dropping mercury electrode (d.m.e.) has been studied in various supporting electrolytes[1–10] and in complexing media by several workers. Chelating agents, viz. EDTA, HEDTA, complexion III, have been employed by some investigators.[11–16] Formate and acetate complexes of europium(III) were studied by Macero and coworkers.[17,18] Zutshi[19] reported results on europium(III) benzoate and salicylate complexes in formamide–water mixtures. Ide[20] noted that $E_{1/2}$ of the first reduction wave of europium(III) in 1,10-phenanthroline and 2,2'-dipyridyl shifted to more positive potentials resulting in a reversible process. Holleck[21] reported complexation of europium(III) with citrates, tartrates, salicylates, and lactates. However, complexation studies of rare earths with amino acids are sparse in the literature. Amino acids possess both nitrogen and oxygen sites available for coordination and stable complexes are expected which can be of analytical importance in separation of rare earths and indirect determination of amino acids. Preliminary studies made by the author[22] on the europium–DL-tryptophan system revealed the formation of one complex [Eu(tryp)]$^{2+}$ with the instability

* Chemistry Department, University of Kentucky, Lexington, Kentucky 40506, U.S.A.

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constant $1 \cdot 60 \times 10^{-7}$. In this note, results on the interaction of L-proline with europium(III) are described.

Experimental

Reagent grade chemicals were used. A $0 \cdot 01$M stock solution of Eu_2O_3 (Moly Corp., U.S.A.) was prepared in the minimum amount of perchloric acid and diluted with distilled water. The depolarizer concentration was $0 \cdot 5$mM in each solution. Sodium perchlorate ($0 \cdot 2$M) was used as the supporting electrolyte. An aqueous solution of L-proline (Nutritional Biochem.) was used as complexing ligand with its concentration varying from 0 to 2M.

PAR Electrochemistry System 170 was employed for the record of $C-V$ curves. Three electrode circuitry was used with the mercury pool as the counter electrode and voltages measured against S.C.E. Triple-distilled mercury (Bethlehem Instrument) was used for the d.m.e. The d.m.e. had the characteristics

$$m^{2/3}t^{1/6} = 1 \cdot 46 \text{ mg}^{2/3} \text{ s}^{-1/2}$$

in $0 \cdot 2$M $NaClO_4$ in the open circuit. Linde's prepurified nitrogen was used for deaeration. The cell temperature was maintained at $25 \pm 0 \cdot 1°$.

Results and Discussion

Europium(III) undergoes one-electron reduction to europium(II) in the first step and the waves are shifted to more negative potentials with increasing concentration of the ligand indicating complex formation between europium(III) and L-proline. The pH of the resulting solutions is altered from $2 \cdot 3$ to $5 \cdot 1$ with addition of L-proline.

Analysis of log-plots indicated the non-reversible nature of the process. The diffusion currents decreased regularly with the increase of proline concentration suggesting the change in the size of depolarizer undergoing complexation. The diminution in diffusion currents is due to the decrease in diffusion coefficient of complexion. The reduction was diffusion-controlled as evidenced from linear plots of i_d against $h^{1/2}$ and exponent of $i-t$ curves being $0 \cdot 19$ in the presence of proline.
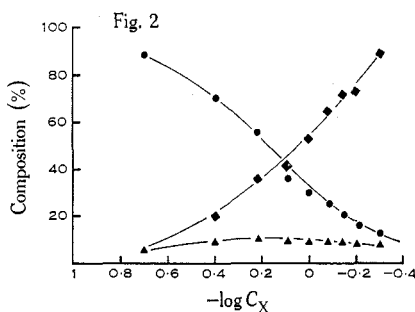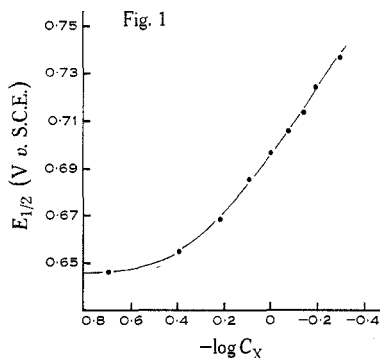

Fig. 1.—Plot of $E_{1/2}$ against $-\log C_X$.
Fig. 2.—Percentage composition for various species of europium(III)–L-proline system.
● Eu^{3+}; ▲ $[Eu(pro)]^{2+}$; ■ $[Eu(pro)_2]^+$.

Since, europium is not reversibly reduced at the d.m.e. and for the study of complex formation, $E_{1/2}^r$ (reversible half-wave potential) is obtained for further calculations of the stability constants of the complexes. The $E_{1/2}^r$ was determined by

Gellings method[23] by plotting $[E-(RT/nF)\ln(i_d-i)/i]$ against i and extrapolating it to $i=0$. The values are given in Figure 1. The standard rate constant of the process (obtained by Gellings method) in the absence of proline was $9\cdot23\times10^{-4}$ cm/s and in the presence of $2\cdot0$M L-proline it became $1\cdot28\times10^{-4}$ cm/s, which is quasi-reversible behaviour.

The plot of $E_{1/2}$ against $-\log C_X$ (C_X = proline concentration) was a smooth curve (Fig. 1) showing the formation of two or more complex species which are in equilibrium. DeFord and Hume's method[24] modified by Irving[25] was adopted for the evaluation of overall formation constants. It was assumed that L-proline was present in relatively large excess so that its concentration at the electrode surface was virtually equal to the concentration in the body of solution. It was also regarded that only europium(II) complex is reduced in the potential range studied and no extraneous effects of europium(III) were present. The normalized curve fitting method developed by DeFord and Hume showed that two complexes species, $[Eu(Pr)]^{2+}$ and $[Eu(Pr)_2]^+$, were present having the overall formation constants $\beta_1=0\cdot3$, $\beta_2=1\cdot78$ respectively. The percentage distribution of europium present in various forms as a function of logarithm of proline is presented in Figure 2.

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