BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2232 (1973)

Polarography of Europium(III)-DL-Tryptophan Complex

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(Received April 1, 1972)

Polarographic studies of europium(III) at the dropping mercury electrode (d.m.e.) in various electrolytes and organic chelating agents have been reported in literature. Holleck[1] claimed that no complexation occurs between Eu(III) and amino acids. However, a recent polarographic study[2] on Eu(III)-L-Proline system indicated definite complexation. In this note, polarographic results on the interaction of Eu(III)-DL-Tryptophan are described.

Experimental

Reagent grade chemicals were used. Solution of europium was prepared by dissolving a weighed amount of Eu_2O_3 (Moly Corp., Colorado) in minimum amount of perchloric acid and diluting with distilled water. M/100 solution of DL-tryptophan (Nutritional Biochem. Corp.) was prepared in double distilled water. The ionic strength was kept constant (μ=0.1) by adding requisite quantity of $NaClO_4$.

PAR Electrochemistry system 170 was used in conjunction with a droptimer for the record of current-voltage curves. The capillary had the characteristics $m^{2/3}t^{1/6}=1.46$ $mg^{2/3}$ $sec^{-1/2}$ in 0.1M $NaClO_4$ in the open circuit. Three electrode circuitry was used with a mercury pool as the counter electrode and voltages measured *vs.* S.C.E. Triple distilled (Bethlehem Instrument) mercury was used for the d.m.e. The temperature of the cell was maintained at 25±0.1C. Linde's prepurified nitrogen was used for deaeration.

Results and Discussion

Solutions containing 0.5 mM Eu(III) with different concentrations of tryptophan (pH=2.4) were polarographed. In each case, a well-defined reduction wave was obtained and $E_{1/2}$ shifted more negatively with increasing concentration of tryptophan. Plots of i_d against h_{eff} were linear depicting it to be a diffusion-controlled process. The plots of log $(i_d-i)/i$ *vs.*$E_{\text{d.e.}}$ were linear but slopes were higher than 59 mV which implied an irreversible process. Although the reduction, in the present case, is diffusion controlled yet is not reversible. $E^r_{1/2}$ (reversible halfwave potential) and kinetic parameters were determined by Gellings[3] method.

The tryptophanate anion [Tr$^-$] concentration at pH=2.4 was calculated with the knowledge of pK value=2.38 of tryptophan. The plot of $E^r_{1/2}$ against $-\log C_x$ is a straight line. Lingane's method[4] for the complex formation studies was applied with the equation:

$$\Delta E_{1/2} = (E^r_{1/2s}) - (E^r_{1/2})_c = \frac{0.0591}{n}\log p + p\frac{0.0591}{n}\log C_x \quad \text{at } 25°C$$

The slope of the plot $(E^r_{1/2})_c$ *vs.* $-\log C_x$ is given by the relation

$$\frac{\Delta E^r_{1/2}}{\Delta \log C_x} = -\frac{0.0591p}{n}$$

and the coordination number, p, is determined. The intercept on the potential axis corresponding to C_x= 1M, gives the instability constant of the complex. In the present case for n=1; p=1 and the intercept= −1.03 V is obtained. The instability constant of the complex $[Eu(Tr)]^{2+}$ is 1.63×10^{-7}.

TABLE 1. $E^r_{1/2}$ AND KINETIC PARAMETERS OF Eu(III)-DL-TRYPTOPHAN SYSTEM

Concn $\times10^3$M Tryptophan	Tr $\times10^{-3}$M	$-E^r_{1/2}$V *vs.* SCE	α	$k_S\times10^3$ cm/sec
0.00	0.000	0.654	0.88	6.25
0.005	0.002	0.668		
0.01	0.004	0.685		
0.02	0.008	0.705		
0.05	0.021	0.736		
0.10	0.041	0.747	0.89	5.75
0.20	0.082	0.762		
0.30	0.123	0.780		
0.40	0.164	0.788		
0.80	0.328	0.804	0.88	5.10
1.00	0.411	0.812		
2.00	0.822	0.831		
3.00	1.233	0.842	0.89	4.86
6.00	2.466	0.862	0.88	4.17
8.00	3.288	0.866	0.87	3.34

The rate constants and transfer coefficients of the process have been evaluated and summarized in Table 1. The apparent rate constants tend to decrease with increasing tryptophan concentration and the reduction appears to be quasireversible.[5]

The author expresses his profound thanks to the Chemistry Department, University of Kentucky and Dr. H. H. Bauer for providing necessary facilities.

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