Monatshefte für Chemie 105, 974—976 (1974)

Tast Polarography of Europium(III)-L-Histidine Complex

By

S. Lal

From the Thomas Hunt Morgan Institute of Genetics, Lexington, Kentucky, U.S.A.

(Received March 8, 1974)

Study of europium(III)-L-histidine complex has been made in sodium perchlorate at $\mu = 0.1$ by tast polarography. The reduction process appears to be quasi irreversible. The apparent rate constants have been determined by *Gellings* method[1]. With the knowledge of $E^r_{1/2}$ and use of *Lingane's* method, one complex Eu(*Histd*)$^{2+}$ with the instability constant 6.77×10^{-5} is reported.

Introduction

Polarography of europium(III) at the dropping mercury electrode (*d.m.e.*) has been carried out both in complexing and noncomplexing media by several workers. *Pleticha* studied complexation of transition metal ions with a variety of amino acids. However, complexation studies of amino acids with europium have not been undertaken excepting the present author's investigations with L-proline[2] and DL-tryptophan[3]. Amino acids possess nitrogen and oxygen sites available for co-ordination and stable complexes are anticipated which can be of analytical importance in separation of rare earths and indirect determination of amino acids. The present communication describes the results on the interaction of europium(III) with L-histidine (*Histd*).

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. 0.01M solution of L-histidine (Eastman Kodak Co.) was prepared in doubly distilled water. The ionic strength was kept constant ($\mu = 0.1$) by adding requisite quantity of $NaClO_4$.

The PAR Electrochemistry system 170 was used in conjunction with a droptimer for the record of current—voltage curves. The capillary had the characteristics $m^{2/3} t^{1/6} = 1.234\ \text{mg}^{2/3}\ \text{sec}^{-1/2}$ 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) Hg was used for the *d.m.e.* The temperature of the cell was maintained at 25 ± 0.1 °C. Linde's prepurified oxygen free nitrogen was used for deaeration.

Results

Solutions containing 0.6 mmoles Eu(III) with different concentrations of L-histidine (5×10^{-4} M — 6×10^{-2} M, pH 1.3–1.7) were studied polarographically. In each case, a well defined reduction wave was obtained and $E_{1/2}$ shifted more negatively with increasing concentration of histidine. Plots of i_d against $h_{\text{eff}}^{1/2}$ were linear depicting it to be a diffusion controlled process. The plots of $\log \frac{i_d - i}{i}$ vs. $E_{d.e.}$ were not linear and slopes were higher than 59 mV which implied a nonreversible process. $E^r_{1/2}$ (reversible half-wave potential) and kinetic parameters were determined by *Gellings's* method[1] (Table 1).

Table 1. *$E^r_{1/2}$ and Kinetic Rate Constants of* Eu(III)-L-*Histidine*

Concn × 10^2M Histidine	[Histd] × 10^2 M	— $E^r_{1/2}$, V vs. *SCE*	$K_{\text{sh}} \times 10^3$ cm/sec
0.00	0.000	0.668	—
0.05	0.015	0.676	2.26
0.10	0.030	0.696	2.46
0.20	0.060	0.714	2.85
0.50	0.155	0.738	3.22
1.00	0.327	0.759	5.32
2.00	0.810	0.785	5.45
4.00	1.620	0.804	5.68
6.00	3.470	0.820	6.40

In *d.c.* polarography, only the first reduction step of Eu(III) to Eu(II) was studied. The half-wave potentials were shifted to more cathodic potentials with increasing ligand concentration indicating complexation. The method of *Lingane*[5] was applied for the determination of co-ordination number, *p*, and the instability constant of the complex. The plot of $E_r^{1/2}$ against — log C_x (histidine anion concentration at a given pH, calculated from its $pK_a = 1.77$) was a straight line yielding p equal to unity as determined from the relation.

$$\frac{\Delta E^{r}_{1/2}}{\Delta \log C_x} = \frac{0.0591\,p}{n}$$

From the intercept on the potential axis corresponding to $C_x = 1\,\text{M}$, the instability constant of the complex $\mathrm{Eu}(Histd)^{2+}$ was 6.77×10^{-5}.

The apparent rate constants, K_{sh}, of the process in varying concentration of histidine were of the order of 10^{-3} cm/sec and the reduction appeared to be quasireversible.

The author expresses thanks to the Chemistry Department, University of Kentucky for the facilities.

References

[1] *P. J. Gellings*, Z. Electrochem. Ber. Bunsenges. Phys. Chem. **66**, 477 (1962).
[2] *S. Lal*, Austral. J. Chem. **25**, 1571 (1972).
[3] *S. Lal*, Bull. Chem. Soc. Japan **46**, 2232 (1973).
[4] *R. Pleticha*, Collect. Czech. Communs. **15**, 807 (1950).
[5] *J. J. Lingane*, Chem. Rev. **29**, 1 (1941).

Dr. S. Lal
Thomas Hunt Morgan Institute
of Genetics
628 North Broadway
Lexington, KY 40508
U.S.A.