POLAROGRAPHIC BEHAVIOUR OF Eu(III) ASPARTATE COMPLEXES

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(Received 18 Jan 1977; accepted March 1977)

The reduction of Eu (III) aspartate complexes in aqueous, aqueous dimethyl formamide, and aqueous-sulfoxide media is diffusion-controlled and irreversible. The reversible half wave potential is shifted to more negative value with aspartate ion concentration, indicating complex formation in solution. The values of overall formation constant are $\beta_1 = 200$, $\beta_2 = 1500$, $\beta_3 = 2 \times 10^4$, $\beta_4 = 8 \times 10^5$ in aqueous medium at 30°C. In aqueous dimethyl formamide four complexes and in aqueous dimethyl sulfoxide five complexes are formed. The stability of the complexes increases linearly with dielectric constant as well as donor number of the solvent used.

Reduction of Eu III) and other rare earth elements in various organic solvents have been reported by Gutmann et al[1,2]. Zutshi[3] made the study of Eu(III) in presence of benzoate and salicylate in aqueous formamide media. Some amino acid complexes of europium (III) have also been studied pH-metrically[4] as well as polarographically[5].

This paper presents the polarographic studies of complexes formed by Eu(III) with aspartate ions in aquoues organic solvent mixture. The solvents used for the study are dimethyl formamide and dimethyl sulfoxide. Overall formation constants have been deter mined.

Experimental

Reagent grade chemicals were used in all the experiments. A manual type of polarographic set-up with Ajco galvanometer was used to measure the current-voltage curves. The d. m. e. had the following characteristics: m = 1.745 mg/sec, t = 4.2 sec. (in open circuit). Reduction was carried out in a 'H' type cell with agar agar plug, saturated with sodium chloride, Solution of Eu(III) ion, as perchlorate, was prepared from reagent grade Eu_2O_3 (J. M. Product) and was then standardized by EDTA titration[6]. Lithium perchlorate was used as a base electrolyte and ionic strength was maintained as 6.3 $\pm$ 0.1 by careful addition of sodium hydroxide solution. Solutions containing 0.5 mM of europium with varying amount of ligand concentration in aqueous and aqueous-organic solvent (20% by volume) media were prepared for the experiments.

Results and Discussion

A single well defined diffusion-controlled wave appeared in each case. The plots of $\log \frac{i}{(i_d - i)}$ vs E are linear in all cases. The values of slope showed the reduction to be irreversible. Hence the reversible half wave potential $E_{\frac{1}{2}}^r$ have been determined using Gelling's[7] treatment. The half wave potential was shifted to a more cathodic direction and diffusion current was found to decrease with increasing concentration of the aspartate ions (Table—1). The plots of $-E_{\frac{1}{2}}^r$ vs - log C_x (C_x is the aspartate ion concentration in moles) gave smooth curve in all cases indicating the formation of two or more complex species in equilibrium with one another.

Hence the classical method of Lingane[8] could not be applied for the determination of formation constants. De Ford and Hume's[9] treatment for the stepwise formation constants has been applied. The stability constants of the various complex species are calculated (Table-2).

Table—2 Values of formation constants of Eu(III) aspartate system at 30°C.

Solvent	Formation constants				
	β_1	β_2	β_3	β_4	β_5
Aqueous	200	1500	2×10^4	8×10^5	—
Aqueous dimethyl formamide	50	3×10^3	11×10^4	10×10^4	—
Aqueous dimethyl sulfoxide	250	5×10^3	15×10^4	27×10^4	65×10^5

It has been observed that in aqueous medium, four complex species are formed at 30°C. having the values of overall formation constant as $\beta_1 = 200$, $\beta_2 = 1500$, $\beta_3 = 2 \times 10^4$, $\beta_4 = 8 \times 10^5$. In aqueous dimethyl formamide four complexes and in aqueous dimethyl sulfoxide five complex species have been formed. (Table 2).

From the results it is indicated that the solvent plays an important role in the complex formation. The

Table—1 Polarographic data of 0.5 mM Eu(III) aspartate complexes

In aqueous medium						In aqueous dimethyl formamide					In aqueous dimethyl sulfoxide				
C_x, M	i_d μA	slope mv.	$-E_{\frac{1}{2}}$, V. (SCE)	$-E^r_{\frac{1}{2}}$, V. (SCE)	$F_0(X)$	i_d μA	slope mv.	$-E_{\frac{1}{2}}$, V. (SCE)	$-E^r_{\frac{1}{2}}$ V. (SCE)	$F_0(X)$	i_d μA	slope mv	$-E_{\frac{1}{2}}$, V. (SCE)	$-E^r_{\frac{1}{2}}$ V. (SCE)	$F_0(X)$
0.00	2.416	88	0.668	0.656		1.635	60	0.675	0.66	—	1.858	72	0.652	0.646	—
0.02	2.193	94	0.730	0.708	8.1	1.487	89	0.722	0.70	4.2	1.691	90	0.721	0.703	9.8
0.04	1.970	91	0.741	0.725	17.7	1.412	118	0.772	0.73	14.0	1.450	85	0.757	0.736	40.5
0.06	1.914	94	0.763	0.741	32.2	1.375	101	0.793	0.76	51.1	1.375	100	0.801	0.767	143.2
0.08	1.858	95	0.774	0.759	67.7	1.375	116	0.828	0.78	114.5	1.338	100	0.818	0.790	351.5
0.10	1.784	98	0.797	0.778	146.2	1.375	135	0.853	0.80	237.4	1.301	102	0.847	0.814	901.8
0.12	1.747	87	0.815	0.792	255.6	1.227	118	0.867	0.82	473.5	1.208	96	0.857	0.834	2090.0
0.14	1.710	98	0.831	0.806	446.2	1.171	118	0.873	0.83	785.6	1.134	104	0.883	0.851	4258.0
0.16	1.635	88	0.836	0.817	712.2	1.134	136	0.891	0.84	1169.9	1.078	87	0.887	0.866	7800.0

stability of the complexes increases with dielectric constant (37 for DMF 847 for DMSO). Similarly, donor number (27 for DMF and 30 for DMSO) confirms the above results.

Acknowledgements : Authors are thankful to C.S.I.R. (New Delhi) for providing Junior Research Fellowship to one of us (KCG) and to Prof. J. N. Gaur, Head of the Department for granting necessary facilities.

REFERENCES

1. G. Victor; Gerald, Monatsh Chem. 100-4 (1969) 1423
2. Ibid, 100-3 (1969) 813.
3. K Zutshi, Polarography 14 3 (1967) 294.
4. O. N. Puplikova, M. A. Savich, Zh. Obshch Khim, 44-5 (1974) 1179.
5. S. Lal, Bull. Chem. Soc. Japan, 46-7 (1973) 2232.
6. S. L. Lyle, Md. M. Rahaman, Talanta, 10 (1962) 1177.
7. P. J. Gelling, Z. Electro Chem. Ber. Bunsenges Physik Chem 66 (1962) 477, 4818799; 67 (1963) 167.
8. J. Lingane, Chem. Rev. 1 (1941 29.
9. DeFord and Hume, J. Am. Chem. Soc. 73 (1951) 5321.
10. T. Sawyer, and J. L. Roberts, Experimental Electro Chemistry for Chemists. 1977, 172.



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