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Polarographic study of Eu(III)-hydroxamic acid complexes

P K BHANSALI and B I NEMADE*

Department of Chemistry, University of Bombay, Vidyanagari, Bombay 400 098, India

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Abstract. Complexes of europium(III) ion with two hydroxamic acids have been investigated by polarographic method of analysis at $30 \pm 0{\cdot}1°$ C and $\mu = 0{\cdot}5$ M (KNO_3). In both hydroxamic acids phenylacetohydroxamic acid (PAHA) and acetohydroxamic acid (AHA), the electrode reaction was found to be quasireversible in nature, hence Gelling's method was used for evaluation of reversible half-wave potential and kinetic parameters. Formation of Eu(III)-hydroxamic acid complex was observed with metal ligand ratio 1 : 2 in aqueous solution.

Keywords. Phenylacetohydroxamic acid ; acetohydroxamic acid ; polarographic method ; quasireversible.

1. Introduction

In different non-complexing media (Vleck 1955, 1959 ; Gierst and Cornelissen 1960) the reduction of $Eu^{3+} \rightarrow Eu^{2+}$ is of irreversible to quasireversible nature. Literature survey revealed that there has been no study of the europium hydroxamic acid system by polarographic technique. Hence the present work has been undertaken.

2. Experimental

The current potential curves were recorded on a manual set-up using dropping mercury electrode (dme) and saturated calomel electrode (SCE) as reference electrode. The ionic strength was maintained at 0·5 with the help of potassium nitrate. Gelatin 0·002% was used as a maximum suppressor. All measurements were carried out at $30 \pm 0{\cdot}1°$ C. The capillary had the following characteristics, $m = 1{\cdot}94$ mg/sec and $t = 4{\cdot}0$ sec in supporting electrolyte potassium nitrate in open circuit. The pH of the solution was measured with an expanded scale pH meter (Electronic Corporation of India Limited, Hyderabad, Model pH 821 B).

* To whom correspondence should be made.

The pH of the experimental solution was adjusted with freshly prepared NaOH or dilute perchloric acid solutions.

PAHA was synthesised by the method given by Blatt (1964). AHA was prepared as described by Fishbein *et al* (1969). The pK values of PAHA and AHA determined by pH titration technique of Irving and Rossotti (1954) were found to be 9·20 and 9·40 respectively (Bhansali and Nemade 1982). Europium solution was prepared by dissolving europium oxide (Koch-light Lab. 99·9% pure) in perchloric acid and was standardised as described by Vogel.

3. Results and discussion

3.1. *Europium*–PAHA *system*

Well defined polarogram was obtained for Eu(III) in 0·5 M potassium nitrate with half-wave potential at −0·670 V *versus* SCE which is in good agreement with the reported values (Chandrasekaran 1970). Above pH = 5·2 formation of precipitate took place hence studies were restricted to a pH range of 4·0 to 5·0. With increase in hydroxamate ion concentrations the half-wave potentials shifted to more negative values indicating complexation. The half-wave potentials were determined from the plots of log $i/id-i$ *versus* E (log-plots) and the slopes of the log-plots were of the order 60–90 mV. The reversible half-wave potential and kinetic parameters, *viz*, α and K_s were evaluated by Gelling's method (Gelling 1962) (figure 1). The plot of $E^{r}_{1/2}$ *versus* pA (data in table 1) resulted in a smooth curve which showed presence of more than one species whose stabilities do not differ appreciably. The data were analysed by DeFord and Hume's (DeFord and Hume 1951) method for evaluation of stability constants. The function $F_0(A)$ was calculated from shift in the half-wave potential obtained from the smooth curve of a plot of $E_{1/2}$ *vs* pA using method of DeFord and Hume (1951).

$$F_0(A) = \text{Antilog}\left[0{\cdot}4343\,\frac{nF}{RT}\,(E_{1/2(s)} - E_{1/2(c)}) + \log\frac{I_{(s)}}{I_{(c)}}\right]$$

$$= 1 + \beta_1[A] + \beta_2[A]^2 + \beta_3[A]^3 + \cdots\cdots \beta_n[A]^n \qquad (1)$$

where, $E_{1/2(s)}$ and $E_{1/2(c)}$ refer to the half-wave potential of the uncomplexed and complexed ions respectively and $I_{(s)}$ and $I_{(c)}$ are the corresponding diffusion currents. β's refer to the overall stability constants, and $[A]$ is the concentration of the ligand. Values of F_j functions obtained at different ligand concentrations $[A]$ are given in table 1. The values of the stability constants obtained are

$$\beta_1 = 2{\cdot}0 \times 10^7 \quad \text{and} \quad \beta_2 = 2{\cdot}7 \times 10^{14}$$

3.2. *Europium*–AHA *system*

In the case of AHA the formation of precipitate was observed at pH > 5·8. The studies were therefore made at pH below 5·8. The slopes of the log-plots are

Table 1. Europium–PAHA system. Effect of ligand concentration on half-wave potential and values of F_j functions.

$[Eu^{3+}] = 0{\cdot}6$ mM, $\mu = 0{\cdot}5$ M KNO_3; Temp. = 30° C

$m^{2/3} \cdot t^{1/6} = 1{\cdot}96$ $mg^{2/3} \cdot sec^{-1/2}$; pK = 9·20

[HA]×10³ M	[A]×10⁷ M	pH	pA	$E_{1/2}$ —V vs.	$E^r_{1/2}$ SCE	a	i_d μA	—log K_s	F_0(A)×10⁻¹ Exptl.	F_1(A)×10⁻⁸	F_2(A)×10⁻¹⁴	F_0(A)×10⁻¹ Calcd.
0	...	...	...	0·670	0·648	0·27	1·88	3·028	...	...	...	...
2·0	0·6607	4·72	7·18	0·684	0·677	0·16	1·82	2·968	0·3519	0·3813	2·744	0·3500
2·0	0·7586	4·77	7·12	0·690	0·684	0·29	1·81	3·028	0·3969	0·3915	2·524	0·4071
2·0	0·7943	4·80	7·10	0·696	0·687	0·14	1·80	2·908	0·4148	0·3963	2·471	0·4292
8·0	1·349	4·43	6·87	0·701	0·691	0·29	1·78	2·888	0·7171	0·4575	1·909	0·8611
24·0	2·089	4·14	6·68	0·717	0·710	0·19	1·76	2·988	1·560	0·6989	2·388	1·696
8·0	2·630	4·72	6·58	0·746	0·732	0·14	1·69	3·228	2·778	1·018	3·109	2·494
4·0	2·884	5·06	6·54	0·748	0·737	0·24	1·68	3·058	3·258	1·095	3·103	2·923
32·0	3·311	4·29	6·40	0·758	0·749	0·26	1·62	3·205	5·525	1·363	2·921	3·722
12·0	3·981	4·82	6·30	0·775	0·770	0·22	1·63	3·088	12·350	2·444	...	...

Table 2. Europium-AHA system. Effect of ligand concentration on half wave potential and values of F_j functions,

$[Eu^{3+}] = 0{\cdot}6$ mM ; $\mu = 0{\cdot}5$ M KNO_3 ; Temp. $= 30°$ C

$m^{2/3} \cdot t^{1/6} = 1{\cdot}96$ $mg^{2/3}.sec^{-1/2}$; pK $= 9{\cdot}40$

$[HA]\times10^3$ M	$[A]\times O^6$ M	pH	pA	$E_{1/2}$ $-V$ vs.	$E_{1/2}{}^r$ SCE	a	i_d μA	$-\log K_s$	F_0(A) Exptl.	F_1(A)$\times10^6$	F_2(A)$\times10^{11}$	F_0(A) Calcd.
0	...	...	...	0·670	0·648	0·27	1·88	3·028	...	...	...	...
16·0	1·738	5·44	5·76	0·677	0·663	0·22	1·83	3·018	1·825	0·4447	1·523	1·796
24·0	2·754	5·46	5·56	0·682	0·674	0·18	1·80	3·008	2·828	0·6636	1·756	2·709
32·0	3·548	5·44	5·45	0·698	0·688	0·18	1·76	2·978	3·782	0·7839	1·702	3·653
40·0	4·786	5·48	5·32	0·700	0·690	0·19	1·77	3·028	5·731	0·9884	1·689	5·526
56·0	6·457	5·46	5·19	0·711	0·700	0·21	1·73	3·038	8·936	1·229	1·625	8·833
40·0	7·079	5·65	5·15	0·715	0·705	0·21	1·71	2·998	9·760	1·237	1·493	10·292
48·0	7·413	5·52	5·13	0·722	0·708	0·16	1·68	3·038	11·144	1·368	1·603	11·127
56·0	8·913	5·60	5·05	0·730	0·716	0·26	1·66	3·058	15·324	1·607	1·601	14·369
56·0	10·720	5·68	4·97	0·741	0·723	0·21	1·62	3·214	20·531	1·822	1·532	21·317

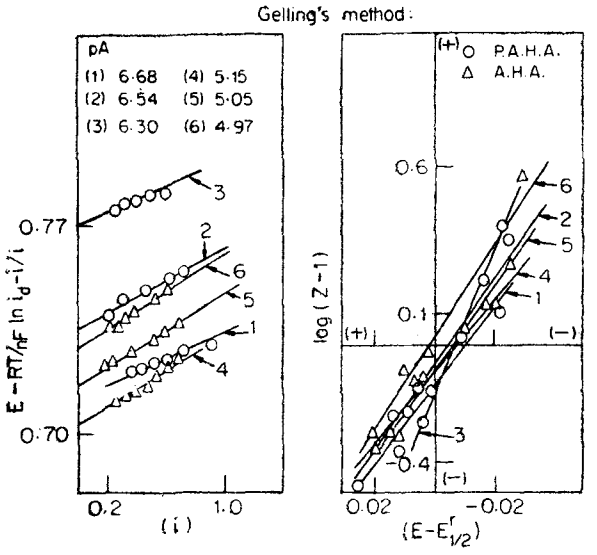

Figure 1.

found in the range 60–87 mV. The reversible half-wave potentials and kinetic parameters were evaluated using Gelling's method (figure 1 and table 2). Two complexes were identified with stability,

$$\beta_1 = 1{\cdot}8 \times 10^5 \text{ and } \beta_2 = 1{\cdot}6 \times 10^{11}.$$

Results showed that complexes formed by PAHA are stronger than those of AHA the hydroxamic acid functional groups $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-OH$ acts as bidentate ligand, and chelation usually occurs (Agrawal 1977), by the substitution of hydrogen atom of hydroxylamine by metal atom and ring closure by carbonyl oxygen atom.

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