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Polarographic Studies on La(III), Sm(III), Eu(III) & Yb(III) Complexes with Diethylenetriaminepentaacetic, Triethylenetetraminehexaacetic & Tetraethylenepentamineheptaacetic Acids

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Diethylenetriaminepentaacetic acid (DTPA), triethylenetetraminehexaacetic acid (TTHA) and tetraethylenepentamineheptaacetic acid (TPHA) form 1 : 1 complexes with La(III), Sm(III), Eu(III) and Yb(III), which are quite stable in acidic medium. The stability constants of these complexes have been determined by the displacement method. The effect of various supporting electrolytes, aqueous alcoholic media, *p*H and surface active substances on the polarographic behaviour of these complexes have been described.

IN recent years, much interest has been shown in the complexes of rare earth with multidentate ligands, especially with aminopolycarboxylic acids[1-6] due to their possible application as laser materials. Polarographic studies on rare earth complexes involve certain difficulties. Since the trivalent rare earths have negative reduction potentials, similar to those of alkaline earth metals, there is possibility of secondary reactions with the medium which may mask the primary wave. A survey of literature reveals that extensive polarographic studies have been carried out on the rare earth complexes with various nitrogen donors[7-11]. However studies on complexes with ligands containing both oxygen and nitrogen donors such as aminopolycarboxylic acids are limited to aqueous media owing to the low solubility of the supporting electrolytes in organic non-aqueous media.

The polarographic behaviour of La(III), Sm(III), Eu(III) and Yb(III) complexes with aminopolyacetic acids in which the carboxylate groups vary from five to seven has been studied and the results are reported in this note. The stability constants of these complexes have been calculated by Schwarzenbach's method. Solvent effect, effect of *p*H, and various supporting electrolytes on the polarographic behaviour of rare earth complexes have also been studied.

Materials and Methods

Nitrates of the rare earth metals were prepared by dissolving weighed quantities of rare earth oxides (Sigma Chemical Co., USA) in dilute nitric acid. The excess of acid was removed by evaporation and the solutions standardized by complexometric titration[12], using Xylenol Orange as an indicator. Extra pure disodium salts of the ligands, viz. diethylenetriaminepentaacetic acid (DTPA), triethylenetetraminehexaacetic acid (TTHA) and tetraethylenepentamineheptaacetic acid (TPHA) were, obtained through the courtesy of Dojindo & Co. Ltd, Japan, and were used as such. A solution of cadmium was prepared by dissolving AR cadmium nitrate.

Polarographic studies were carried out on a manual Toshniwal polarograph, in conjunction with a Pye-Scalamp galvanometer, using a d.m.e. and potentials were measured against a saturated calomel electrode (SCE). The capillary characteristics was $m^{2/3}\ t^{1/6} = 2{\cdot}06\ mg^{2/3}\ sec^{-1/2}$.

The solutions were deaerated by bubbling purified nitrogen gas for about 10 min before recording the polarograms at $30^\circ \pm 0{\cdot}1^\circ$.

The ligand concentration employed was $1{\cdot}0 \times 10^{-2}M$. Acetic acid-sodium acetate buffer solution was used in all the cases except when alternate procedure is described. The buffer concentration was maintained at $0{\cdot}1M$ with respect to both acid and base form. Reagent grade potassium nitrate was added to maintain the ionic strength and to bring the concentration up to $0{\cdot}5M$. Distilled ethyl alcohol was used and supporting electrolytes LiCl and $(C_2H_5)_4NBr$ were of (BDH) AR grade. Triton X-100 (Rohm & Haas Co., Philadelphia, USA) was used as maxima suppressor. Doubly distilled water was used for the preparation of all the solutions. *p*H measurements were made with a Toshniwal (C. No. -42-1) *p*H meter using glass electrode. All other chemicals were of extra pure grade.

Results and Discussion

Polarographic study — Polarograms of La(III), Sm(III), Eu(III) and Yb(III) in the presence of

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DTPA, TTHA and TPHA exhibit a large maximum at [rare earth ion] $> 10^{-3}M$. The maximum is easily suppressed by the addition of surface active agents but the half-wave potential is strongly affected by the presence of even small amounts of such maxima suppressors. Hence all polarograms were recorded by keeping the concentration of rare earths below $10^{-3}M$. The nature of the polarographic waves was studied[13]. It was found that reduction in all the cases was diffusion-controlled and the waves were found to be irreversible as evinced from the log plots[14]. The polarographic data are recorded in Table 1. The method of determining the stability constant for reversible wave could not, therefore, be applied.

Stability constants — The stability constants were determined by using Schwarzenbach's displacement method[15] using cadmium as indicator ion.

$$K = \frac{(\%\ Cd^{2+})^2}{(100 - \%\ Cd^{2+})^2}$$

The stability constants were calculated from above equation and their values are given in Table 2.

Solutions containing cadmium-TTHA complex (0·001M), $R(NO_3)_3$ (0·001M), sodium acetate (0·01M), acetic acid (0·01M) were prepared and potassium nitrate was added to keep the ionic strength constant (0·1). Triton X-100 was added to suppress the maximum and solutions were diluted accordingly. Similar solutions were also prepared at an ionic strength of 1·0. All the solutions were placed in the thermostat for 48 hr and were well shaken to ensure complete reaction and then polarograms were recorded. The i_d value of each rare earth ion was calculated, the amount of free cadmium in the above solution was calculated by taking blank polarogram of Cd^{2+} in potassium nitrate. Two well-defined waves appeared, as expected, the first wave corresponding to Cd-TTHA complex and the second wave to free rare earth ion.

The results of the present amperometric titrations indicate that rare earth (III) forms 1:1 complexes with TTHA, DTPA and TPHA which are quite stable in the *p*H range 4-6, 5-6 and 2-6 respectively. The effect of ionic strength on the stability constant has also been studied and the results show that the stability constant decreases with an increase of ionic strength.

A close inspection of stability constants (Table 2) show that DTPA forms the most stable complexes with rare earths. TTHA and dodecadentate ligand TPHA forms comparatively less stable complexes. It is supposed that coordination number may decrease with the steric hindrance caused by the large size of the ligand, as the rare earths (III) ions decreases in size.

Effect of dielectric constant of the medium — A relation has been shown to exist between variation of the dielectric constants of the different aqueous-alcoholic mixtures and the half-wave potential becomes more and more positive as this constant diminishes (Table 1). The $E_{1/2}$ and slope values for various rare earth and their complexes in 25 and 50% aq. ethanol are given in Table 1. The results indicate that $E_{1/2}$ becomes more positive with an increase in alcohol content of the medium, whereas diffusion current (i_d) diminishes. According to the slope of $E_{d.m.e.}$ vs. log $(i/i_d - i)$ plot, the reduction of these ions at d.m.e. becomes more irreversible as the proportion of ethanol increases.

Effect of surface active substances — The effect of surface active substances on the polarographic waves of rare earths. TTHA, DTPA and TPHA complexes was investigated using strongly adsorbed ionic and non-ionic surfactants. It has been generally observed that the polarograms were

TABLE 1 — POLAROGRAPHIC DATA ON RARE EARTHS AND THEIR COMPLEXES

[Supporting electrolyte for rare earths, LiCl 0·1M; and for rare earth complexes $(C_2H_5)_4NBr$, 0·1M; maximum suppressor, triton X-100, 0·01%]

Rare earth or rare earth complexes	EtOH (25%)				EtOH (50%)			
	*p*H	$E_{1/2}$ (V)	Slope[c]	I	*p*H	$E_{1/2}$ (V)	Slope[c]	I
La	3·00	−1·90	0·030	3·121	3·00	−1·88	0·090	2·461
La*	3·00	−1·82	0·040	2·378	—	—	—	—
Sm*	3·00	−1·74	0·050	2·021	3·00	−1·80	0·040	2·216
Eu*	2·90	−0·68[a]	—	0·714	2·80	−0·72[a]	0·080	0·953
		−1·35[b]		1·778		−1·32[b]	0·035	1·834
Yb*	2·80	−1·82[b]	0·028	1·520	2·90	−1·80[b]	0·030	1·886
La (DTPA)	3·00	−1·98	0·044	2·935	3·00	−1·97	0·040	2·782
La (TTHA)	3·10	−1·96	0·062	2·377	3·00	−1·94	0·060	2·219
La (TPHA)	3·20	−2·02	0·055	2·336	3·00	−2·00	0·060	2·110
Sm (DTPA)	5·20	−1·88	0·032	2·937	5·00	−1·85	0·044	2·719
Sm (TTHA)	5·00	−1·91	0·066	2·125	5·10	−1·88	0·056	2·091
Sm (TPHA)	5·00	−2·03	0·063	1·983	5·00	−2·01	0·061	2·247
Yb (DTPA)	4·00	−1·87	0·080	1·762	4·00	−1·86	0·066	1·640
Yb (TTHA)	4·10	−1·93	0·065	1·450	4·10	−1·90	0·073	1·590
Yb (TPHA)	4·30	−2·06	0·058	1·640	4·10	−1·98	0·054	1·450

(a) Half-wave potential of first wave.
(b) Half-wave potential of second wave.
(c) Slope of $E_{d.m.e.}$ vs log $(i/i_d - i)$ plot.
*At EtOH, 75%.

TABLE 2 — STABILITY CONSTANTS OF RARE EARTH (III) COMPLEXES WITH DTPA, TTHA AND TPHA

[Temp., 30°±1°; ionic strength = 0·1 (KNO_3)]

Rare earth	log k		
	DTPA complex	TTHA complex	TPHA complex
La	19·32	19·52	19·10
Sm	22·80	19·54	20·50
Eu	22·91	19·57	20·70
Yb	22·59	19·46	19·82

strongly distorted in the presence of even very small amount of non-ionic (0·005%), Triton X-100 and anionic (0·002%) sodium dodecyl sulphate. The electrocapillary curve of mercury shows that the addition of Triton X-100 to the solution causes a large decrease in the drop time of the capillary, the electrocapillary maximum shifts to the positive side with increasing concentration of Triton X-100. These facts show that an adsorption of Triton X-100 occurs on the mercury electrode; the film formation of surface-active substances can be regarded as a rapid process. The inhibiting effect of the absorbed film of Triton X-100 on the electron transfer renders the current potential curve more irreversible[16].

Effect of pH — As the pH of the solution increases, the $E_{1/2}$ shifts towards more negative values. The half-wave potential of Eu-TTHA complex was, measured in the pH range of 3 to 10 (borax-NaOH, H_3PO_4-boric acid CH_3COOH-NaOH, NH_4Cl-NaOH buffer solutions). In the case of Yb-TPHA complex the half-wave potential shifted to the more negative values with increasing pH from 4·40 to 5·45, and became constant in the pH range 5·45 to 6·45, because of the formation of stable complex species. The limiting current i_d decreased gradually with increasing pH and the electrode process was irreversible.

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