ELECTRODE KINETICS OF Eu^{3+}/Eu^{2+} REACTION BY CYCLIC VOLTAMMETRY

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The paper is a detailed study of the cyclic voltammetric behaviour of Eu^{3+} at HMDE in molar solutions of KCl, KBr, KI, KSCN and in 0·1M-EDTA solution with an indigenously built equipment. The computed values of the rate constants at various scan rates show good agreement with those reported by other electrochemical methods. In addition, the results indicate participation of a bridged activated complex in the electron-transfer step, the rate constants showing the trend $SCN^- > I^- > Br^- > Cl^-$ usually observed for bridging order of these anions in homogeneous electron-transfer reactions. The results for Eu–EDTA system, however, indicate involvement of an outer sphere activated complex in the electrode reaction.

The electrochemical behaviour of Eu^{3+}/Eu^{2+} couple at d.m.e. has aroused wide interest in recent years and is often adopted[1–3] as a typical model for testing theories of double layer correction. The most interesting and intriguing aspect about the electrochemistry of europium in various supporting electrolytes is that it exhibits a range of rate constants characterising not only nearly irreversible or quasi-reversible behaviour but also reversible mode of electron transfer fer[4,5]. The electrode kinetic parameters for this lanthanide couple in various supporting electrolytes have been evaluated by impedance measurement[4], complex plane analysis[1,2], conventional polarography[6], Kalousek polarography[7], chronopotentiometry[8] and potential step chronocoulometry[9]. In all these methods, for the evaluation of apparent rate constant, it is essential to know *a priori* the standard potential or to measure the formal potential of the couple in the medium of interest. The triangular wave voltammetric technique provides another simple method whereby both the transfer coefficient (α) and apparent standard rate constant (k_s) can be determined without measuring the standard or formal potential of the system.

In this paper, the cyclic voltammetric behaviour of Eu^{3+} at HMDE has been studied in solutions of 1M-KCl, KBr, KI, KSCN and also in 0·1M-EDTA, at various voltage scan rates. The computed values of α and k_s have been compared with those obtained by other methods.

EXPERIMENTAL

Cyclic voltammograms were recorded with a multipurpose instrument called Electrochemoscan[10] (Figs 1 and 2*) fabricated in this laboratory. Based on operational amplifier circuitry with ECC 83 valves, the present unit is a modification of the one proposed by Bhagat and Santha-

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* See insert facing p. 1776.

nam[11], and has in addition, positive feedback iR drop compensation facility. The voltammograms corresponding to low scan rates were recorded on a X–Y recorder (Rikadenki Kogyo Co, Japan, Model BW 133) at sensitivity 20 mV s^{-1}, after backing off major portion of the initial potential with a portable potentiometer (Toshniwal). A storage oscilloscope DM 64 (Telequipment) with Polaroid camera attachment (Tektronix, Type C-27) was used for recording/photographing the cyclic curves at scan rates greater than 1 V s^{-1}. Average of triplicate experiments was used for each system and the measured potentials were reproducible within ±5 mV. The pH of all solutions were measured with Beckman Expandomatic SS-2 pH-meter.

An improved cell set-up with linear electrode arrangement[12] was employed to minimise shielding of the working electrode and to ensure good reproducibility and accuracy. A syringe-type HMDE (Metrohm Ltd., Herisau), with area 0·032 cm^2 was used as the working electrode. The auxiliary platinum bead electrode, with an area 0·13 cm^2, was placed within 2 mm of the HMDE on one side, whereas the Luggin capillary of s.c.e. was located within 1 mm on the opposite side of the drop. All solutions were deoxygenated by bubbling pure nitrogen and the temperature was kept constant at 30 ± 0·1°C by Ultrathermostat, Type NBE.

A stock solution (0·02M) of europium was obtained by dissolution of pure Eu_2O_3 (M/s Rare Earth Products, England) in HCl and fuming thrice with perchloric acid. The exact strength was checked by titration[13] with standard EDTA using Xylenol orange as indicator. Other chemicals used were either G.R. or AnalaR grade.

RESULTS AND DISCUSSION

Cyclic voltammograms were obtained for 1 mM solution of Eu(III) in 1M-KCl, 1M-KBr, 1M-KI and 1M-KSCN at pH 2·4 and different scan rates. The behaviour

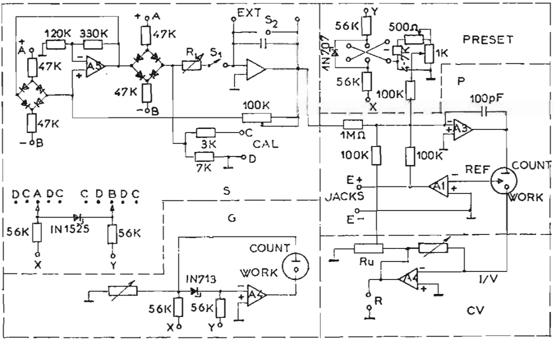

FIG. 1

Simplified circuit diagram

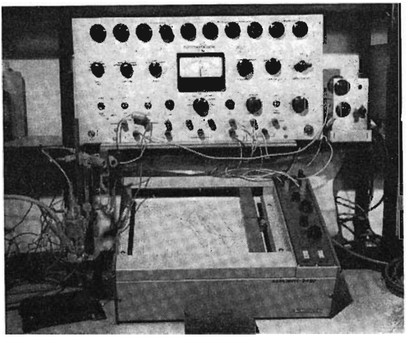

FIG. 2

Electrochemoscan

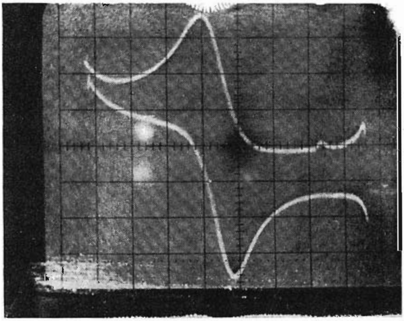

FIG. 3

Cyclic voltammogram — 1 mM-Eu in 1M-KSCN, scan rate 1·6 V s^{-1}

of europium in 0·1M-EDTA was studied at pH 9·5 using borax buffer, keeping the ionic strength constant at 1 by the addition of NaCl. The cyclic *i–E* curves for europium in chloride, bromide and iodide supporting electrolytes were recorded with X–Y recorder whereas for thiocyanate and EDTA systems a storage oscilloscope was used (Fig. 3*). The cathodic peak potential $(E_p)_c$, the anodic peak potential $(E_p)_a$ as also half-peak potential for the cathodic wave $(E_{p/2})_c$, were measured for the systems at various sweep rates and are included in Tables I–V.

Nicholson[14,15] has derived an expression for the calculation of standard rate constant k_s from the observed separation ΔE_p between the anodic $(E_p)_a$ and cathodic $(E_p)_c$ peak potential values of a cyclic voltammogram. In this method, a previous knowledge or actual measurement of the value of the standard or formal potential is not necessary. Further it is possible[15,16] to compute the transfer coefficient α from the values of the cathodic peak potential $(E_p)_c$ and the cathodic half-peak potential $(E_{p/2})_c$ by means of the relation

$$0{\cdot}048/[(E_{p/2})_c - (E_p)_c] = \alpha n\,. \qquad (1)$$

Nicholson[14] has shown that

$$\psi = v^{\alpha} k_s / \sqrt{(\pi a D_0)} \qquad (2)$$

with

$$v = (D_0/D_R)^{1/2}\,, \quad a = nF/RT\,, \qquad (3), (4)$$

where D_0 and D_R are the diffusion coefficients of the oxidised and reduced species. The symbol ψ is a function of ΔE_p and its value can be obtained by interpolation from Table I given by Nicholson[15]. The diffusivity values for the oxidised and reduced

TABLE I

Cyclic voltammetric data for Eu^{3+}/Eu^{2+} in 1M-KCl. 1 mM-Eu; pH 2·4; 30 ± 0·1°C. Area of HMDE 0·032 cm^2. Potentials *vs* S.C.E.

Scan rate $V\,s^{-1}$	$(E_p)_a$ V	$(E_p)_c$ V	$(E_{p/2})_c$ V	ΔE_p V	ψ	α	$k_s \,.\, 10^4$ $cm\,s^{-1}$
0·0154	−0·525	−0·730	−0·625	0·205	0·115	0·46	4·3
0·035	−0·495	−0·720	−0·625	0·225	0·090	0·50	5·0
0·037	−0·490	−0·720	−0·640	0·230	0·084	0·60	4·7
0·052	−0·475	−0·735	−0·640	0·260	0·068	0·50	4·6
0·055	−0·465	−0·730	−0·650	0·265	0·065	0·60	4·4

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* See insert facing p. 1776.

TABLE II

Cyclic voltammetric data for Eu^{3+}/Eu^{2+} in 1M-KBr. 1 mM-Eu; pH 2·4; 30 ± 0·1°C. Area of HMDE 0·032 cm^2. Potential *vs* S.C.E.

Scan rate V s^{-1}	$(E_p)_a$ V	$(E_p)_c$ V	$(E_{p/2})_c$ V	ΔE_p V	ψ	α	$k_s \cdot 10^3$ cm s^{-1}
0·0147	−0·558	−0·672	−0·602	0·114	0·41	0·69	1·3
0·0335	−0·558	−0·690	−0·606	0·132	0·29	0·57	1·4
0·0471	−0·556	−0·694	−0·598	0·138	0·26	0·50	1·5
0·0727	−0·550	−0·698	−0·600	0·148	0·22	0·49	1·6
0·1025	−0·548	−0·706	−0·608	0·158	0·19	0·49	1·6

TABLE III

Cyclic voltammetric data for Eu^{3+}/Eu^{2+} in 1M-KI. 1 mM-Eu; pH 2·4; 30 ± 0·1°C. Area of HMDE 0·032 cm^2. Potentials *vs* S.C.E.

Scan rate V s^{-1}	$(E_p)_a$ V	$(E_p)_c$ V	$(E_{p/2})_c$ V	ΔE_p V	ψ	α	$k_s \cdot 10^3$ cm s^{-1}
0·0162	−0·576	−0·660	−0·592	0·084	1·00	0·70	3·2
0·0350	−0·554	−0·644	−0·570	0·090	0·78	0·65	3·7
0·0536	−0·556	−0·650	−0·562	0·094	0·68	0·54	4·0
0·0765	−0·544	−0·642	−0·559	0·098	0·61	0·58	4·3
0·1120	−0·538	−0·638	−0·554	0·100	0·58	0·57	4·9

TABLE IV

Cyclic voltammetric data for Eu^{3+}/Eu^{2+} in 1M-KSCN. 1 mM-Eu; pH 2·4; 30 ± 0·1°C. Area of HMDE 0·032 cm^2. Potentials *vs* S.C.E.

Scan rate V s^{-1}	$(E_p)_a$ V	$(E_p)_c$ V	$(E_{p/2})_c$ V	ΔE_p V	ψ	α	$k_s \cdot 10^2$ cm s^{-1}
0·176	−0·605	−0·675	−0·605	0·07	2·5	0·69	2·5
0·224	−0·585	−0·660	−0·575	0·075	1·5	0·57	1·7
0·994	−0·570	−0·650	−0·580	0·08	1·2	0·68	2·8
1·560	−0·560	−0·650	−0·570	0·09	0·8	0·60	2·4

forms of europium in various media are needed for the computation of apparent rate constant by this method. In the present work the values of D_0 and D_R in chloride, bromide, iodide and thiocyanate media were taken from the data (Table VI) of earlier workers. The value of D_0 for europium in EDTA medium was determined polarographically as $4{\cdot}3 \,.\, 10^{-6}\ cm^2\ s^{-1}$ whereas D_0/D_R was assumed to be unity. The computed values of α and k_s for europium in different supporting electrolytes and at various scan rates are included in Tables I–V. It can be seen that the results are in good agreement with those reported (Table VI) by earlier workers on the basis of other methods.

TABLE V

Cyclic voltammetric data for Eu^{3+}/Eu^{2+} in 0·1M-EDTA. 1 mM-Eu; 0·075M borax; ionic strength[1] (NaCl); pH 9·5; 30 ± 0·1°C. Area of HMDE 0·032 cm^2. Potentials *vs* S.C.E.

Scan rate $V\ s^{-1}$	$(E_p)_a$ V	$(E_p)_c$ V	$(E_{p/2})_c$ V	ΔE_p V	ψ	α	$k_s \,.\, 10^2$ $cm\ s^{-1}$
0·123	−1·155	−1·230	−1·160	0·075	1·6	0·68	1·3
0·179	−1·155	−1·230	−1·160	0·075	1·6	0·68	1·5
0·225	−1·155	−1·230	−1·167	0·075	1·6	0·66	1·7
0·996	−1·140	−1·240	−1·170	0·100	0·58	0·68	1·3
1·562	−1·145	−1·260	−1·190	0·115	0·39	0·68	1·3

TABLE VI

Diffusivity values and kinetic parameters for europium

Supporting electrolyte	D_{O2} $10^6\ cm^2\ s^{-1}$	D_R $10^6\ cm^2\ s^{-1}$	k_s cm^{-1}	α	Ref.
1M-KCl	8·5	11·5	$(3{\cdot}2-4{\cdot}9) \,.\, 10^{-4}$	0·59	2
			$2{\cdot}1 \,.\, 10^{-4}$	—	4
			$1{\cdot}7 \,.\, 10^{-4}$	0·53	22
1M-HBr	6·8	8·6	—	—	23
1M-KI	6·3	8·3	$(2{\cdot}8-4) \,.\, 10^{-3}$	0·5 —0·6	1
			$1{\cdot}6 \,.\, 10^{-3}$	—	4
1M-KSCN	5·6	7·3	$(2{\cdot}6-3{\cdot}3) \,.\, 10^{-2}$	0·59—0·63	2
			$8 \,.\, 10^{-3}$	—	4
			$1{\cdot}5 \,.\, 10^{-2}$	—	9
0·1M-EDTA	4·3[a]	—	$1{\cdot}6 \,.\, 10^{-2}$	9·62	26

[a] Denotes present work.

The results of the present study indicate that the apparent rate constant and hence the d.c. polarographic reversibility of Eu^{3+}/Eu^{2+} system increases in the order $Cl^- < Br^- < I^- < EDTA \leqq SCN^-$. Of these ligands only EDTA forms with Eu^{3+} a stable chelate with coordination number 1 and log β equal to 17·4 (Schwarzenbach and coworkers[17]). The appreciable free energy change due to chelation shifts the peak potentials of europium to more negative values and also increases the rate constant for the electrode reaction[18]. It is possible that in this case the electron transfer proceeds through an outersphere activated complex mechanism.

On the contrary Eu^{3+} forms only weak complexes or ion pairs with thiocyanate and halides, the formation constants being 2·9, 0·9, 0·65 and 0·5 for thiocyanate, chloride, bromide and iodide respectively[19].

The half wave potential for the reduction of Eu^{3+} shifts to more positive values in the order $SCN^- > I^- > Br^- > Cl^-$ (ref.[7]) and this trend is in agreement with the corresponding increase in polarizability of the ligands. It appears that with these systems a bridged activated complex is involved in the electrode process, the ligand – bridge serving as a conducting link for electron transfer between the oxidised and reduced species. Radioactive tracer studies[20] on the homogeneous electron exchange reaction between Eu^{2+} and Eu^{3+} in HCl medium indicate that the rate-determining step involves aquated monochloro species of europium. The observed trend in the values of the apparent rate constant for europium in these systems is suggestive of a ligand-bridged electron transfer mechanism in which the normal bridging order $SCN^- > I^- > Br^- > Cl^-$ is maintained.

The effect of anions on the kinetics of electron transfer processes is complex and can involve nonspecific interactions arising from coulombic forces within the double layer and/or specific effects arising from complex formation and ligand bridging. While considering the influence of water molecules in governing the potential distribution close to the electrode surface one cannot preclude the possible effect due to reorientation and exchange of coordinated water on the electrode kinetics[22]. A significant question that remains unsettled is the exact nature of the europium species which participate in the rate-determining step of the electrode reaction in various media. Actually europium undergoes electrode reaction in a potential region where Cl^-, Br^-, I^- and SCN^- anions are strongly adsorbed on the electrode. De Kreuk and coworkers[1,2] applied Frumkin correction based on the value of Φ_2 potential in the presence of halide and thiocyanate supporting electrolytes. They obtained true rate parameters for Eu^{3+}/Eu^{2+} reaction which were constant and essentially potential independent only for chloride and iodide systems. The computed value of the true rate constant in thiocyanate medium was an order of magnitude higher and the results showed better consistency for a model based on participation of europium monothiocyanato species in the charge transfer step. Weaver and Anson[3], however, support a ligand-bridged pathway in which a thiocyanate moiety is attached to both mercury and europium. It is clear that further work is needed for a better understanding of the electrochemical behaviour of europium in various media.

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