Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 89, Number 4, August 1980, pp. 381–385.

Electrode kinetics of Eu^{3+}/Eu^{2+} reaction by cyclic voltammetry

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MS received 12 November 1979; revised 30 May 1980

Abstract. The cyclic voltammetric behaviour of Eu^{3+}/Eu^{2+} couple at hanging mercury drop electrode (HMDE) has been studied in chloride, bromide, iodide, thiocyanate and EDTA supporting electrolytes. The apparent rate constant and transfer coefficient for these systems have been calculated at various voltage scan rates, without using the data for standard or formal potential. The values have been compared with those obtained by earlier workers through other electrochemical methods.

Keywords. Cyclic voltammetry; rate constant; europium; halides; thiocyanate; EDTA.

1. Introduction

The nuances in electrode behaviour of Eu^{3+}/Eu^{2+} systems have been investigated earlier by techniques like polarography, impedance measurement, chronopotentiometry and chronocoulometry (Gierst and Cornelissen 1960; Kinard and Philp 1970; Randles and Somerton 1952; Weaver and Anson 1975; De Kreuk *et al* 1970, 1971; Radhakrishnan and Sundaram 1972; Rodgers and Anson 1973). This paper deals with the cyclic voltammetric behaviour of Eu^{3+} at HMDE in solutions of 1M KCl, KBr, KI, KSCN and also in 0·1 M EDTA. The values of apparent rate constant (k_s) and transfer coefficient (α) have been computed without using formal potential data and the results are compared with those obtained by other methods.

2. Experimental

Cyclic voltammograms were recorded with a multipurpose instrument called Electrochemoscan (Kapre and Radhakrishnan 1979) 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 Santhanam (1971) and has in addition, positive feedback IR drop compensation facility. The voltammograms, corresponding to low scan rates were recorded on an X–Y recorder (Rikadenki

Kogyo Co., Japan, Model BW 133) at sensitivity 20 mV sec^{-1}, after backing off a 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 sec^{-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 (Damokos and Juhasz 1966) 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 (0·02 M) of europium was obtained by dissolution of pure Eu_2O_3 (Rare Earth Products, England) in HCl and fuming thrice with perchloric acid. The exact strength was checked by titration (Woyski and Harris 1963) with standard EDTA using xylenol orange as indicator. Other chemicals used were either G.R. or AnalaR grade.

3. Results and discussion

Cyclic voltammograms were obtained for 1 mM solution of Eu(III) in 1 M KCl, 1 M KBr, 1 M KI and 1 M KSCN at pH 2·4 and different scan rates. The behaviour of europium in 0·1 M 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 an X–Y recorder whereas for thiocyanate and EDTA systems a storage oscilloscope was used. The photographic replica of a typical cyclic voltammogram for Eu(III) in 1 M KSCN is shown in figure 1. The cathodic

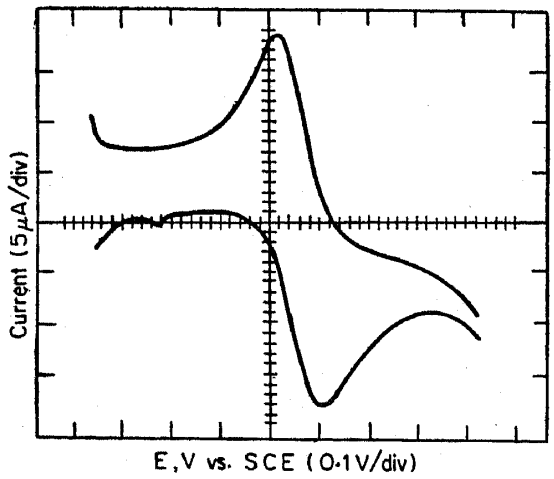

Figure 1. Cyclic voltammogram—1 mM Eu in 1 M KSCN, scan rate 1·6 V sec^{-1},

peak potential $(E_p)_c$, the anodic peak potential $(E_p)_a$ as also the half-peak potential for the cathodic wave, $(E_{p/2})_c$, were measured for all the systems at various sweep rates and are included in tables 1 and 2.

Table 1. Cyclic voltammetric data for Eu^{3+}/Eu^{2+} in KCl, KBr and KI. Eu = 1 mM; pH = 2·4; temperature = 30 ± 0·1° C; area of HMDE = 0·032 cm^2.

Supporting electrolyte	Scan rate V sec^{-1}	$(E_p)_a$ V vs SCE	$(E_p)_c$ V vs SCE	$(E_{p/2})_c$ V vs SCE	$\triangle E_p$ V	ψ	α	k_s cm. sec^{-1}
1 M KCl	0·0154	−0·525	−0·730	−0·625	0·205	0·115	0·46	$4·3 \times 10^{-4}$
	0·037	−0·490	−0·720	−0·640	0·230	0·084	0·60	$4·7 \times 10^{-4}$
	0·052	−0·475	−0·735	−0·640	0·260	0·068	0·50	$4·6 \times 10^{-4}$
	0·055	−0·465	−0·730	−0·650	0·265	0·065	0·60	$4·4 \times 10^{-4}$
1 M KBr	0·0147	−0·558	−0·872	−0·602	0·114	0·41	0·69	$1·3 \times 10^{-3}$
	0·0335	−0·558	−0·690	−0·606	0·132	0·29	0·57	$1·4 \times 10^{-3}$
	0·0471	−0·556	−0·694	−0·596	0·138	0·26	0·50	$1·5 \times 10^{-3}$
	0·0727	−0·550	−0·698	−0·600	0·148	0·22	0·49	$1·6 \times 10^{-3}$
	0·1025	−0·548	−0·706	−0·608	0·158	0·19	0·49	$1·6 \times 10^{-3}$
1 M KI	0·0162	−0·576	−0·660	−0·592	0·084	1·00	0·70	$3·2 \times 10^{-3}$
	0·0350	−0·554	−0·644	−0·570	0·090	0·78	0·65	$3·7 \times 10^{-3}$
	0·0536	−0·556	−0·650	−0·562	0·094	0·68	0·54	$4·0 \times 10^{-3}$
	0·0765	−0·544	−0·642	−0·559	0·098	0·61	0·58	$4·3 \times 10^{-3}$
	0·1120	−0·538	−0·638	−0·554	0·100	0·58	0·57	$4·9 \times 10^{-3}$

Table 2. Cyclic voltammetric data for Eu^{3+}/Eu^{2+} in KSCN and EDTA. Eu = 1 mM; temperature = 30 ± 0·1° C; area of HMDE = 0·032 cm^2.

Supporting electrolyte	Scan rate V sec^{-1}	$(E_p)_a$ V vs SCE	$(E_p)_c$ V vs SCE	$(E_{p/2})_c$ V vs SCE	$\triangle E_p$ V	ψ	α	k_s cm. sec^{-1}
1 M KSCN	0·176	−0·605	−0·675	−0·605	0·07	2·5	0·69	$2·5 \times 10^{-2}$
pH = 2·4	0·224	−0·585	−0·660	−0·575	0·075	1·5	0·57	$1·7 \times 10^{-2}$
	0·994	−0·570	−0·650	−0·580	0·08	1·2	0·68	$2·8 \times 10^{-2}$
	1·560	−0·560	−0·650	−0·570	0·09	0·8	0·60	$2·4 \times 10^{-2}$
0·1 M EDTA + 0·075 M	0·123	−1·155	−1·230	−1·160	0·075	1·6	0·68	$1·3 \times 10^{-2}$
Borax(μ = 1)	0·179	−1·155	−1·230	−1·160	0·075	1·6	0·68	$1·5 \times 10^{-2}$
pH = 9·5	0·225	−1·155	−1·230	−1·167	0·075	1·6	0·66	$1·7 \times 10^{-2}$
	0·996	−1·140	−1·240	−1·170	0·100	0·58	0·68	$1·3 \times 10^{-2}$
	1·562	−1·145	−1·260	−1·190	0·115	0·39	0·68	$1·3 \times 10^{-2}$

The rate constant k_s was determined from the working curve of Nicholson (1965) in which the peak-to-peak separation $\triangle E_p$ is plotted against ψ. Some relevant relations are

$$\psi = \gamma^{\alpha} k_s/(\pi a D_O)^{1/2}, \tag{1}$$

$$\gamma = (D_O/D_R)^{1/2}, \tag{2}$$

and $$a = nFv/RT, \tag{3}$$

where v is the scan rate and D_O and D_R are the diffusion coefficients of the oxidised and reduced species respectively. The transfer coefficient α was determined from the relation (Nicholson and Shain 1964; Adams 1969).

$$[(E_{p/2})_c - (E_p)_c]/0{\cdot}048 = \alpha n. \tag{4}$$

In the present work the values of D_O and D_R in chloride, bromide, iodide and thiocyanate media were taken from the data (table 3) of earlier workers. The value of D_O for europium in EDTA medium was determined polarographically as $4{\cdot}3 \times 10^{-6}$ cm^2 sec^{-1}, whereas D_O/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 1 and 2. It can be seen that the results are in good agreement with those reported (table 3) by earlier workers on the basis of other methods.

The results of the present study indicate that for Eu^{3+}/Eu^{2+} system k_s increases in the order : $Cl^- < Br^- < I^- < EDTA \leqslant SCN^-$. Of these ligands only EDTA forms with Eu^{3+} a stable chelate (Schwarzenbach *et al* 1954). It is possible that in this case the electron transfer proceeds through an outer sphere activated complex mechanism.

Table 3. Diffusivity values and kinetic parameters for europium.

Supporting electrolyte	D_O 10^6 cm^2 sce^{-1}	D_R 10^6 cm^2 sec^{-1}	k_s cm^{-1}	α	Citation
1 M KCl	8·5	11·5	$(3{\cdot}2$–$4{\cdot}9) \times 10^{-4}$	0·59	De Kreuk *et al* (1971)
			$2{\cdot}1 \times 10^{-4}$	..	Randles and Somerton (1952)
			$1{\cdot}7 \times 10^{-4}$	0·53	Chandrasekaran and Sundaram (1971)
1 M HBr	6·8	8·6	..	..	Niki and Mizota (1976)
1 M KI	6·3	8·3	$(2{\cdot}8$–$4) \times 10^{-3}$	0·5–0·6	De Kreuk *et al* (1970)
			$1{\cdot}6 \times 10^{-3}$	..	Randles and Somerton (1952)
1 M KSCN	5·6	7·3	$(2{\cdot}6$–$3{\cdot}3) \times 10^{-2}$	0·59–0·63	De Kreuk *et al* (1971)
			8×10^{-3}	..	Randles and Somerton (1952)
			$1{\cdot}6 \times 10^{-2}$	..	Rodgers and Anson (1973)
0·1 M EDTA	4·3*	..	$1{\cdot}6 \times 10^{-2}$	0·62	Kisova *et al* (1972)

* Denotes present work.

Europium(III) forms only weak complexes with thiocyanate, chloride, bromide and iodide, the formation constants being 2·9, 0·9, 0·65, and 0·5 respectively (Rodgers and Anson 1973; Choppin and Ketels 1965). It is apparent that the observed dependence of k_s for europium in these systems cannot be explained on the basis of the relative tendencies of these anions for complex formation. Radioactive tracer studies (Meir and Garner 1952) on the homogeneous electron exchange between Eu^{2+} and Eu^{3+} in HCl medium indicate that the rate determining step involves aquated monochloro species of europium. Further for Eu–SCN system there is evidence (De Kreuk *et al* 1971; Weaver and Anson 1975) to show that $Eu(SCN)^{++}$ species are involved in a bridged electron-transfer process in which a thiocyanate moiety is attached to both mercury and europium. Kinard and Philp (1970) who employed Kalousek polarography to study Eu^{3+}/Eu^{2+} reaction in various media showed that the reversibility increased in the order $SCN^- > I^- > Br^- > Cl^-$. It appears reasonable to conclude that a ligand-bridged activated complex is involved in Eu^{3+}/Eu^{2+} reaction. The observed trend of k_s which is also the trend of these anion polarisabilities is in accord with this view.

Acknowledgement

The authors are thankful to Dr M Sankar Das, Analytical Chemistry Division, for his interest in the work.

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