

POLAROGRAPHY OF EUROPIUM IN AQUEOUS AND AQUEOUS METHANOLIC SOLUTIONS

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ABSTRACT

The standard rate constants for the reduction of europium in perchlorate and chloride media and the formal rate constants in sulphate, acetate and lactate solutions are reported. The rate increases in the order of increasing polarisability of the anion or the increasing stability of the complex, viz., perchlorate < sulphate < lactate \approx acetate.

The effect of methanol on the polarography of europium has been studied. In perchlorate and chloride media, the half-wave potential shifts to negative values and then to positive values as the methanol content is increased. In acetate solutions, the shift is continuously to negative potentials. This is attributed to the effect of complex formation in acetate media and ion-pairing in perchlorate and chloride media. The effect of viscosity on the diffusion current was found to obey the Stokes-Einstein equation.

INTRODUCTION

THE reduction of europium (III) to europium (II) involves a change in the inner 4f shell. The reduction is therefore expected to be irreversible.¹ The chemical composition of the supporting electrolyte should have little effect on the nature of the electrode process since the outermost shell would remain unaltered in the reduction. It is interesting, however, to note that the rate of the electrode process is altered by the kind and concentration of the anion in the supporting electrolyte. The effect of the solvent is also considerable, the electrode process being reversible in acetonitrile,² quasi-reversible in aqueous ethanol³ and irreversible in acetone.⁴ A study of the polarography of europium in complexing and non-complexing media in aqueous and methanolic solutions is reported here.

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EXPERIMENTAL

Current-potential curves were obtained with a manual polarograph using a three-arm electrolysis cell and a saturated calomel electrode (S.C.E.) as the reference electrode. Divalent europium was obtained *in situ* by constant potential electrolysis using a potentiostat.⁵ Measurement of pH was made with a Cambridge Bench type pH meter. Experiments were carried out at $30 \pm 0.5^\circ \text{C}$ with a dropping mercury electrode having a drop-time of 6.4 sec. and a flow-rate of 1.2 mg. of mercury per sec.

A stock solution of europium (III) perchlorate was prepared from the oxide (M/s. Rare Earth Products Ltd., England). Other chemicals were of reagent grade. Methanol (E. Merck, G. R.) was used without further purification as there was no significant change in the residual current with the sample redistilled over fused calcium chloride. The test solutions contained about 2 mM perchloric acid to prevent hydrolysis of europium in chloride and perchlorate media.

RESULTS AND DISCUSSION

The half-wave potentials in aqueous solutions of perchlorate, chloride, sulphate, acetate and lactate are shown in Fig. 1. Since complex formation

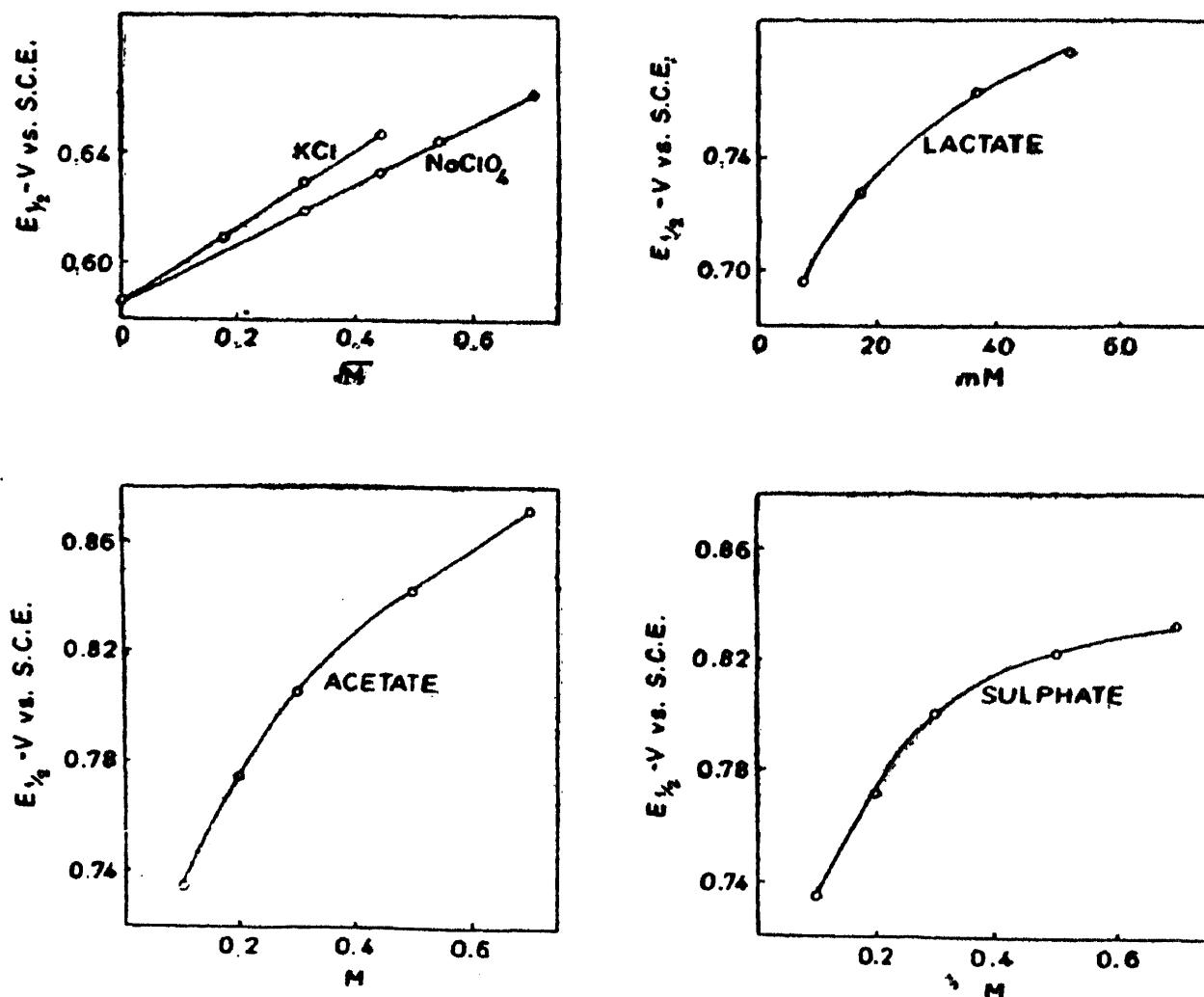


FIG. 1. $E_{1/2}$ Vs. Concentration of Ligand,

in perchlorate and chloride media could be considered negligible, a plot of $E_{\frac{1}{2}}$ vs. the square-root of the ionic strength was extrapolated to zero ionic strength to obtain the standard potential, viz., -0.586 V vs. S.C.E. This value agrees with the values of -0.592 V vs. S.C.E., in 0.05 M sodium perchlorate, reported by Gierst and Cornelissen⁶ and -0.35 V vs. N.H.E., reported by Anderson and Macero.⁷ The value of -0.43 V vs. N.H.E., reported by McCoy⁸ applies only for the europium-formate system.

The rate constants were calculated by the methods of Koutecky⁹ and Randles.¹⁰ In Koutecky's method, $\log K_f$, obtained from the experimental values of i/i_d and the tabulated values of $F(X)$ and X was plotted against the applied potential, E . The rate constant (Table I) was read off at the standard potential in perchlorate and chloride media and at the formal potential, obtained from the composite polarograms, in other media. The standard potential could not be obtained from the polarographic data in these solutions because of complexation. In Randles' method, the rate constant was obtained¹¹ from a plot of $\log h/1 + \exp \beta\eta$ vs. η , the overpotential.

TABLE I

Rate constants for europium in aqueous media

M	Rate constant $\times 10^4$ cm./sec.			
	Chloride	Perchlorate	Sulphate	Acetate
0.05	74
0.10	..	3.8	3.4	12.6
0.20	37	2.3	4.5	9.3
0.30	2.1	2.0	5.3	6.6
0.50	1.8	1.5	..	4.1
0.70	3.5
1.0	1.7	1.7

The standard rate constant reported in this work in chloride solutions agrees with Randles' value of 2.1×10^{-4} cm. sec.⁻¹ in 1 M potassium chloride

by the a.c. impedance method.¹² A value of 4×10^{-4} cm. sec.⁻¹ has been reported for 1M perchloric acid.¹³ The formal rate constant for lactate solutions in the range of 0.01 to 0.06 M has been calculated to be $(1.6 \pm 0.4) \times 10^{-3}$ cm. sec.⁻¹. The rate constants obtained for chloride solutions indicate that the reduction of europium approaches reversibility at low concentrations of chloride. The value generally decreases with the increasing concentration of the anion. The rate constant increases in the order of increasing polarisability of the anion or the increasing stability of the europium complexes, *viz.*, perchlorate < sulphate < lactate \approx acetate.

The formal potential, E_f° , in acetate and lactate media was more negative than in perchlorate solutions indicating complexation. The concentrations of the acetate and lactate ions were calculated from the pH of the solution and the corresponding pK values (4.76 for acetate¹⁴ and 3.86 for lactate¹⁵). The plot of E_f° vs. pA (Fig. 2) gave a straight line with the value of two corresponding to the change in the number of ligands attached to the depolariser during reduction. Hence the electrode reaction can be written as



or

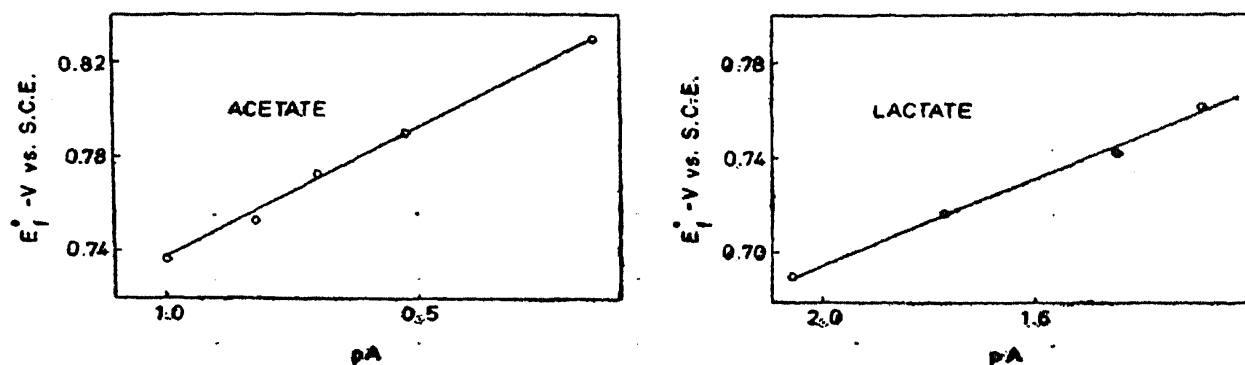


FIG. 2. Plot of E_f° Vs. pA.

where A represents the ligand. The latter reaction is more likely since the large size and small charge of divalent europium do not favour¹⁶ complex formation. Since it has been reported¹⁷ that $\text{Eu}(\text{CH}_3\text{COO})_3$ is the predominant species in the solution under the experimental conditions, it appears that the europium complex undergoes a structural change prior to the electrode reaction.

The reduction of europium was studied in aqueous methanolic solutions of perchlorate, chloride and acetate containing 25, 50 and 75 per cent (V/V) methanol. The results are given in Fig. 3. In perchlorate and chloride media, the half-wave potential shifted at first to negative and then to positive values with the increase in concentration of methanol. In acetate solutions the shift was towards negative potentials. If the free energy of transfer, ΔG° , of one mole of solute from a solvent of dielectric constant ϵ_1 to another of dielectric constant ϵ_2 is purely electrostatic in nature, we have, according to Born's equation,¹⁸

$$\Delta G^\circ = \frac{Ne^2}{2r} \left[\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1} \right] \quad (3)$$

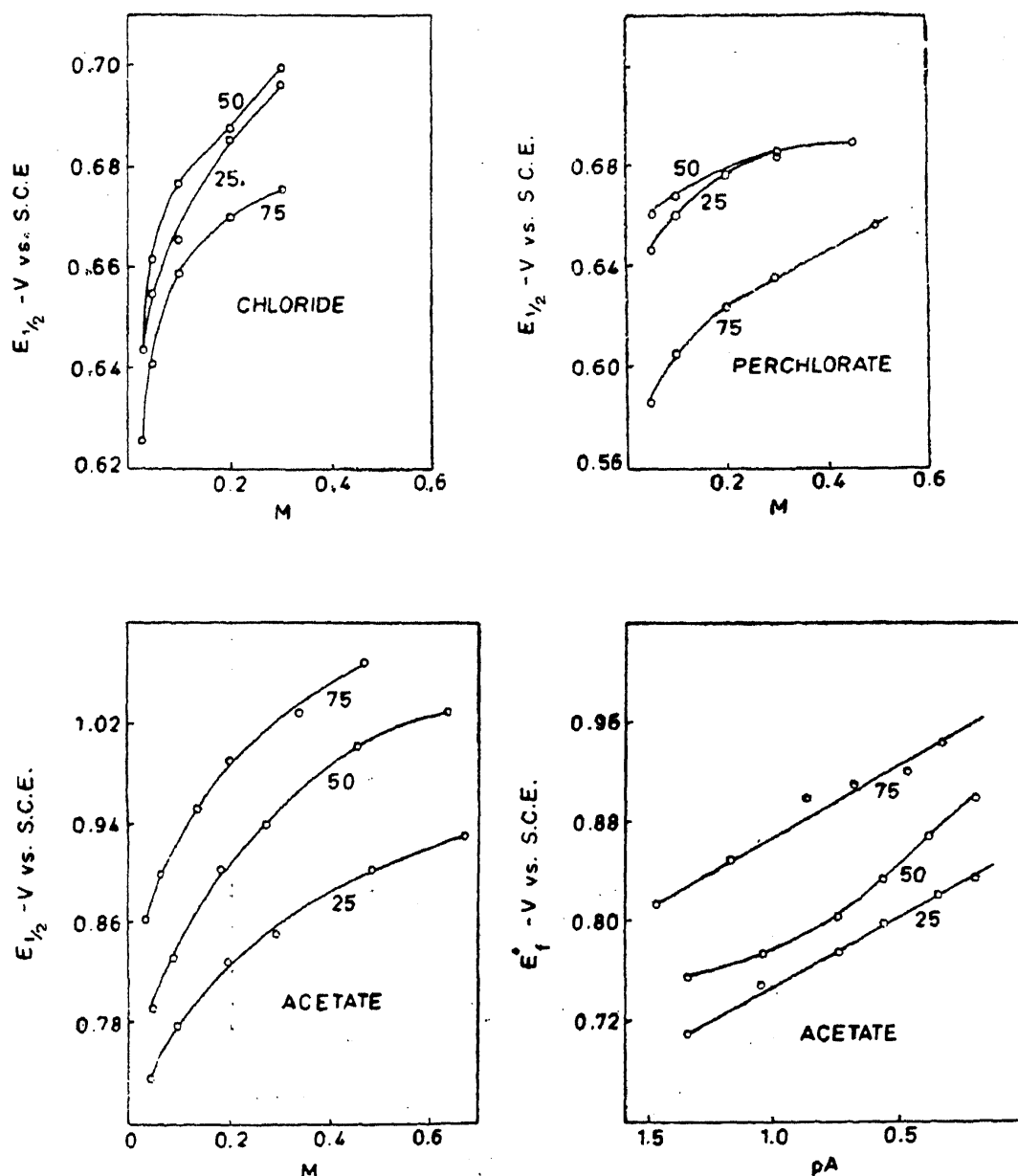


FIG. 3. $E_{1/2}$ and E° , in Methanol.

where r is the radius of the solute ion or molecule, N is the Avagadro number and e is the electronic charge. The free energy of transfer can also be written in terms of the standard/formal potentials as

$$\Delta G^\circ \simeq F \Delta E_f^\circ \quad (4)$$

Deviations from the linear dependence of ΔG° on the reciprocal of the dielectric constant occur when the effect of the solvent is not purely electrostatic in nature. The dependence of the formal potential on the dielectric constant¹⁹ in perchlorate, chloride and acetate media is shown in Fig. 4. In perchlorate and chloride media, the formal potential is shifted to positive values while the shift is to negative potentials in acetate media. These results can be interpreted on the basis of complex formation. The large size of the europium acetate complex favours the arrangement of methanol molecules around the solute at high methanol content. This causes a decrease in the free energy resulting in the shift of the formal/half-wave potentials to negative values. In perchlorate and chloride media, ion-pairing may occur in the double layer at high concentrations of methanol resulting in a

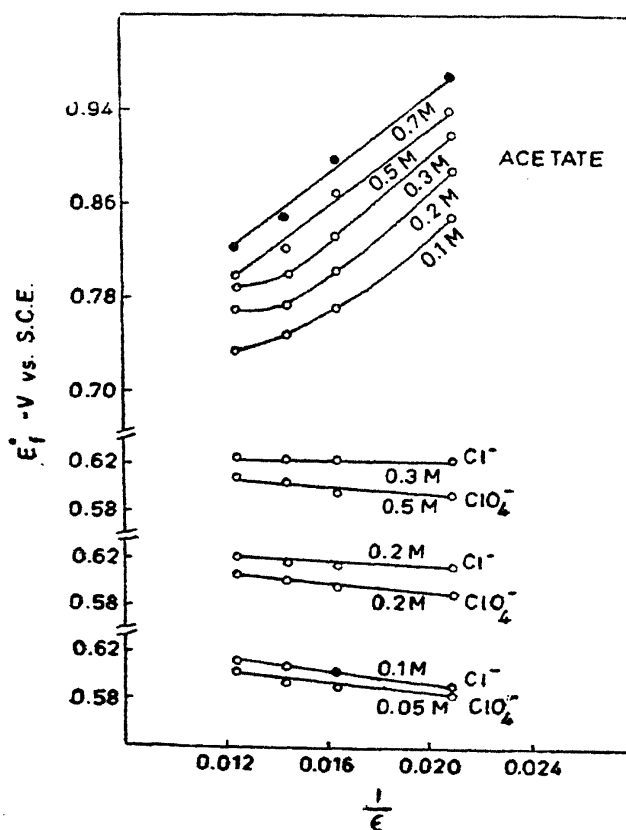


FIG. 4. Plot of E_f° Vs. ϵ^{-1} .

decrease of the repulsion between the electrode and the europium ion. Hence the rate of reduction is enhanced and the half-wave potential is shifted to positive values.

The standard potential in aqueous methanolic solutions of perchlorate and chloride was found to be the same as that in aqueous solutions. The standard rate constants were calculated for these media whereas only formal rate constants were calculated for acetate solutions. The rate constants (Table II) in aqueous methanol indicate that the electrode reaction is quasi-reversible.

TABLE II

Rate constants for europium in methanol media

Methanol %	Rate constant $\times 10^4$ cm./sec.								
	25			50			75		
M	0.05	0.20	0.50	0.05	0.20	0.50	0.05	0.20	0.50
Chloride	1.9	0.8	0.6	1.9	1.1	0.6	3.0	1.7	..
Perchlorate	2.9	1.8	1.3	2.1	1.5	0.8	12.5	3.3	1.6
Acetate	4.5	2.8	2.0	3.4	1.0	0.9	3.2	1.9	1.3

The nature of the europium acetate complex in aqueous methanol was studied by plotting E°_f vs. $\log(\text{acetate})$ using the pK values²⁰ for acetic acid in aqueous methanol (Fig. 3). The plot resulted in a straight line for 25 and 75 per cent methanol with a value of two for the change in the number of ligands as in aqueous solutions. A curve was obtained for 50 per cent methanol indicating the presence of more than one species.

The change in the viscosity of the solvent alters the diffusion coefficient of the electroactive species and hence the diffusion current. According to Stokes-Einstein equation,²¹ the diffusion current, i_d , is inversely proportional to the square root of the viscosity, η , of the solution. Hence the product

$i_d\eta^{\frac{1}{2}}$, should be a constant. This has been verified for the system under study (Table III).

The reduction of europium occurs at potentials close to the point of zero charge of mercury and hence the polarographic behaviour will be influenced significantly by double layer effects. This has not been taken into account in the present work and will form the subject for further studies.

TABLE III
Effect of viscosity on the diffusion current

		Methanol per cent			
		0	25	50	75
KCl	i_d (μ A)	1.45	1.15	1.08	1.09
	* $i_d\eta^{\frac{1}{2}}$	4.3	4.2	4.2	3.8
NaClO ₄	i_d (μ A)	1.51	1.28	1.11	1.15
	$i_d\eta^{\frac{1}{2}}$	4.5	4.7	4.4	4.0
NaOOCCH ₃	i_d (μ A)	1.41	1.14	1.01	1.11
	$i_d\eta^{\frac{1}{2}}$	4.2	4.2	4.0	3.9

* η values obtained from Reference 22.

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