# Polarography of europium(III) in water-dimethylformamide mixtures

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Abstract. The kinetics of the electrochemical reduction of europium(III) in water-N, N dimethyl formamide mixtures in potassium chloride medium has been studied. The formal rate constant for the reduction increases markedly from $10^{-4}$ cm sec$^{-1}$ in low concentrations to $10^{-2}$ cm sec$^{-1}$ at high concentrations of the solvent. The effects of solvent on the formal potential and diffusion current are discussed.

Keywords. Polarography ; europium ; dimethylformamide.

## 1. Introduction

The effect of solvents on the kinetics of electrode processes is of interest since any change in the coordination shell of the depolariser during electron transfer may contribute to the activation energy, due to the energy required for reorganisation of the solvent molecules of the reactant and product. The effect of solvents on the reduction of europium(III), proposed as a model for simple electrode reactions, has been studied by polarographic and other electrochemical techniques in non-aqueous solvents (Coetzee and Wei-San Siao 1963; Gritzner et al 1965; Gutmann and Peychal-Heiling 1969; Cokal and Wise 1966; Hush and Dyke 1974) as well as mixed solvents containing water as one component (Almagro et al 1966; Rabockai and Jordan 1974; Behr et al 1979). The present paper describes the polarographic behaviour of europium(III) in water-N, N-dimethylformamide (DMF) mixtures containing potassium chloride so as to enable the variation of dielectric constant and viscosity over a wide range and also to ensure fairly high solubility for the supporting electrolyte thereby minimising both mass transfer by migration and iR drop.

## 2. Experimental

A manual polarograph with three electrodes was used for the current-potential measurements. The d.c. potential was applied between the dropping mercury

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electrode (DME) and mercury pool and the effective potential was measured across the DME and a saturated calomel electrode using a digital voltmeter (M/s PLA Electro Appliances, Model DPM-1). The saturated calomel electrode was connected to the electrolysis cell through an agar-saturated potassium chloride bridge. A potentiostat based on the circuit of Greenough *et al* (1951) was used for the electrolytic generation of europium(II) *in situ*. Measurements were made at 30 ± 0·5° C with a capillary having the following characteristics: $m = 1\cdot07$ mg/sec and $\tau = 5\cdot0$ sec (open circuit). No maximum suppressor was found necessary. Deaeration of the test solutions was carried out with nitrogen presaturated with the same solvent mixture. The currents reported here have been corrected for the residual current.

A stock solution of europium was prepared by dissolving europium oxide (M/s Rare Earth Products Ltd., England; greater than 99·9% purity) in 1:1 hydrochloric acid, evaporating to dryness, fuming with perchloric acid (Baker analysed reagent; 70%) and dissolving in double-distilled water. The europium content was estimated gravimetrically as oxide as well as by titration with EDTA. The final test solution was 0·1 mM with respect to perchloric acid.

DMF (Koch–Light Laboratories Ltd., England) was used without further purification and potassium chloride (E. Merck, G.R.) was recrystallised twice from double-distilled water.

## 3. Results and discussion

Cathodic and composite polarograms were obtained in 25, 50 and 75% (V/V) DMF at different concentrations of potassium chloride, in the range of 0·1 to 1·0 M, as the supporting electrolyte. The limited solubility of potassium chloride at higher concentrations of DMF, however, restricted the measurements to 0·7 M and 0·3 M in 50 and 75% DMF respectively. A few typical polarograms, which are well-defined, are shown in figure 1. For a given composition of the
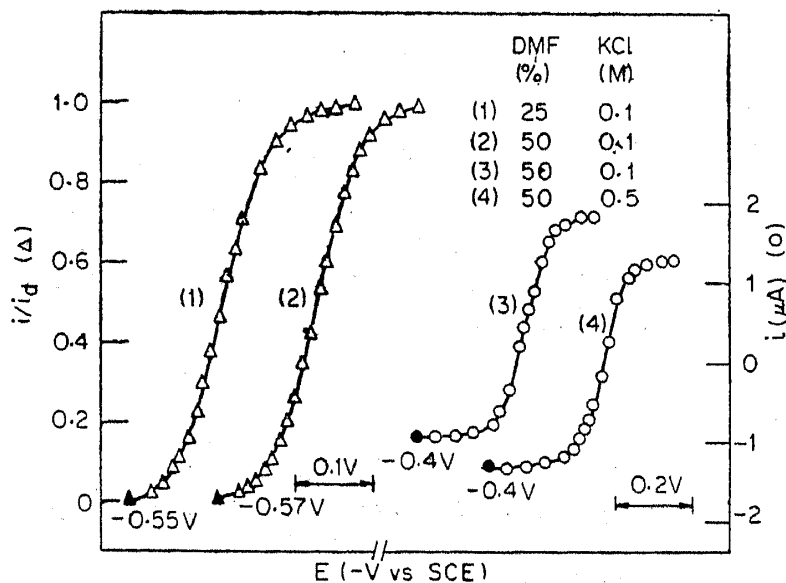


**Figure 1.** Cathodic and composite polarograms.

solvent, the polarograms were increasingly drawn out with increasing concentrations of the supporting electrolyte for 25 and 50% DMF, as indicated by the slope of the log-plots. The shape of the polarograms and the values of slope did not vary with the concentration of potassium chloride in 75% medium where the reduction approached d.c. reversibility as indicated by the log-plot (table 1). The extent of acceleration of the electrode reaction was determined quantitatively by calculating the kinetic parameters. The reversible potential, $E_\gamma$, was determined at the zero current from the S-shaped composite polarograms (figure 1) and the formal potential, $E_f^o$, was calculated from

$$E_r = E_f^o + \frac{RT}{nF} \ln \frac{(i_d)_c}{(i_d)_a},$$

(1)

where $(i_d)_c$ and $(i_d)_a$ refer to the cathodic and anodic diffusion currents respectively. The kinetic parameters were calculated by the method of Randles (1959) using the expression (Sathyanarayana 1964),

$$\log \frac{h}{1 + \exp f\eta} = \log \left[ \left( \frac{3}{7D} \right)^{\frac{1}{2}} k_s \right] - \frac{a f \eta}{2 \cdot 303},$$

(2)

where $\eta$ refers to the overvoltage, $a$ is the transfer coefficient, $k_s$ is the formal rate constant and $f$ is given by $nF/RT$. The formal rate constant was calculated from the intercept of a plot of (figure 2) log $[h/1 + \exp f\eta]$ as a function of $\eta$, using the diffusion coefficient calculated from the cathodic polarograms. The formal rate constant decreased with increasing concentrations of potassium chloride for 25 and 50% DMF (table 1). The reduction was quasireversible with the rate constant of $10^{-4}$ cm sec$^{-1}$ while a rapid increase in the rate constant was observed for the reduction in 75% medium. The acceleration of the rate of reduction confirmed the slope of 60 mV observed for the log plots.

Increase in the rate constant for the reduction of europium(III) in water–DMF mixtures has been attributed by Behr *et al* (1979) to preferential solvation of europium ions by DMF. The reduction of europium in water-formamide mixtures, reported by Rabockai and Jordan (1974), indicates that double layer effects
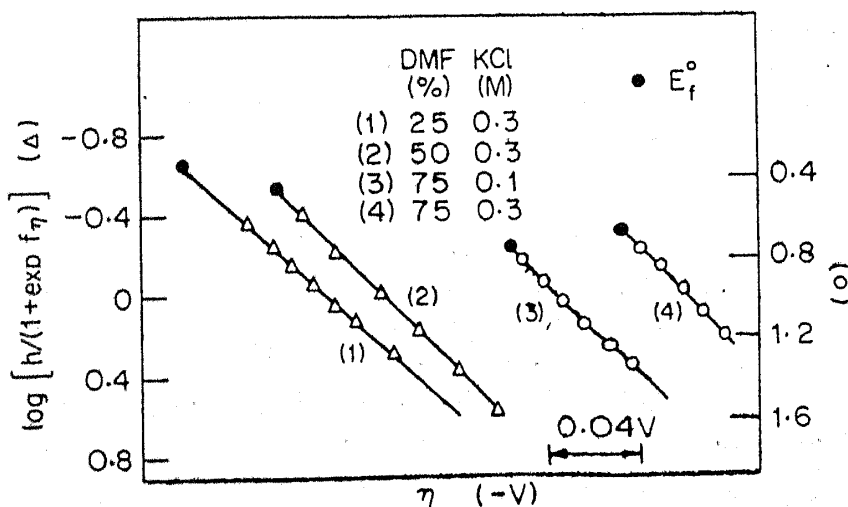


Figure 2. Determination of kinetic parameters.

**Table 1.** Values of kinetic parameters.

| DMF Vol. % | KCl $M$ | $i_d/C$ $\mu A/mM$ | $E_{1/2}$ $-V$ vs | $E_f^o$ S.C.E. | Slope mV | $k_s \times 10^3$ cm/sec. | $\alpha$ |
|---|---|---|---|---|---|---|---|
| 25 | 0·1 | 1·99 | 0·672 | 0·658 | 66 | 0·12 | 0·55 |
|    | 0·3 | 1·97 | 0·682 | 0·666 | 68 | 0·07 | 0·57 |
|    | 0·5 | 1·96 | 0·697 | 0·683 | 73 | 0·06 | 0·57 |
|    | 1·0 | 1·96 | 0·710 | 0·696 | 74 | 0·05 | 0·54 |
| 50 | 0·1 | 1·21 | 0·697 | 0·685 | 62 | 0·07 | 0·64 |
|    | 0·3 | 1·21 | 0·702 | 0·689 | 68 | 0·06 | 0·62 |
|    | 0·5 | 1·20 | 0·710 | 0·694 | 70 | 0·05 | 0·62 |
|    | 0·7 | 1·19 | 0·714 | 0·700 | 72 | 0·04 | 0·61 |
| 75 | 0·1 | 1·27 | 0·716 | 0·716 | 60 | 1·32 | 0·65 |
|    | 0·2 | 1·25 | 0·728 | 0·727 | 60 | 1·21 | 0·66 |
|    | 0·3 | 1·24 | 0·733 | 0·733 | 60 | 1·00 | 0·65 |

may play an important role in the acceleration of reaction rate. The similarity of the effect of changes in the energy of solvation and changes in the double layer effects in the correction for the observed rate constant has been discussed by Behr *et al* (1975) in the reduction of zinc in water–ethanol and water–acetone mixtures.

For a given concentration of potassium chloride the plot of $E_f^o$ vs $1/\epsilon$, $\epsilon$ being the dielectric constant of the mixed solvent, was not linear (figure 3). The dielectric constants for mixed solvents were estimated by interpolation from the values for the pure solvents assuming a proportionality of the dielectric constant to the weight per cent of the solvent. This indicated that factors other than solvation based on electrostatic concepts were to be considered. The plot of $E_f^o$ vs log [DMF] resulted in a straight line with a slope of 60 mV indicating a change in the coordination of europium by one DMF molecule during the electron transfer step. A variation of one DMF molecule in the coordination in the reduction of europium in pure DMF has been reported by Hush and Dyke (1974). The negative shift in the formal potential with increasing concentration of DMF has been interpreted in terms of preferential solvation in ammonium perchlorate media (*loc. cit.*).

The variation of viscosity with the change in the solvent composition alters the diffusion coefficient and hence the diffusion current. Since the surface tension and hence the drop-time also vary with the concentration of the organic solvent, the diffusion current constant, rather than the diffusion current, can be correlated to the viscosity $\eta_s$. Hence the diffusion current constant was determined for 10, 25, 50, 60 and 75% DMF in 0·3 M potassium chloride (table 2). The product of the diffusion current constant and the square-root of the viscosity of water DMF mixture (Hale and Parsons 1960) was nearly constant indicating little variation in the radius of solvated europium ion.
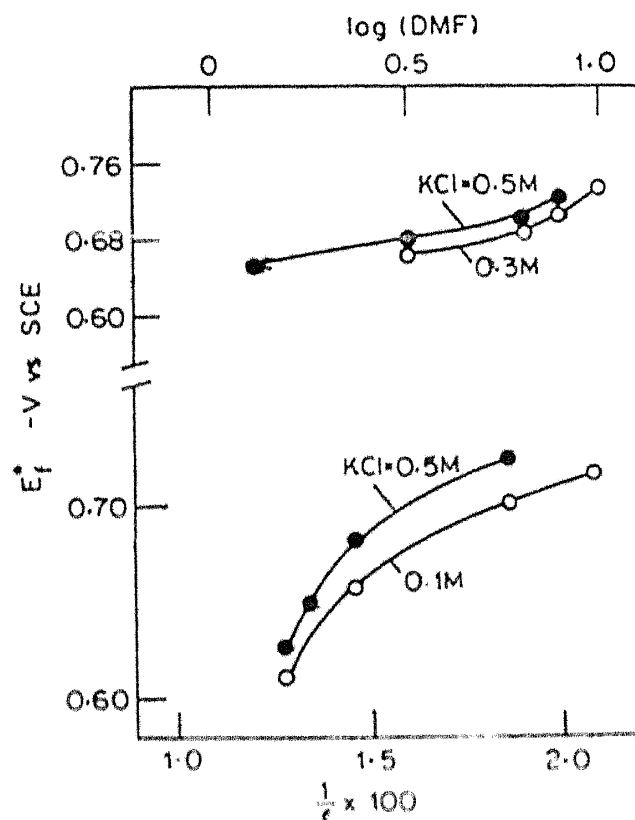
**Figure 3.** Variation of formal potential with dielectric constant and log (DMF).

**Table 2.** Effect of viscosity.

Supporting electrolyte : $0 \cdot 3$ M KCl.

| DMF %(V/V) | Diffusion current constant, $I_a$ $\mu A/(mM\ mg^{2/3}\ sec^{1/6})$ | Viscosity, $\eta_s$ $p$ | $I_d\,\eta_s^{1/2}$ |
|---|---|---|---|
| 10 | $1 \cdot 520$ | $0 \cdot 0184$ | $0 \cdot 21$ |
| 25 | $1 \cdot 322$ | $0 \cdot 0233$ | $0 \cdot 20$ |
| 50 | $0 \cdot 904$ | $0 \cdot 0387$ | $0 \cdot 18$ |
| 60 | $0 \cdot 903$ | $0 \cdot 0399$ | $0 \cdot 18$ |
| 75 | $0 \cdot 924$ | $0 \cdot 0336$ | $0 \cdot 17$ |

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