Chronopotentiometry Reduction of Eu^{3+} Ion in Propylene Carbonate/Dimethylsulphoxide Mixtures

V. J. EASOW, K. A. KHASGIWALE, M. M. MEHTA AND M. SUNDARESAN
Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 085

Presented at E.C.S.I. A.T.M. (1980) Bangalore

THE effect of addition of 0-2% by volume of dimethylsulphoxide to propylene carbonate on the chronopotentiometric reduction of Eu ion has been investigated. No significant changes were observed in the diffusion coefficients upto 1%. Also quarter wave potentials and transition periods showed a regular relationship with increasing DMSO content upto 1%, while at 2% the electrochemical characteristics were markedly different. Reversibility was observed only at 2%. The kinetic parameters and α na factors have been calculated. Plausible explanation has been offered on this behaviour on the basis of competing coordination and mass effects.

THE polargraphic reduction of rare earths in dimethylsulphoxide and dimethylformamide[1] and propylene carbonate (PC)[3] has been reported by Gutman et al. Gutman and Heiling[2] have studied the reduction of europium by polarography and reported the half wave potentials, diffusion coefficients diffusion currents and the reversibility of the electrochemical reductions in different solvent and electrolytes. Gutman[3] has also reported about some a.c. oscillopolarographic and cyclic voltammetric studies. Dey[4] uses chronpotentiometry to ascertain the role of water in Propylene Carbonate(PC). Other than these there does not appears much systematic study done in this direction. In a recent publication Chitre et al[5]. have reported the chronopotenticmetric study of the reduction of Cu^{++}, Pb^{++}, Co^{++}, Cd^{++} and Eu^{+++} in PC The present work is aimed at an investigation of the effect of addition of Dimethyl Sulphoride (DMSO) to PC on the chronopotentiometric reduction of europium.

EXPERIMENTAL

Reagents : All reagents used in the experiments were of analytical reagent grade. PC after preliminary purification was distilled at 4 mm Hg pressure, collecting the fraction at 102°C. The method of purification has been detailed in a recent publication[5]. DMSO from Koch-Light Laboratories was purified before use. The water contents of both the reagents were checked by Karl Fischer titration. Europium perchlorate was prepared by the recommended procedure and was dried at 110°C in vacuum for several hours. DMSO and PC mixtures were prepared by volume taking all precautions to avoid contact with moisture.

The electrolysis cell design was adopted from that of Delahay and Mattax[6] and consisted of a mercury pool as the working electrode, a platinum wire as an auxiliary electrode and a saturated calomel electrode (SCE) with a special non-aqueous salt bridge[7] as the reference electrode.

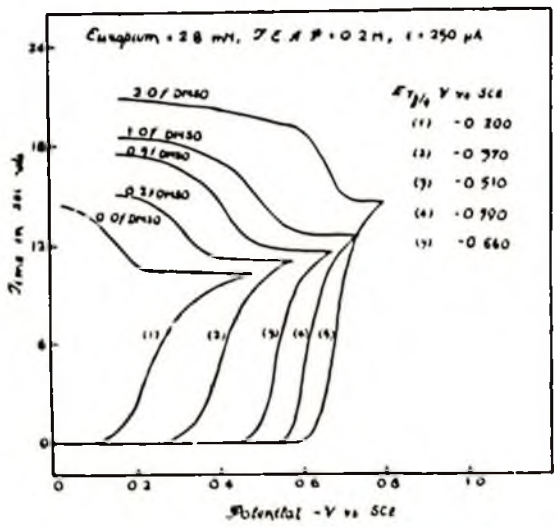
The aparatus used has been described in detail elsewhere[5]. Precautions were taken to keep the resistance of the assembled cell less than 1 K Ω. The potential-time curves were recorded on a Honeywell strip chart recorder.

5 ml of the solution containing the requisite amounts of the solvents and the solute were taken for each experiment. The solution was freed from dissolved oxygen and was thermostated at 25°C.

RESULTS

A typical set of chronopotentiograms of 2.8 mM europium perchlorate with 0.2 M tetraethyl ammonium perchlorate as the supporting electrolyte in PC solutions containing 0, 0.2, 0.5 1.0 and 2.0% DMSO (by volume) is given in Fig. 1. The chronopotentiograms were repeated at several other concentrations ranging from 1-3 mM of europium perchlorate and at constant currents ranging from 200-400 μ A. Each of these experiments were repeated 3 times in order to ensure reproducibility.

Fig. 1



Chronopotentiogram, Europium in D/MSO-PC mixtures

DISCUSSION

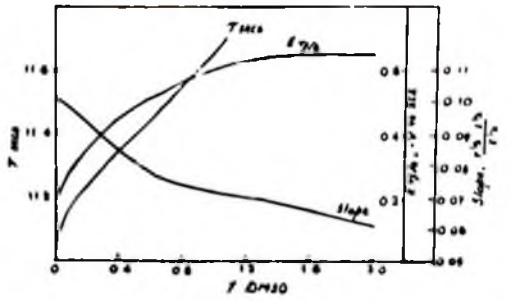
Figure 2 shows the variation of τ, $E\tau_{/4}$ and slopes of the plates of E vs log $\frac{(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})}{t^{\frac{1}{2}}}$ as a function of the concentration of DMSO in PC. Here τ is the transition time, $E\tau_{1/4}$ is the forward quarter wave potential and t is the time at any particular potential. Sand's equation[8], viz.,

$$\tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} n F.A.D^{\frac{1}{2}}C^{o}}{2i} \qquad (1)$$

was found to be obeyed at all the concentrations of both the solvent and solute, as confirmed by the constancy of $\frac{i\tau^{\frac{1}{2}}}{C}$, thereby confirming that the electrode processes are diffusion controlled. The plots of E against log $\frac{(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})}{t^{\frac{1}{2}}}$ indicates that except at 2% of DMSO, the reduction was irreversible. However, the intercept on the Y axis which should be equal to $E_{\frac{1}{2}}$ or the half-wave potentials in the various media agreed within 10 mV with the quarter wave potentials.

Fig 2

Variation of chronopotentiometric parameters with DMSO concentration (%)



Plots were also drawn following Delahay's equation[9].

$$E - E_{\frac{1}{2}} + \frac{RT}{nF} \ln \frac{\tau^{\frac{1}{2}} - (\tau + t')^{\frac{1}{2}} - t'^{\frac{1}{2}}}{(\tau + t')^{\frac{1}{2}} + t'^{\frac{1}{2}}} \qquad (2)$$

where t is the time at any potential. These plots also confirmed the earlier results. The anodic quarter wave potentials gave a difference of the order of about 30mV from the cathodic quarter wave potentials. In short the different diagnostic criteria suggested by Reinmuth[10] were attempted for determining reversibility.

For obtaining the formal heterogeneous rate constant, $k^{\circ}_{f,h}$ the value of $k_{f,h} = \frac{\pi^{\frac{1}{2}} D^{\frac{1}{2}}}{2\tau^{\frac{1}{2}}}$ was found out in each case. Here D is the diffusion coefficient in $Cm^2.sec^{-1}$ calculated from Sand's equation. Thereafter $k^{\circ}_{f,h}$ can be calculated from the equation[9].

$$k_{f,h} = k^{\circ}_{f,h} \exp \left[\frac{\alpha n_a F}{RT} E_{\frac{1}{4}=0} \right] \frac{\alpha n_a F}{RT}$$

The calculation of αn_a and $E_{\frac{1}{4}=0}$, where α is the transfer coefficient nA in the number of electrons involved and $E_{\frac{1}{4}=0}$ is the potential of electrolysis, can be done by plotting E vs log $\frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{\tau^{\frac{1}{2}}}$ as per the equation[9].

$$E = \frac{RT}{\alpha n_a F} \ln \frac{nAFC^{\circ}k^{\circ}_{f,h}}{i} + \frac{RT}{\alpha n_a F} \ln \left(1 - \frac{t^{\frac{1}{2}}}{\tau}\right)$$

The first term of the right hand side of the equation can be taken as a constant and therefore a plot of E against log $1 - \left(\frac{t}{\tau}\right)^{\frac{1}{2}}$ will yield a straight line with slope of $\frac{2.303\,RT}{\alpha n_a F}$. On extrapolation, this straight line yields the value of $E_{\frac{1}{4}=0}$. Having thus determined both $E_{\frac{1}{4}=0}$ and αn_a $k^{\circ}_{f,h}$ can be calculated. The values of $E_{\frac{1}{4}=0}$, αn_a and log $k^{\circ}_{f,h}$ are given in Table 1 as a function of DMSO concentration.

TABLE 1

Formal heterogeneous rate constants for europium in 0.2 M tetraethylammonium perchlorate in PC - DMSO mixtures

Concentration of DMSO %	α na	$-E_{\tau/4}$ V vs NHE	$-\log K^{f}_{f,h}$
0	0.241	—0.124	3.104
0.2	0.476	—0.108	2.714
0.5	0 503	0.230	5.565
1.0	0 787	0.330	3.003
2 0	0 443	0.384	6.476

CONCLUSIONS

Primarily the object of the study was to investigate the difference in the behaviour of the reduction of Eu^{3+} ion as the solvent properties underwent changes on mixing. Propylene carbonate with a viscosity of 2.53 CP and a dielectric constant of 67 is an ideal aprotic solvent whole DMSO has a viscosity of 1.92 CP and a dielectric constant of 46 7. An addition of upto 2% of DMSO to PC should not change the electrochemical characteristics which are observed in PC. However marked difference is obtained in our experiments as can be seen from the results. (in Fig. II). Gutman[11] in a polarographic study of lanthanide elements has noticed similar effects with the addition of water to PC, even though he has not specified the water content of pure PC. Lanthanum which gave a well defined single wave in pure PC gave distorted waves, with wave heights increasing upto 25%. The $E_{\frac{1}{4}}$ shift from pure PC to PC containing 2% water was of the order of 100 mV on the negative side. The behaviour of addition of DMSO to PC in our case also follows a similar pattern. As can be seen from Fig. 2 the shift in $E_{\tau/4}$ or the polarographic have wave potential is of the order 400 mV on the negative side, while the transition time, diffusion coefficients and reversibie nature shows marked difference only at 2%.

The change in dielectric constant and viscocity by the addition of DMSO is not high enough to warrant such a change in behaviour. Assuming a coordination number of eight for Eu the quantity of DMSO required to replace all PC from the coordination sphere of Eu is only 0.16%. Hence if it were only a purely replacement reaction, further addition of DMSO should not change the electrochemical behaviour. Thus it is to be assumed that a mass law reaction must be taking place with DMSO completing for the coordination sites. A Similar behaviour-a significant half wave potential change towards more negative side and a drastic change in transfer coefficient on the addition of DMSO to PC-has been reported in the polarographic reduction of the fluoromethane sulphonates of lead, thallium and cadmium[12]. Further studies are in progress to investigate the effect of addition of higher percentage of DMSO.

REFERENCES

1. V. Gutman, G. Geitzner and G. Schober, *Montasch*, 96 (1956) 1056.
2. V. Gutman and G. Peychal Heiling, *Montasch*, 100 (1969) 1423.
3. V. Gutman, M. Kogleing and M. Michelmayer, *Montasch*, 99 (1968) 699.
4. A. N. Dey, *J. Electrochem. Soc.*, 114 (1967) 823.
6. R. S. Chitre, K. A. Khasgiwale and M. Sundaresan, *J. J. Electrochem. Soc. India*, 29-2 (1980) 71.
6. P. Delahay and C. C. Mattax, *JACS*, 76 (1954) 874.
7. I. S. Kosmali, *Soviet Electrochemistry*, 4 (1968) 1316.
8. A. J. Bard, *Electroanalytical Chemistry*, Vol. 2. Marsl Dekker, Inc., N.Y. (1967).
9. P. Delahay and T. Berzins, *JACS*, 75 (1953) 4205.
10. W. H. Reinmuth, *Anal. Chem*, 32 (1960) 1514.
11. V. Gutman and G. Peychal Heiling, *Z. Anal. Chem.*, 6 (1969) 248.
12. J. Massaux and G. Duckaerts, *J. Electroanalchem.*, 59 (1975) 311.