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Effect of Solvents and Supporting Electrolytes on the Electrochemical Behaviour of Ferrocene/Ferricenium Redox System

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Cyclic voltammetric measurements were made using freshly polished glassy carbon to test ferrocene as a function of solvents and electrolyte composition. Apparent heterogeneous electron transfer rate constant, k°_{app}, of 0.0186, 0.0172, 0.0169 and 0.00487 cm/s were observed in 0.1 M $NaClO_4/CH_3CN$, 0.1 M $NaClO_4$/DMF 0.1 M $NaClO_4$/DMSO and 0.1 M $(C_2H_5)_4NClO_4$, respectively. The results of this work suggest that rate constant in several solvents revealed the expected trend of decreased rate in the lower dielectric constant. On the basis of the experimental results we concluded that increasing the ionic conductivity of solution decreases the magnitude of Ru (uncompensated cell resistance) and increases the electron transfer rate constant.

Key Words: Glassy carbon, Cyclic voltammetry, Ferrocene, Supporting electrolyte.

INTRODUCTION

Studies on the transport properties of electrolytes in different solvent media are of great importance in obtaining information as to the solvation and association behaviour of ions in solutions[1]. We have investigated these properties for several electrolytes in different solvents. The ferrocene/ferricenium redox couple was selected as a test system to investigate. Ferrocene is routinely used as a model in kinetic studies because it demonstrates ideal electrochemical behaviour in a variety of solvents. The one electron oxidation of ferrocene to the stable ferricenium cation is a simple electron transfer reaction in that there are no complications arising from adsorption or associated chemical reactions. Generally this redox couple exhibits highly reversible, well-defined voltammetric responses at a variety of electrode materials (Pt, Au, GC)[2, 3].

Cyclic voltammetric data are presented for GC obtained as a function of the scan rate, solvent and electrolyte composition. Apparent heterogeneous electron transfer rate constant, k°_{app}, were calculated from the dependence of the peak potential separation, ΔE_p, on the scan rate, according to the theory developed by Nicholson[4, 5]. The present paper reports the relationship between conductivity and uncompensated resistance of solution and rate constant.

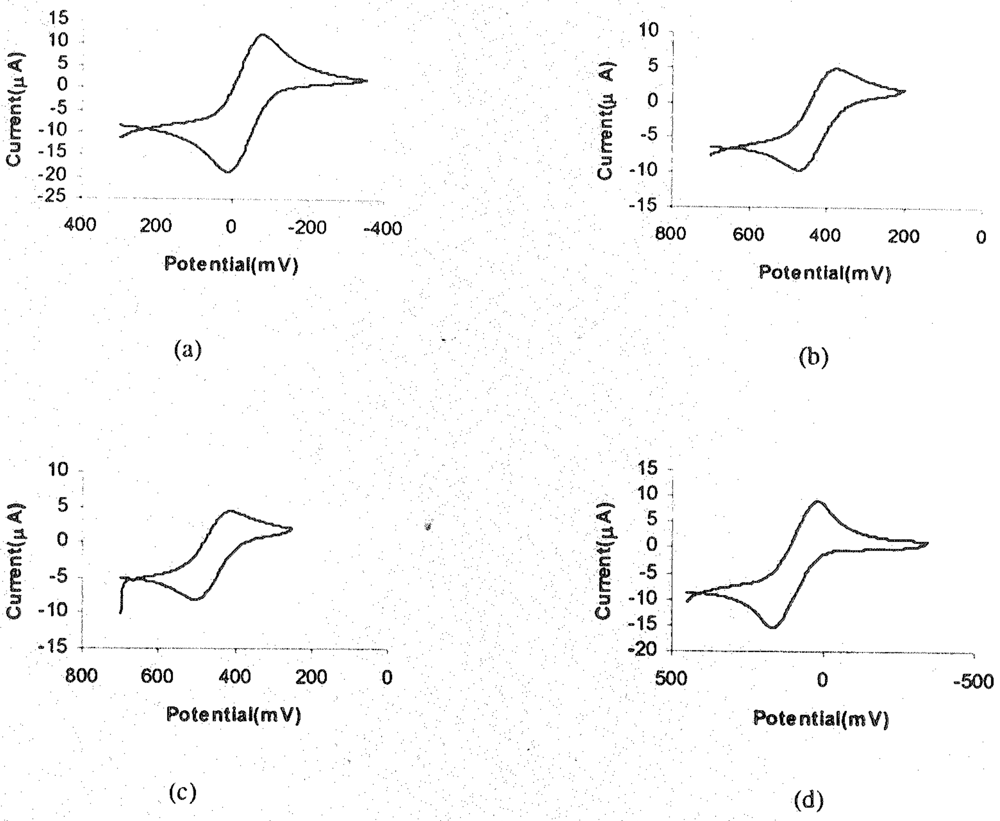
EXPERIMENTAL

Ferrocene (Fluka), sodium perchlorate (Fluka) and tetraethylammonium perchlorate (Fluka) were used as received. Dichloromethane (Fluka), acetonitrile (Fluka), dimethylsulfoxide (Merck) and dimethylformamide (Merck) were used as solvents. GC electrode (metrohm) was used for some cyclic voltammetric measurements. This electrode was polished smooth, using slurry of 0.3 μm alumina in ultrapure water. The polishing was performed on felt pads. The electrode was rinsed with ultrapure water between each polishing step.

All electrochemical measurements were performed using a computer controlled potentiostat-galvanostat (model 263A; EG&G instrument). Ag/AgCl/KCl (sat) electrode was used as a reference electrode and a Pt wire as a counter electrode. A standard three electrode glass cell was employed. In an effort to minimize ohmic distortion, low analyte concentration (0.1, 1 mM) and iR compensation were used.

RESULTS AND DISSCUSION

The oxidation of ferrocene is a one-electron process leading to a chemically stable ferricenium cation. Fig. 1 shows a cyclic voltammetric i-E curve at 0.1 (v/s) for (0.1, 1) mM ferrocene in different solvents such as acetonitrile, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and dichloromethane containing



(a) (b)

(c) (d)

Fig. 1. Voltammograms: (a) 1 mM ferrocene in 0.1 M (($(C_2H_5)_4NClO_4/CH_3CN$), (b) 1 mM ferrocene in 0.1 M (($(C_2H_5)_4NClO_4$/DMF), (c) 1 mM ferrocene in 0.1 M (($(C_2H_5)_4NClO_4$/DMSO), (d) 1 mM ferrocene in 0.1 M (($(C_2H_5)_4NClO_4/CH_2Cl_2$)

0.1 M supporting electrolyte, like sodium perchlorate, tetraethyl ammonium perchlorate.

ΔE_p was recorded at different electrolyte/solvent systems and the values used to calculate k°_{app}[4,5]. This method relates ΔE_p to the dimensionless kinetic parameter, Ψ, and is useful for determining the rate constants for redox systems with peak separation of 65–200 mV.

Table-1 lists the k°_{app} values for freshly polished glassy carbon. The k°_{app} values were calculated assuming that $D_o = D_R$ and $\alpha = 0.5$. The diffusion coefficient for ferrocene in acetonitrile[6] was taken as $D_R = 2.4 \times 10^{-5}$ cm^2 s^{-1}. The value used in dichloromethane, $D_R = 2.0 \times 10^{-5}$ cm^2 s^{-1} was calculated from the Stckes-Einstein relation.

TABLE-1

THE k°_{app} VALUE FOR DIFFERENT SOLVENT/SUPPROTING GEL ELECTROLYTE SYSTEM BY SCAN RATE OF 0.1 v/s, ACCORDING TO THE THEORY DEVELOPED BY NICHOLSON

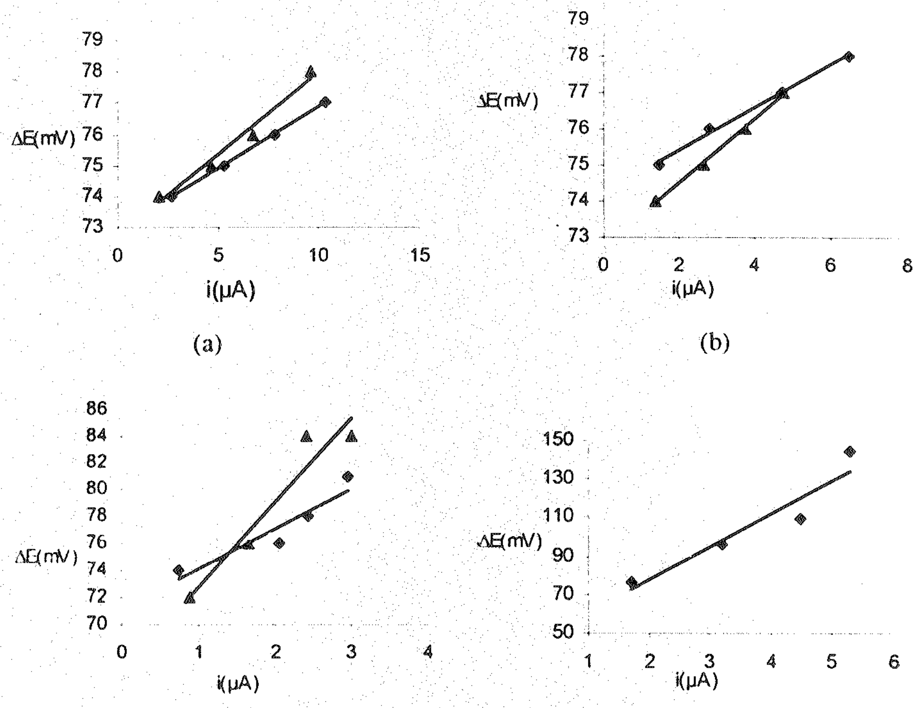
Solution (1 mM ferrocene)	k°(cm/s)
0.1 M ($NaClO_4/CH_3CN$)	1.86×10^{-2}
0.1 M ($(C_2H_5)_4NClO_4/CH_3CN$)	1.67×10^{-2}
0.1 M ($NaClO_4$/DMF)	1.72×10^{-2}
0.1 M ($(C_2H_5)_4NClO_4$/DMF)	1.22×10^{-2}
0.1 M ($NaClO_4$/DMSO)	1.69×10^{-2}
0.1 M ($(C_2H_5)_4NClO_4$/DMSO)	1.22×10^{-2}
0.1 M ($(C_2H_5)_4NClO_4/CH_2Cl_2$)	4.87×10^{-2}

There is an effect of the solvent at electrode with k°_{app}, for example in CH_2Cl_2 being a factor 4–6 times lower than in CH_3CN. The difference is attributed to a dielectric constant for CH_2Cl_2 that is a factor 4.3 times less than that for CH_3CN ($\xi = 9.08$ *vs.* 38.8). The difference in dielectric constant is a little less than the difference in rate constants. The effect of lower solvent dielectric constant on the cyclic voltammetric response, from which k°_{app} is determined, is manifested in the following way:

The solution will have a lower ionic conductance because of less effective charge separation. The ionic strength will be reduced, hence the ion conductivity will be less. The lower ionic conductivity increases the magnitude of iRu. In the experiment, the cell current, i, is measured as a function of E_{ppl}, which is the applied potential between the working and reference electrodes. The contribution of cell or monolayer resistance to the observed ΔE_p results was evaluated by varying the concentration of the electroactive species. Results for 4 concentraion of ferrocene are listed in Table-2 for unmodified GC. At a given scan rate (0.1 v/s) the increase in peak separation with higher concentration (and peak current) should be caused by uncompensated resistance. Since the peak separation due to electron transfer kinetics should be constant with concentration. The iR corrected ΔE_p is related to the peak current (i_p) and uncompensated resistance (Ru) by the following equation:

$$\Delta E_p \text{ (observed)} = \Delta E_p \text{ (corrected)} + 2i_pR_u$$

A plot of ΔE_p (observed) versus i_p has a slope of 2Ru andan intercept of ΔE_p (corrected)[7]. These plots for several solvent/supporting electrolyte systems are shown in Fig. 2 and Ru values have been calculated and shown in Table-2.



(a) (b)

(c) (d)

Fig. 2. Plot of ΔE_p (observed) *vs.* i_p from voltammograms for determination of Ru:
(a) ■ 0.1 M ($NaClO_4/CH_3CN$), ▲ 0.1 M ($(C_2H_5)_4NClO_4/CH_3CN$),
(b) ■ 0.1 M ($NaClO_4$/DMF), ▲ 0.1 M ($(C_2H_5)_4NClO_4$/DMF),
(c) ■ 0.1 M ($NaClO_4$/DMSO), ▲ 0.1 M ($(C_2H_5)_4NClO_4$/DMSO),
(d) ■ 0.1 M ($(C_2H_5)_4NClO_4/CH_2Cl_2$).

TABLE-2

COMPARISON OF k°_{app}, Ru AND K VALUE FOR 0.1 mM FERROCENE IN DIFFERENT SOLVENT/SUPPORTING GEL ELECTROLYTE SYSTEM FOR GC ELECTRODE

Solution	k°_{app} (cm/s) 1 mM Ferrocene	Ru (Ω)	K (1/Ω cm)
0.1 M ($NaClO_4/CH_3CN$)	1.86×10^{-2}	197.8	1.16×10^{-2}
0.1 M ($(C_2H_5)_4NClO_4/CH_3CN$)	1.67×10^{-2}	265.05	1.04×10^{-2}
0.1 M ($NaClO_4$/DMF)	1.72×10^{-2}	253.5	5.34×10^{-2}
0.1 M ($(C_2H_5)_4NClO_4$/DMF)	1.22×10^{-2}	440.85	3.81×10^{-2}
0.1 M ($NaClO_4$/DMSO)	1.69×10^{-2}	1479.3	2.70×10^{-2}
0.1 M ($(C_2H_5)_4NClO_4$/DMSO)	1.22×10^{-2}	3152.3	2.28×10^{-2}
0.1 M ($(C_2H_5)_4NClO_4/CH_2Cl_2$)	4.87×10^{-2}	8713.5	1.24×10^{-2}

On the basis of this experiment and its results we can get that solvent/supporting electrolyte system by more ion conductivity has less Ru (uncompensated resistant) and so it is due to the increase of k^{o}_{app} (rate constant) that we can conclude that the solvents by high dielectric constant such as CH_3CN, DMF and DMSO have conditions better than CH_2Cl_2 by lower dielectric constant and a comparison of rates measured in these solvents revealed the expected trend of decreased rates in the lower dielectric solvent, dichloromethane.

Conclusions

The results of this work suggest that rate constant in several solvents revealed the expected trend of increased rate in the higher dielectric constant. On the basis of the experimental results we concluded that increasing the ionic conductivity of solution decreases the magnitude of Ru (uncompensated cell resistance) and increases the electron transfer rate constant.

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