A STUDY ON FERROCENE / FERROCENIUM COUPLE BEHAVIOR IN THE DISSOLVABLE IONIC LIQUID N, N-DIMETHYLAAMMONIUM N', N'-DIMETHYLCARBAMATE (DIMCARB)

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ABSTRACT

Ferrocene/ferricenium redox couple behavior is studied by cyclic and linear scan voltammetry at gold and glassy carbon micro- and macrodisc stationary and rotating electrodes in the room temperature distillable ionic liquid N,N-dimethylammonium N', N'-dimethylcarbamate (DIMCARB). Bulk electrolysis experiments are carried out as well. It is found that the redox reaction studied deviates from its reversibility. The values of the diffusion coefficients of ferrocene and ferricenium cation at gold are \( \sim 10^{-6} \text{cm}^2 \text{s}^{-1} \) and \( \sim 10^{-7} \text{cm}^2 \text{s}^{-1} \), correspondingly, while at glassy carbon they are \( \sim 10^{-7} \text{cm}^2 \text{s}^{-1} \). The rotation disc electrode and constant potential bulk electrolysis measurements show that ferrocene oxidation is interfered by a fast chemical reaction. The examination of all data obtained leads to the suggestion that ferricenium acting as an oxidizing agent brings about decarboxylation of the ionic liquid’s anions. It is concluded that the redox couple studied cannot be used as an internal voltammetric reference standard in DIMCARB.

Keywords: ferrocene/ferricenium, reference potential standard, ionic liquids, diffusion coefficients.

INTRODUCTION

As a non-conventional class of novel solvents room temperature ionic liquids are becoming increasingly important. This expanding interest has lead to the development of new families and generations of ionic liquids with targeted properties and a diversified range of applications [for an example 1-6 and the numerous references therein]. Some specifically designed ionic liquids may reversibly switch their polarity to induce solubility changes of products and/or catalysts making their separation and purification feasible. The polarity change in these “switchable solvents” is achieved by addition of \( \text{CO}_2 \) to a mixture of two liquid components (amidines and an alcohol [7], a primary amine/amidine mixture [8] or secondary amines [9]). A carbamate salt is formed which can then be assumed as an ionic liquid. Mixtures of adducts of \( \text{CO}_2 \) and dialkylamines of the general formula \( \text{Me}_2 \text{NH} : \text{CO}_2 \) (where \( R \) and \( R' \) stand for alkyl groups), i.e. dialcarbs are distillable ionic liquids of low cost of synthesis and high, tuneable conductivities achieved by varying the \( RR' \text{NH} : \text{CO}_2 \) ratio. In case of \( R = R' = \text{methyl} \), a series of liquids containing the dimethylcarbamate ion is produced. A highly conductive, stable liquid, referred as DIMCARB [10,11] is obtained when the \( \text{Me}_2 \text{NH} : \text{CO}_2 \) ratio drops to 1.8:1. It has been used in organic synthesis as a solvent and as a convenient and safe source of dimethylamine.
[10]. It is highly suitable for electrochemical studies [11] as well.

Quasi-reference electrodes are used in organic solvents and ionic liquids when a high level of potential reproducibility is not required. But meaningful data comparisons require a calibration against a well defined reference system. This is usually achieved by voltammetric measurements of the quasi-reference electrode versus the formal potential of an electrochemically reversible couple. As ferrocene is soluble and stable in many solvents and exhibits reversible one-electron behavior [12], the ferrocene/ferricenium couple is recommended by IUPAC as an internal standard for calibration purposes.

The aim of this study is to follow ferrocene voltammetry in DIMCARB providing data for ferrocene/ferricenium couple behavior as a reference potential standard.

EXPERIMENTAL

Linear sweep, cyclic voltammetric, rotating disc and bulk electrolysis experiments were performed using BAS 100B/W Version 2.3 electrochemical workstation. The experiments in CH₃CN (0.1 M Bu₄NPF₆) were carried out in a standard three electrode cell with gold or glassy carbon microdisc working electrode, a gold wire and a glassy carbon Cypress electrode as a counter electrode, respectively, and a Ag / Ag⁺ (0.1 M AgNO₃ in CH₃CN) double junction reference electrode. The voltammetric experiments carried out in DIMCARB employed the same configuration and counter electrodes. The choice of the latter was determined in the course of the preliminary experiments carried out.

It was verified that the electrode surface pretreatment was of great importance. Partial fouling resulting from ferrocene polymerization reaction [13] with CH₃OH was observed (the presence of is commented below). Therefore all electrodes used were pretreated prior to each experiment through polishing on a moist polishing cloth with 0.3 μm alumina (Buehler) and sonication in distilled water for 15 min. This procedure was followed by the effective electrode area determination. The latter was based [14] on the measurement (with 100 % IR compensation) of the steady-state current value (Iₘₚ) obtained in the course of a reversible one-electron oxidation in a 1 mM solution of ferrocene in CH₃CN (0.1M Bu₄NPF₆). Cyclic voltammetry with a scan rate of 0.002 Vs⁻¹ was applied. The equation used was:

\[ I_{st, state} = 4nFDC^0 \left( r_0 \right)_{disk} \]

where \( C^0 \) and \( D \) were the bulk concentration and the diffusion coefficient of ferrocene, correspondingly, \( r_0 \) was the disc radius, while the other symbols had their usual meaning. Illustrative stationary curves recorded at the working electrodes studied are presented in Fig. 1.

Rotating disc and constant potential bulk electrolysis experiments were carried out in a two-compartment...
ment cell with gold and glassy carbon rotating discs, a Pt gauze counter electrode and a reference electrode as described above. Metrohm 628-10 (MEP Instruments Pty. Ltd.) RDE assembly was used.

Acetonitrile (Merck, HPLC grade, 99.9 %) and ferrocene (BDH) were used as supplied by the manufacturer. Tetrabutyl ammonium hexafluorophosphate (Bu₄NPF₆) was purchased from GFS Chemicals and recrystallized twice from C₆H₁₂OH. DIMCARB was synthesized at the Research Centre for Green Chemistry of Monash University [10, 11].

Oxygen dissolved in DIMCARB was removed by degassing with N₂ for 5 min. Longer duration leads to disruption of the dynamic equilibria characteristic for DIMCARB [10]. All experiments were carried out at ambient temperature (20±2°C).

RESULTS AND DISCUSSION

DIMCARB is a mixture [10,11] containing CO₂, Me₂NH, Me₂N–COOH, [Me₂NH⁺][Me₂N–CO₂]⁻, Me₂NCOO⁻, MeNHCOO⁻ and H₂O⁺. The potential ranges available in this ionic liquid are governed [15] by the following reactions:

\[
\begin{align*}
\text{Me}_2\text{NCOO}^- + H_2O &\rightarrow 2e^- \\
&\rightarrow \text{MeNHCOO}^- + HCHO + 2H^+ \\
2\text{Me}_2\text{NH}^+ + 2e^- &\rightarrow 2\text{Me}_2\text{NH} + H_2
\end{align*}
\]

As Fig. 2 shows they commence at higher potentials at glassy carbon when compared to those at Au microdisc electrode, i.e. the potential window of glassy carbon is shorter than that at Au. Besides, the currents recorded at glassy carbon are lower than those found for the process at.

Illustrative cyclic voltammograms recorded at both electrodes studied are presented in Fig. 3. As expected the scan rate increase leads to currents increase, to the oxidation and the reduction peak potential shift to higher and lower values, correspondingly. All data obtained are treated in correspondence to the diagnostic criteria [12] for a reversible redox couple. It is found that the magnitude of the ratio of oxidation and reduction peak currents is not close to unity. This is in fact evident from the voltammograms shown in Fig. 3. Furthermore, the peak-peak separations, i.e. the difference in oxidation and reduction peak potentials or ΔEₚ-values are not close to the theoretical separation of 55 mV expected for a one electron reversible couple at 20°C. The ΔEₚ-values obtained show a tendency to decrease with increasing scan rate as illustrated in Fig. 4. It should be noted that it cannot be explained with a transition from steady state behavior at a slower scan rate to transient behavior at faster scan rates as expected for ferrocene oxidation in ionic liquids [16]. It is now well recognized that in ionic liq-
uids the oxidation and reduction peak currents increase systematically with the scan rate increase in accordance with Randles-Sevcik equation [12]:

\[ I_p = 0.4463 \sqrt{\frac{n^3 F^3 A c^0 D^{1/2}}{R T V^{1/2}}} \]  

(4)

where \( n \) is the number of electrons, \( A \) is the electrode area (cm\(^2\)), \( D \) is the diffusion coefficient (cm\(^2\)s\(^{-1}\)), \( c^0 \) is the bulk concentration (mol cm\(^{-3}\)), \( V \) is the scan rate in Vs\(^{-1}\), while the other symbols have their usual meaning. The data concerning the oxidation and reduction process taking place at the working electrodes studied are treated in correspondence with the linearized form of Eq. (4). Some of the dependences obtained are shown in Figs. 5 and 6. It is seen once again that the ratio of the peak currents deviates from the value expected. The lines presented do not pass through the origin which is in accord with findings in other ionic
Fig. 6. Scan rate dependence of the oxidation (1) and reduction (2) peak current obtained for a glassy carbon microdisc electrode of an effective area of $6.01 \times 10^{-7} \text{cm}^2$ in 3.0 mM solution of ferrocene in DIMCARB.

Fig. 7. Scan rate dependence of the oxidation peak current obtained in linear scan voltammetry experiments carried out at Au microdisc electrode (1) of an effective area of $2.73 \times 10^{-7} \text{cm}^2$ in 3.5 mM solution of ferrocene in DIMCARB and a glassy carbon microdisc electrode (2) of an effective area of $8.17 \times 10^{-7} \text{cm}^2$ in 3.0 mM solution of ferrocene in DIMCARB.

Fig. 8. Illustrative cyclic voltammograms recorded in 1.7 mM solution of ferrocene in DIMCARB at Au rotating disc electrode at 2000 rpm and a scan rate of 0.200 Vs$^{-1}$, 0.300 Vs$^{-1}$ and 0.400 Vs$^{-1}$, correspondingly (a) and 1.003 Vs$^{-1}$, 2.007 Vs$^{-1}$ and 3.011 Vs$^{-1}$, correspondingly (b).

Liquids. The values of their slopes are used to estimate the diffusion coefficient $D$ of ferrocene and ferricinium cation. They are $\sim 10^{-5} \text{cm}^2\text{s}^{-1}$ for ferrocene and $\sim 0.5 \text{cm}^2\text{s}^{-1}$ for ferricinium cation for Au, while for glassy carbon both $D$ values are $\sim 10^{-7} \text{cm}^2\text{s}^{-1}$. It is worth noting that ferrocene concentration has no effect if the electrode surface has been properly pretreated. The $D$ values just reported are higher than those found in DIMCARB [11]. Moreover, the ratio of the values estimated for the oxidation and the reduction process taking place at Au is much greater than that found in other ionic liquids [16-18], although it can be even 7.80 [16]. Additional information concerning the diffusion of ferrocene can be obtained by linear scan voltammetry application. Some of the dependences of the oxidation peak current vs. the scan rate square root are shown in Fig. 7. The $D$ values estimated for both working electrodes are of the order pointed above.

The experiments carried out with gold and glassy carbon rotating disc electrodes show that peak shaped
Fig. 9. Current vs. time dependence recorded during bulk electrolysis of 3.655 \times 10^{-3} moles of ferrocene in DIMCARB at Au macrodisc electrode. The experiment is carried out at a constant potential of 0.300 V, a value in the range of the anodic peak recorded in DIMCARB.

voltammograms are recorded. They are indicative of a significant contribution from transient diffusion controlled behavior. It is worth noting that at a constant rotation rate no reduction peaks are recorded at low scan rates, while no oxidation peaks are outlined at high scan rates. Some of the voltammograms recorded at Au are presented in Fig. 8. The curves obtained with a glassy carbon rotating electrode are of the same form but the effect is not so well outlined.

The bulk electrolysis experiments carried out at a constant potential value in the range of ferrocene oxidation peak show as well that the cation generated electrochemically takes part in a fast chemical reaction. This is well illustrated by the current vs. time curve presented in Fig. 9. As it is seen the curve recorded does not have the form expected, i.e. the current decreases only within ca 50 s. Then the current starts to increase steadily to reach a value which remains unchanged for additional ca 3000 s.

The above type of behavior suggests that the redox couple reversibility is interfered by a fast chemical reaction. The latter can be attributed to an oxidative transformation of the carboxylate ions present in DIMCARB. This suggestion seems reasonable as ferricenium cation instability \cite{11,19,20} mainly determined by its oxidizing properties \cite{20-25} is well recognized. Besides, oxidative decarboxylation with ferricenium participation is used for carbon surfaces modification \cite{26,27}. On the other hand, \( CO_2 \) is a product of the reaction considered. It should be added that gas evolution has been observed in course of the preliminary experiments carried out using Pt microdisc electrode in studying ferrocene/ferricenium behavior in DIMCARB. The fact that \( CO_2 \) is present in the system is investigated by the coincidence of the value of the diffusion coefficient found in case of ferrocene electrooxidation at \( Au \) and those of \( CO_2 \) diffusion coefficients reported in five ionic liquids \cite{28}. They all are of the order of \( 10^{-6} \) \( cm^2 s^{-1} \). As the rate of the chemical step is determined by the proceeding ferrocene electrooxidation, its effect on the redox couple reversibility should vary with the electrode material used. The experimental data obtained show that it is the greatest at \( Pt \) and the lowest at a glassy carbon electrode.

CONCLUSIONS

The electrochemical behavior of ferrocene/ferricenium redox couple in DIMCARB is studied with the application of cyclic and linear scan voltammetry at stationary and rotating macro and micro \( Au \) and glassy carbon electrodes varying the scan and rotation rates in wide ranges. Constant potential bulk electrolysis experiments are carried out as well. The voltammetric experimental data obtained show that: (i) the ratio of the peak currents of ferrocene oxidation and ferricenium reduction is greater than one; (ii) the peak separation is not close to that expected for an electrochemically reversible process and shows a tendency to decrease with scan rate increase; (iii) the peak currents increase systematically with scan rate increase although the linear dependences obtained do not pass through the origin of the coordinate system as expected in accordance with Randles-Sevcik equation. The diffusion coefficients values derived from these lines slopes are \( \sim 10^{-6} \) \( cm^2 s^{-1} \) for ferrocene and \( \sim 10^{-7} \) \( cm^2 s^{-1} \) for ferricenium cation at \( Au \), while for glassy carbon both \( D \) values are \( \sim 10^{-7} \) \( cm^2 s^{-1} \). The rotating disc electrode and bulk electrolysis measurements indicate that the redox couple reversible behavior is affected by a fast chemical reaction which is more pronounced at \( Au \) than at a glassy carbon electrode. It is suggested that ferricenium acting
as an oxidizing agent brings about decarboxylation of DIMCARB anions. The rate of this reaction which is comparable to the voltammetric timescale affects the reversibility of ferrocene/ferricinium redox reaction and hence it cannot be used as a reference potential standard in DIMCARB.

REFERENCES

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