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Characterization of decamethylferrocene and ferrocene in ionic liquids: argon and vacuum effect on their electrochemical properties

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The electrochemistry of decamethylferrocene (DmFc) has been studied in organic solvent systems and proven to be a superior internal reference redox standard to ferrocene (Fc). However, the electrochemical information on this redox couple in ionic liquids is still limited. Therefore, the voltammetric and amperometric behaviour of DmFc was investigated under argon and vacuum conditions in six different ionic liquids and compared to that of Fc under the same experimental conditions. Consequently, the concentration, the heterogeneous electron-transfer rate constant (k^0), volatility, and diffusion coefficients (D) of Fc and Fc$^+$, as well as the solubility, k^0, and D values for DmFc and DmFc$^+$ were determined under argon and vacuum conditions by fitting the experimental chronoamperometric and voltammetric data with numerical and digital simulations. The rate of mass transport of ferrocene and decamethylferrocene was observed to decreases between 6–37% by changing the working atmosphere from argon to vacuum. The $D_{\mathrm{Fc}}/D_{\mathrm{Fc+}}$ ratios are in the range 1.31-2.01 in the different ILs. Importantly, the $D_{\mathrm{DmFc}}/D_{\mathrm{DmFc+}}$ ratio is ≈ 1 in 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)amide, 1-methyl-1-butylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, and 1-methyl-3-ethylimidazolium tris(pentafluoroethyl)trifluorophosphate. The experimental mid-point potential and half-wave potential of Fc$^{0/+}$ vs. DmFc$^{0/+}$, as well as the formal potential obtained after correction for inequality in the respective diffusion coefficients of both redox processes are presented. Even though DmFc is not freely soluble in the different ILs, the results presented in this work suggest that the DmFc$^{0/+}$ redox process is less dependent than Fc on the IL nature. This is a very relevant finding for the application of this transition-metal sandwich complex as an internal reference redox system in IL solutions.

1. Introduction

The standard redox potential, and more frequently the formal redox potential obtained experimentally, is often the basic thermodynamic quantity used to characterize a redox system. In aqueous media, redox potentials are usually measured relative to reliable and generally accepted reference electrodes, such as the silver|silver chloride (e.g., Ag|AgCl, 3 M NaCl) and the saturated calomel electrodes[1,2]. Unfortunately, no universally accepted reference electrodes exist for work in ionic liquid solvent systems [3]. Besides, the small volume of ionic liquid generally used, in general several tenths or hundreds of microlitres, in order to perform simple and cost-efficient research, make the accurate construction of such reference electrodes more technically complicated in comparison to what is known from aqueous and organic solvent systems. In view of this problem, electrode potentials obtained in ionic liquid systems have been generally reported versus silver or platinum wire quasi-reference systems (QRE). The problem with using this arrangement is that the potential of the QRE is unknown and likely to change during the electrochemical experiment [3]. Recently, an activated carbon QRE has been proposed as a more stable alternative respect to silver and platinum wire [4]. Aqueous or organic solvent-based silver|silver chloride electrodes have also been used as reference systems in ionic liquids. The problem with using these electrodes in ionic liquid systems is that impurities are being introduced into the system during the measurements, affecting the IL physicochemical properties. This issue, in conjunction to the unknown liquid-junction potential build at the reference electrode/IL interface, could sensitively affect the electrochemical measurements [3]. Ionic liquid-based silver|silver chloride electrodes are nowadays the most reliable reference electrodes to work within ILs [5], mainly when the IL inside and outside the reference compartment is the same. However, the potential of this reference electrode is IL-dependent, and not potential

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comparison can be made between different ILs, In addition, an unknown liquid-junction potential could appear at the reference electrode/IL interface if the IL part of the reference electrode is different to that present in the working solution [6].

In view of this problem, internal reference scales (or internal reference redox systems), IRRS, which are reversible redox systems used to provide a known and stable reference point in non-aqueous solvents in conditions where reliable reference electrodes are difficult to be established and/or stabilized, have continuously been used within ionic liquids [3,7–9]. Indeed, quasi-reference electrodes in combination with in-situ calibration with IRRS, such as ferrocene (Fc), decamethylferrocene (DmFc) or cobaltocenium (Cc^+) have been seen to provide an attractive approach for the development of potential scales in ILs [3]. The IRRS accomplish these objectives by eliminating the liquid-junction potential commonly associated with more traditional reference systems when there are different electrolytes, different electrolyte concentrations, and/or different solvents inside and outside the reference compartment [10].

Albeit voltametric studies on the ferrocene/ferrocenium redox process have been extensively reported in ionic liquid systems, the available electrochemical information on this redox couple in ILs is still limited. For example, although it is well understood that the standard redox potential of Fc is highly dependent on solvation effects by the organic solvent and supporting electrolyte used [11–13], just recently the IL solvation effect on Fc was reported [2,3,14,15]. Interestingly, detailed studies on the effect of dissolved argon on the diffusivity of ferrocene in ILs have been restricted to 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)amide IL, [emim][NTf_2] [16], and the ratio of the diffusion coefficient for the reduced and oxidised component never reported under this gas condition. In addition, the ferrocene volatilization from an ionic liquid have been restricted to two bis(trifluoromethylsulfonyl)amide- and one tetrafluoroborate-containing ionic liquids [17–19]. Therefore, the exact usefulness of the available data to understand what happens in different ionic liquids and atmospheres is still uncertain.

The electrochemistry of decamethylferrocene has been studied in organic solvent systems and proven to be a superior redox standard to ferrocene [13,20,21]. It was concluded that the methyl substitution on the cyclopentadienyl ring prevents both specific and nonspecific interaction between DmFc and external molecules by hindering the access of solvent and supporting electrolyte molecules both to the metal centre and to the ring [13,20,21]. Meanwhile, the applicability of DmFc as an IRRS in ILs was recently addressed by studying the effect of ionic liquid structure on the mid-point potentials of Fc and DmFc [2,3,15]. The ILs were used either in dichloromethane, where the IL was added as the supporting electrolyte, as well as under neat conditions. The first of these experiments was performed using DmFc as the IRRS, which in this organic solvent system is less sensitive to solvation effects [13]. A variation of 0.034 V in the redox potential of Fc vs. DmFc was observed when the supporting electrolyte was changed from 0.1 M 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [bmim][OTf], to 0.1 M 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, [emim][FAP] [15]. The IL solvation effect is even more pronounced under neat conditions, where a variation in the redox potential of Fc vs. $DmFc^{0/+}$ of about 0.100 V is observed when the IL was modified from [bmim][OTf] to [emim][FAP] [15].

Despite these observations suggesting that the redox potential of Fc could be tuned by changing the anion component of the IL as well as by mixing the ILs with another organic solvent system and that the $DmFc^{0/+}$ couple is less solvent dependent, more studies are required to verify the validity of this assumption. Furthermore, information about DmFc solubility, diffusion coefficient, and effect of argon and vacuum on its electrochemical behaviour is not yet available.

The present study reports the voltammetric and amperometric behaviour of both Fc and DmFc under two different atmospheric conditions in six different ionic liquids. The selected IL anions possess different donor properties, which will allow the verification of their effect on the redox potential of the metallocenes under study. Exceptions are the [FAP]-containing ILs, which will shine light about the effect of the cations on the mentioned potentials. The concentration, volatility, heterogeneous electron-transfer rate constant (k^0), and diffusion coefficients of Fc and Fc^+, as well as the solubility, k^0, and mass-transport properties of DmFc and $DmFc^+$ were determined by fitting the experimental chronoamperometric and voltammetric data with numerical and digital simulations. The effect of argon and vacuum on these values is also discussed. In addition, the experimental half-wave potential and mid-point potential of Fc/Fc^+ vs. DmFc/$DmFc^+$, as well as the formal potential after correction for inequality in the diffusion coefficients of both redox processes under argon and vacuum atmosphere are also presented. Provision of this fundamental information provides a basis for accurate comparison of redox processes in different ionic liquids.

2. Experimental

Reagents. High purity grade (>99.0%) 1-methyl-3-butylimidazolium hexafluorophosphate, [bmim][PF_6], 1-methyl-3-butylimidazolium tetrafluoroborate, [bmim][BF_4], 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)amide, [bmim][NTf_2], 1-methyl-3-butylimidazolium trifluoromethanesulfonate, [bmim][OTf], 1-methyl-1-butylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, [bmpyr][FAP], 1-methyl-3-ethylimidazolium tris(pentafluoroethyl)trifluorophosphate, [emim][FAP], were purchased from Merck. The structure of these ionic liquids was reported elsewhere [15]. Ferrocene, Fc or $[Fe^{II}(\eta^5\text{-}C_5H_5)_2]$ (98%, Aldrich), decamethylferrocene, DmFc or $[Fe^{II}(\eta^5\text{-}C_5(CH_3)_5)_2]$ (97%, Aldrich), and tetrabutylammonium hexafluorophosphate, Bu_4NPF_6 (≥99.0%, Fluka) were used as received without further purification.

Apparatus and Procedures. Voltammetric experiments were performed at room temperature (21 ± 1 °C) with a Gamry Reference 3000 potentiostat (Gamry, USA). The voltammograms and chronoamperograms were obtained using a conventional two-electrode arrangement, consisting in a 6.2 μm diameter carbon fibre (CF) working electrode (ALS, Japan) and a platinum wire as a quasi-reference electrode (QRE), being the QRE surface area immersed into the IL larger than the working electrode area. It is worth mentioning that a two-electrode system constituted by a micron-scale working electrode and a reference/counter electrode is suitable for this work, since the very low current, in the order of picoampere (10^{-12} A), passing through the system leads to negligible electrolytic change within the QRE. In addition, the uncompensated resistance present in the system becomes small enough to neglect. This fact was further validated by comparing volammograms of a 14.91 mM Fc in [emim][FAP] obtained with a two-electrode arrangement with that obtained inside an argon-filled glove box with a three-electrode system. To this end, the same CF working electrode, Pt counter electrode, IL solution, and argon atmosphere was used for both experiments. However, in the three-electrode arrangement, the voltammograms were recorded using a Ag/AgCl,R reference electrode (where R represent the IL under study) separated by a porous glass frit from the test solution. For this comparison, the potential of the obtained voltammograms were normalised relative to the decamethylferrocene|decamethylferrocenium, $DmFc^{0/+}$, potential