

Electrochemistry of ferrocene-modified redox ionic liquids

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Research on ionic liquids (IL) is motivated in large part by the almost endless possibilities of chemical modifications that can be made to one of their components to impart a specific functionality to the melt. A neat example of functionalized ionic liquid is found through the modification of alkylimidazoliums with a ferrocenyl redox moiety, resulting in an intrinsically electroactive liquid.¹⁻⁴ Work on redox active polyether hybrid molten salts and other related systems⁵⁻⁷ demonstrated that the investigation of such redox ionic liquids phases can lead to new knowledge on electron transfer in liquid phases due to the intimate proximity of redox centers that cannot be achieved in solute-solvent systems. However, the current library of redox ionic liquids contains almost exclusively structures based on the modification of alkyimidazoliums, with the exception of reports on ferrocene-functionalized phosphonium ionic liquid⁷ and on metallocenium ionic liquids.^{8,9} The design and synthesis of new structures is required in order to further understand the effect of the redox group on ionic liquids properties and to study the electron transfer taking place in these melts.

This contribution describes the properties of new electroactive ionic liquids which are obtained by the modification of either the alkyimidazolium cation or the bis(trifluoromethane)sulfonamide anion (Fig. 1). The electrochemical behavior of such redox ionic liquid phases was studied with the aim of understanding the interaction taking place between the anion and the cation. In particular, the redox ionic liquid obtained by the anion modification with ferrocene (ferrocenylsulfonyl-(trifluoromethylsulfonyl)imide, FcTFSI) showed an unusual behavior at high concentrations and in the absence of supporting electrolyte (see cyclic voltammograms in Fig. 2). The formation of a zwitterion upon oxidation of the anionic ferrocene-modified TFSI generates a diffusion layer with different properties from those of the bulk, decreasing mass transport of species at the electrode.

The effect of the type of ionic liquid, the nature of the substituent and on the alkyl chain length on the electrochemical and physico-chemical properties of the ionic liquids will be discussed with the aim of understanding the role of these parameters in the transport and electron transfer properties in redox ionic liquids.

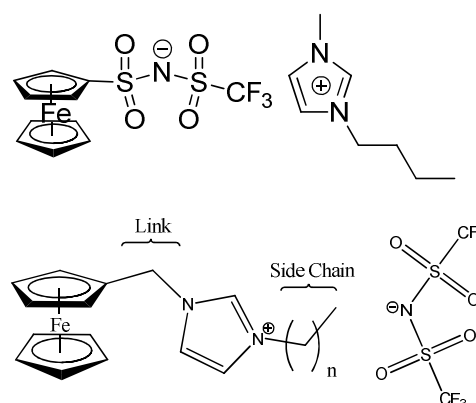


Fig. 1. Ionic liquid ions modified with ferrocene.

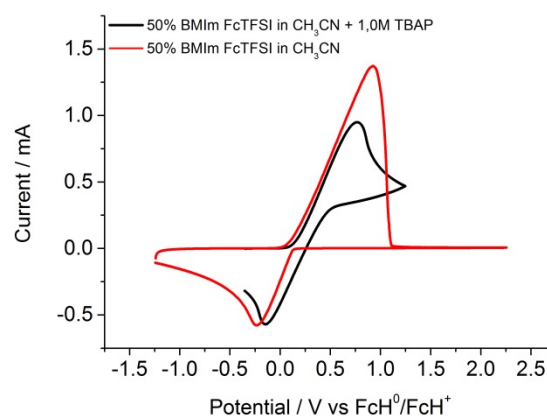


Fig. 2. Cyclic voltammograms ($100 \text{ mV} \cdot \text{s}^{-1}$) obtained for a 50% v/v solution of BMIM FcTFSI in CH_3CN with (black line) or without (red line) 1.0 M TBAP as supporting electrolyte.

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