



Electrochemical and physicochemical properties of redox ionic liquids using electroactive anions: influence of alkyimidazolium chain length



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ABSTRACT

Ferrocenylsulfonyl(trifluoromethylsulfonyl)imide [FcNTf] is reported as a redox anionic species used to obtain an electroactive ionic liquid with a typical alkyimidazolium cation. Here, several of these redox ionic liquids (RILs) were prepared by combining FcNTf with alkyimidazolium cations in order to understand the influence of symmetry and alkyl chain length on the RIL system. The physicochemical and electrochemical properties are characterized for $[C_xC_yIm][FcNTf]$, where x and y were varied between 1 and 8, both in the pure, undiluted state and in solutions of acetonitrile. In pure form, the ionic conductivity of $[C_xC_yIm][FcNTf]$ was found to range between 0.22 and 0.42 mS cm^{-1} at 60°C , and the alkyl chain length was found to have a similar effect on viscosity as in conventional imidazolium-NTf₂ ionic liquids. While an increase in alkyl chain length increases viscosity and decreases mass transport, it was found to have no effect on the redox potential of the ferrocene center. The cyclic voltammetry of $[C_xC_yIm][FcNTf]$ solutions diluted in acetonitrile exhibited behavior which depends on concentration and on the presence of a supporting electrolyte. At concentrations above 50 wt.% and in the absence of any supporting electrolyte, the electroactive anion was found to deposit as a dense film on the electrode upon oxidation. This behavior is linked to formation of Fc^+NTf^- zwitterions, which accumulates in the double-layer and precipitates on the electrode surface. This study also investigates the electrochemical properties of film deposition.

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1. Introduction

Ionic liquids (ILs) are composed entirely of ions and present a melting point below 100°C [1,2]. Their potential application in the field of electrochemistry is very attractive due to the potential – depending on the selected ion – to obtain liquid phases with a low vapour pressure, good thermal and chemical stability, good ionic conductivity, and a large electrochemical window of stability. Ionic liquids become increasingly appealing when considering the numerous possibilities for structure modification and ion combinations. The incorporation of functional groups on the cation or anion structure can be used in order to accomplish specific tasks for a specific application [3–5]. The use of redox-active ionic liquids (RILs) is increasingly prevalent in the literature for fundamental studies on electron transfer in concentrated phases as well as for application in energy storage devices. Redox ionic liquids may be considered intrinsically electroactive with the presence of redox-active

counter-ions. Examples of RILs include iodide-based ([I]) [6–8], metal complexes based on ([Ru],[Co],[Fe]) [9,10] and metallocenium [11] or viologen ($[C_4VC_7]$) [12]–based counter ions. Additionally, ILs may be made electroactive by grafting a redox functional group on a common cation or anion structure. Functional groups such as ferrocenyl (Fc) [13–21], 2,5-di-tert-butyl-1,4-dimethoxybenzene (DDB) [22], 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) [23,24], and metal complexes [25,26] have been reported in the literature. Redox ionic liquids could replace traditional redox systems which are used in several electrochemical applications to transfer electrons in homogeneous or heterogeneous reactions. Related to energy storage and conversion RIL can increase the specific energy in pseudocapacitors [6,27], achieve internal electron transfer in dye-sensitized solar cells [8,23] and act as redox shuttles in lithium-ion batteries to prevent cathode over-oxidation [15,28].

Designing redox-active ILs with improved properties is required to achieve an application in this area, but insufficient fundamental understanding of the relationship between various structure properties is currently impeding progress. While most examples of RILs were obtained through modification of the cation, our group reported on the first example of anion modification with ferrocene in order to generate an electroactive ionic liquid.

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A ferrocenylsulfonyl(trifluoromethylsulfonyl)imide anion (FcNTf) [14] was combined with 1-butyl-3-methylimidazolium, and the resulting RIL's physicochemical and electrochemical properties were discussed in a previous paper. Since only one cation was used in the aforementioned study, the effect of its structure on the ionic liquid's properties was not established. Systematic studies of the effect of structural modifications of the cation in conventional ionic liquids have been previously reported, for example by Watanabe [29,30]. In this study, we wish to determine the role of the imidazolium alkyl's chain length on the transport and electrochemical properties of electroactive ionic liquids employing a redox anion.

To do so, seven different RILs were prepared based on the ferrocenylsulfonyl(trifluoromethylsulfonyl)imide anion (FcNTf) and imidazolium cation (C_xC_yIm). Their structures are presented in Fig. 1. The effect of alkyl chain length and symmetry on the imidazolium was investigated for all cation structures, and viscosity, conductivity and redox properties were measured for the RIL, in pure form as well as in acetonitrile solutions. These properties were compared with conventional, unmodified IL systems found in the literature. Results of cyclic voltammetry experiments on the RIL at high concentrations are discussed to provide additional data on the electrochemistry of these redox liquid phases.

2. Experimental section

2.1. Materials

All reagents and precursor chemicals were obtained from Sigma-Aldrich unless otherwise stated, and all solvents were obtained from Fisher. The trifluoromethanesulfonamide was ordered from Synquest Laboratories. All products were used as received.

2.2. Synthesis of RILs

Synthesis of the redox anion ferrocenylsulfonyl(trifluoromethylsulfonyl)imide (FcNTf) was performed in accordance with a method published earlier [14]. All alkylimidazolium cations were prepared following established procedures, and detailed synthetic steps for the imidazolium cations $[C_1C_2Im]$, $[C_4C_4Im]$, $[C_2C_2Im]$ and $[C_1C_8Im]$ are provided in Fig. S1B [31]. In short, a solution of the corresponding alkylimidazole and alkylhalides was mixed in an acetonitrile solution. The resulting reaction product was washed with ethyl ether and the final product dried under vacuum at 75 °C before characterization (yield: 98%). For the synthesis of $[C_1C_1Im]$ and $[C_8C_8Im]$, a different procedure (Fig. S1C) was used due to a low reaction yield of pathway B and some difficulty in eliminating

impurities from the final product. In this case, sodium imidazolate was added to a 10 ml of THF solution. Two molar equivalents of alkyl halide (1-iodomethane, bromooctane) were then added to the mixture. The mixture was maintained under reflux for four hours. The resulting substance was washed with THF, followed by dichloromethane and diethyl ether (yields: 67% and 99%). The final steps in RIL synthesis consisted of a recombination reaction of cation and redox anion from the metathesis reaction with NaFcNTf dissolved in water, carried out in an ultrasonic bath for two hours (Fig. S1D). This step was followed by intensive washing with water to eliminate the sodium halide salt. The RILs were dried overnight under vacuum and stored in the glove box for further analysis. Following this drying step, the resulting water concentration in undiluted RIL was found at 144 ppm for $[C_1C_2Im][FcNTf]$ and 170 ppm for the $[C_1C_4Im][FcNTf]$. These values are similar to those reported for vacuum-dried unmodified ionic liquids [32].

2.3. Characterization

All synthesized compounds were characterized by 1H , ^{13}C and ^{19}F NMR on a Bruker ADVANCE 300 MHz spectrometer at room temperature and by mass spectrometry (MS) on an Agilent ESI-LC-MSD TOF. Elemental analysis was performed on an EAS 1108 apparatus from Fisons Instruments SPA. Detailed results of this characterization are provided in the supporting information. The presence of water in IL was determined through coulometric Karl Fisher titration (Mettler Toledo Coulometric KI Titrator). The determination of w_{H_2O} was performed three times for each sample. The density measurement was made through a very simple method with an electronic balance (Mettler Toledo XS105 Dual Range) and a 1 ml syringe. The viscosity values were obtained by a viscometer from Cambridge Applied Systems between 50 °C and 80 °C, at temperature intervals of 4 °C. Thermal properties were obtained by DSC analysis on a TA Q2000. Two heating cycles were done on each RIL with a scan rate of 1 °C min⁻¹ at temperatures ranging -70 °C to 100 °C. The ionic conductivity was measured by AC impedance using a Parstat 2273 potentiostat from Princeton Applied Research, with a flow conductivity Orion (018012) cell composed of two platinized Pt electrodes that were calibrated daily with a standard solution of 0.117 M KCl (0.015 S cm⁻¹ at 25 °C). The measurement was carried out from 1 MHz to 1 Hz at 25 °C- 80 °C, at temperature intervals of 4 °C. A BioLogic SP-50 potentiostat was used for cyclic voltammetry (CV) and AC impedance measurements, using a three-electrode setup composed of a silver wire quasi-reference electrode, a Pt wire counter electrode, and a platinum disk working electrode with a surface area of 0.0194 cm². All RILs were diluted in acetonitrile solution with 1 M TBAP and the total volume of solution in the cell for each experiment was about 1.5 mL. All potentials are reported to the

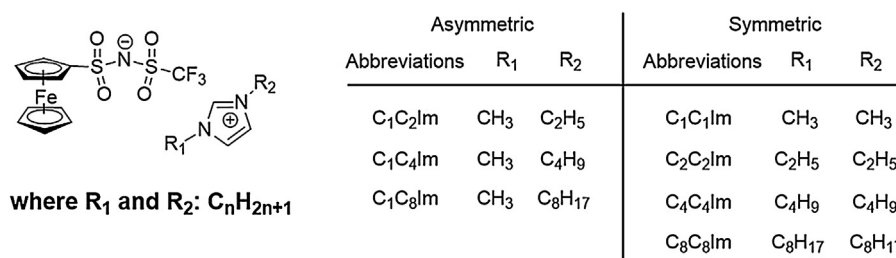


Fig. 1. General structure of $[C_xC_yIm][FcNTf]$ with cation structure variations and abbreviations.

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