



## Convective mass transport in ionic liquids studied by electrochemical and electrohydrodynamic impedance spectroscopy

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### ABSTRACT

In this work, the role of convective mass transport in two ionic liquids (ILs) that differ by the anions 1-butyl-2,3-dimethyl-imidazolium bis(trifluoromethanesulfonyl)imide ([BMMI][Tf<sub>2</sub>N]) and 1-butyl-2,3-dimethyl-imidazolium tetrafluorborate ([BMMI][BF<sub>4</sub>]) were studied in the presence of ferrocene (Fc) as a redox tracer. A rotating disk electrode (RDE) system was used, and the use of electrochemical (EIS) and electrohydrodynamic (EHD) impedance spectroscopies allowed for a deeper analysis of mass transport and charge transfer at the surface of the electrode. The two ILs showed a viscoelastic character that was observed using a parallel plate geometry viscometer with a high storage-to-loss modulus ratio in a frequency domain where the RDE response was characterized by significant elongational flow kinematics. As a general conclusion, the observed effects were interpreted as unbalanced contributions of the elongational flow close to the electrode surface, which induced an anisotropic diffusivity that increased along the flow lines, and the effect of Fc and Fc<sup>+</sup> as structure breakers or strengtheners in the diffusion layer. Finally, from EIS analysis, it was established that increasing the overpotential in the anodic direction yielded an increased Schmidt number, which indicated a detrimental effect on the mass transport of Fc<sup>+</sup>, whose production rate was also increased under the same conditions. EIS showed that the anion had an effect on the reaction rate of Fc oxidation and on the double-layer capacitance value.

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### 1. Introduction

After the pioneering work of Osteryoung and co-workers related to the redox ferrocene (Fc) reaction in ionic liquids (ILs) [1], there have been many published works devoted to the study of diffusion in ILs using macro [2–9] or microelectrodes [10–23]; however, only a few of these studies were performed using convective diffusion conditions, such as rotating disk electrodes (RDE) [5,23], hydrodynamic sono voltammetry [24], and high-speed channel electrodes [25]. Mass transport studies that were performed in quiescent conditions and used electrochemical techniques with microelectrodes provided values of the Fc diffusion coefficient  $D_{Fc}$  in a wide Fc concentration range though some of them limited to one Fc concentration [11,12,14,15,17]. Among those works,  $D_{Fc}$  was found to be both depend [2,11,12] or independent [7,15,18] on its concentration. This influence still remains a controversial issue

because Fc concentration can change during the dissolution and drying processes of Fc in ILs [7,26], and this change could be the reason for the variation of the observed diffusion coefficient. Moreover, it is known that the dissolution of gases [18,27], salts and even neutral species [31,32] can completely change the rheological characteristics of ILs by modifying their short-range structure or by producing a phase transition [31,32]. Based on these assumptions, even that is not surprising that the diffusion coefficient of an electroactive species could change with its concentration, there are strong evidences which show that  $D_{Fc}$  does not change with Fc concentration.

Osteryoung and co-workers [23] showed that it is not easy to achieve steady-state conditions as a consequence of the very high viscosity when using a RDE in ILs, and this high viscosity results in a very large value for the Schmidt number ( $Sc = \nu/D$ , where  $\nu$  is the kinematic viscosity and  $D$  is the molecular diffusion coefficient), which causes a large effect on the transient response. This effect should be of concern in situations where convection is able to play a crucial role in liquids, such as in the fast-growing area dealing with electrodeposition in ILs [33,34], because optimizing this process requires stirring. Another example is in the analysis of data issued from scanning electrochemical microscope

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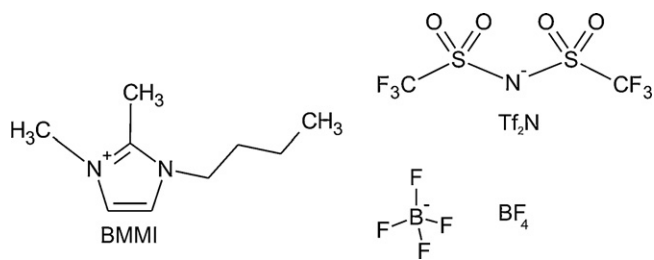


Fig. 1. Schematic structure of the organic cation and anions of the ILs under study.

(SCEM) measurements in ILs, where tip scanning creates local fluid motion [13,19,21,35].

Another critical issue when dealing with convection in ILs is their possible complex non-Newtonian rheological behavior, such as shear-thinning fluids within specific shear rate domains. This complex behavior is due to the presence of structures that are broken by flow or water addition [36,37]. In addition, increasing the viscosity or diffusivity by introducing salts or colloidal particles is known to influence the local structure of ILs and the transport quantities of ILs [38,39]. In fact, depending on the nature of the cation or anion, different structural organizations of ILs are expected that involve either ion-pairing or micelle formation, and they may have a strong impact on the rheological behavior of these fluids [31].

Moreover, when an electrochemical reaction proceeds, there is a change in the electrical charge and negatively or positively charged species are produced. This phenomenon also influences the physico-chemical properties of the ILs close to the interface, which affects transport processes, the structure and characteristics of the double layer [20] and the heterogeneous electron transfer rate constant [11,21]. The electron transport properties in ILs in which Fc groups have been attached to the imidazolium center by different linkers have been investigated. Electron transport was measured in undiluted ILs, and electron transport proceeded by electron hopping reactions of the  $\text{Fc}^+/\text{Fc}$  couple [40].

Despite the complexity of the electrochemical reactions in ILs, it is crucial to understand the kinetics of heterogeneous charge transfer reactions in these media [41]. The aim of this work is to contribute to the understanding of the convection phenomenon of redox active molecules, and this is the first experimental approach to characterize the simultaneous changes in transport processes that are expected to take place in ILs in the presence of a redox reaction. The oxidation of Fc in two different ILs, 1-butyl-2,3-dimethyl-imidazolium bis(trifluoromethanesulfonyl)imide ([BMMI][Tf<sub>2</sub>N]) and 1-butyl-2,3-dimethyl-imidazolium tetrafluoroborate ([BMMI][BF<sub>4</sub>]) (schematic structures shown in Fig. 1) was chosen for this study, being the investigations performed over a wide Fc concentration domain. In spite of the increasing in viscosity caused by the introduction of a methyl group in the cation C-2 position [42], these ILs were selected after considering their differential transport properties and their chemical stability against lithium metal, caused by the presence of a methyl group in the cation C-2 position [43], which is of vital importance considering their application as electrolyte in Li-batteries.

Among several techniques, like ac voltammetry combined with RDE recently proposed by Bano et al. [44], in which is possible to get information about diffusion coefficient and electrode mechanism and kinetics in one single experiment, in the present contribution, the measurements were done under convection conditions that were also induced by a RDE, but impedance spectroscopy (electrohydrodynamical spectroscopy (EHD) and electrochemical impedance spectroscopy (EIS)) were used as the measuring techniques.

## 2. Experimental

### 2.1. Preparation of the ILs

The [BMMI][Tf<sub>2</sub>N] synthesis was described in previous work [43]. [BMMI][BF<sub>4</sub>] was obtained by dissolving [BMMI][Br] salt in aqueous HBF<sub>4</sub> (Aldrich), and the solution was stirred overnight. [BMMI][BF<sub>4</sub>] was dissolved in dichloromethane, washed with water, and rotary evaporated. Both ILs were stored under an argon atmosphere in a Labmaster 130 glovebox (H<sub>2</sub>O and O<sub>2</sub> levels were less than 1 ppm).

### 2.2. Ferrocene dissolution in the ILs

Fc (98% purity – Aldrich) powder was dissolved in both ILs by mechanical stirring according to previously reported methods [7]. This solution was centrifuged at 15,000 rpm for 5 min and the upper phase was carefully transferred to a new tube. After that, the concentration of Fc was determined by using a standardized procedure that employs Cu(II) to oxidize the sample and was completed by EDTA titration [45,46]. A representative titration curve of Fc in [BMMI][BF<sub>4</sub>] is shown in Fig. A1 (Appendices). From these curves, the concentrations were obtained and were used to make a plot of the absorbance at 442 nm (a representative spectrum of Fc is shown in Fig. A2, Appendices) as function of the concentration of Fc solutions in both ILs (Fig. A3, Appendices). At this point, it is important to mention that the absorbance values were corrected by colloidal tail as it was mentioned in Ref. [7]. The molar extinction coefficient is  $990 \pm 30 \text{ dm}^2 \text{ mol}^{-1}$  for both ILs and is in agreement with the values reported by Vorotyntsev et al. [7]; the extinction coefficient, along with the absorbance value at 442 nm, was used to determine the concentration of the prepared Fc solutions. Fc concentration did not change along the electrochemical measurements, as it is possible to observe by absorbance spectra taken before and after the experiments (Fig. A4, Appendices). The concentrations of water in both ILs and in the Fc solutions were determined using the Karl Fischer method, and in all cases, the concentration of water was between 300 and 500 ppm, being incremented to 700 ppm after 10 h.

### 2.3. Electrochemical cell and electrodes

For electrochemical measurements a dedicated electrochemical cell was designed. The cell is made of Plexiglass® with a 2 mL internal volume and a PTFE O-ring, which allows the RDE to rotate freely and ensure an airtight passage during the rotation of the electrode. The working electrode is made of  $\varnothing$  1 mm (electrode area  $\sim 7.85 \times 10^{-3} \text{ cm}^2$ ) platinum wire with a  $\varnothing$  3 mm-insulating sheath letting only the circular cross-section in contact with the IL solution (Fig. 2). The maximum accessible rotation speed was 3100 rpm with stability greater than 0.1% above 100 rpm. A platinum mesh (3 cm<sup>2</sup>) was used as an auxiliary electrode, and a Ag wire was used as a pseudo-reference electrode. The working electrode was polished with emery paper down to 2400 grit size, rinsed with alcohol and deionized water, and was dried under warm air flux.

It was verified that the geometrical characteristics of the cell fulfilled the required validity conditions of the Levich theory with two known Newtonian solutions: 0.5 mol dm<sup>-3</sup> KCl solution in pure water (with an Sc number of 10<sup>3</sup>) and in 83%/17% glycerol/water mixture that approached the expected values of viscosity and Sc number of the investigated ILs. The obtained limiting current as a function of  $\Omega^{1/2}$  ( $\Omega$  being the angular disk velocity) curves for both ILs at 0.5 V (vs. Ag) are straight lines that cross the origin of the axes when extrapolated, as expected, based on the theory (Fig. A5, Appendices). Similarly, both the EHD and EIS diagrams displayed characteristic features of Newtonian liquids, and all EHD

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