



Ionic liquids for solid-state electrolytes and electrosynthesis



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ABSTRACT

The aim of this work was to demonstrate that ionic liquids (ILs) as electrolytes for several applications have been explored. We have explored their potential as solvent-free electrolytes dispersed in natural polymer matrix and as electrolytes for electrosynthesis. The ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate ([C₂mim][C₂SO₄]) was dispersed in gelatin and agar, producing free-standing-electrolyte membranes thermally stable up to 200 °C and an ionic conductivity of $9.73 \times 10^{-5} \text{ S cm}^{-1}$ at 30 °C and $2.37 \times 10^{-3} \text{ S cm}^{-1}$ at 100 °C for Gelatin[C₂mim][C₂SO₄] and $1.10 \times 10^{-5} \text{ S cm}^{-1}$ at 30 °C and $7.24 \times 10^{-4} \text{ S cm}^{-1}$ at 100 °C for Agar[C₂mim][C₂SO₄] films. These samples were then tested in electrochromic devices (ECDs) revealing electrochemical reversibility during more than 200 color/bleaching cycles. Moreover, the electrochemical behavior of (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) bromide, [Ni(tmc)]Br₂, at a glassy carbon electrode in the absence and in the presence of unsaturated halides in the ionic liquids, [C₂mim][C₂SO₄] and N,N,N-trimethyl-N-(2-hydroxyethyl) ammonium bis(trifluoromethylsulfonyl)imide ([N_{1112(OH)}][NTf₂]), has been examined by cyclic voltammetry. It was observed that [Ni(tmc)]²⁺ complex was reduced in a reversible one-electron step and the electro-generated [Ni(tmc)]⁺ complex catalytically reduced the carbon–halogen bond of unsaturated halides. The obtained results showed that the investigated ionic liquids are good candidates for use as electrolytes in either solid or liquid form.

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1. Introduction

The choice of the solvent is a critical factor in the development of new materials, synthesis routes and electrosynthetic processes. For instance, a lot of chemical reactions have been performed in aprotic solvents however their toxicity, hazards and high cost make them unattractive media. To overcome these problems ionic liquids (ILs) can be considered a promising alternative to volatile organic solvents (VOCs) either for organic reactions [1,2] or new materials synthesis [1,3]. In comparison to VOCs the ILs possess almost null volatility under ambient conditions [4], good solvation properties for polar and non-polar compounds, low combustibility [5], excellent thermal stability, high conductivity and the possibility of recycling [3]. Consequently, during the last decade, a large number of papers concerning ILs have been published and its denomination as a “green solvent” has appeared. Among these publications electrochemical synthetic processes [6] without any added supporting electrolyte and/or solvent and the evaluation of the redox behavior of

electroactive substrates have been described [6,7]. The use of ILs in other electrochemical technologies such as batteries, fuel cells, solar cells, photovoltaic devices and metal deposition is also largely investigated [8].

In connection with our current interest to seek for new electrochemical eco-friendly methodologies, in this work, we present some selected research results involving current electrochemical applications of ILs to the development of innovative electrolytes for both, ECDs and novel electrosynthesis methodologies. The exploration of the types of mechanism that could be employed for electrosynthesis in such media, that were previously only reported in aprotic solvents that present toxicity or hazard concerns is also presented in this study. Thus ionically conducting membranes based on gelatin and agar and containing room temperature ionic liquids (RTILs) were prepared and characterized by ionic conductivity measurements, thermal analyses and electrochemical stability. Then, these membranes were applied and tested in small ECDs. Moreover, the preliminary studies of electrochemical behavior of [Ni(tmc)]Br₂ complex at a glassy carbon electrode in the absence and in the presence of unsaturated halides in different RTILs has also been examined by cyclic voltammetry.

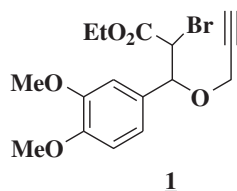
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2. Experimental section

2.1. Reagents and materials

Nickel(II) bromide (Aldrich, 98%), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tetramethylcyclam, tmc, ACROS, 97%) was used as received. Deaeration procedures were carried out with zero-grade argon (Air Products). Published procedures were employed for the preparation of $[\text{Ni}(\text{tmc})]\text{Br}_2$ [9] and ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)-3-propargyloxy-propanoate (**1**) [10].



The ionic liquids used in this work were 1-ethyl-3-methylimidazolium ethylsulfate ($[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$) (IoLiTec; purity of more than 99%) and N,N,N-trimethyl-N-(2-hydroxyethyl) ammonium bis(trifluoromethylsulfonyl)imide ($[\text{N}_{1112}(\text{OH})][\text{NTf}_2]$), which was synthesized with a purity above 99%, as described in a previous paper [11].

In order to reduce water and volatile compounds to negligible values, all samples were dried under vacuum at 10^{-1} Pa and vigorously stirred at ca. 47 °C for at least 24 h. Coulometric Karl-Fischer titrations using Metrohm 831 KF Coulometer revealed always less than 300 ppm of water. This value is a conservative estimate that takes into account the uncertainty associated with the handling of the samples.

2.2. Polymer electrolyte preparation

Samples were prepared according to an optimized procedure described elsewhere by Raphael et al. [12,13]. 0.5 g of agar (Aldrich) was dispersed in 30 mL of Milli-Q water and heated under magnetic stirring for a few minutes up to 100 °C for complete dissolution. Next, 0.5 g of $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$, 0.5 g of glycerol (Himedia, 99.5%) as plasticizer and 0.5 g of formaldehyde as crosslinking agent (Panreac) were added to this solution under stirring. Gelatin-based samples were prepared by dissolving 2 g of colorless gelatin (Dr. Oetker®) and 0.5 g of $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ in 15 mL of Milli-Q water under heating up to 50 °C and magnetic stirring for a few minutes for complete dissolution. Then, 1.25 g of glycerol as plasticizer and 0.25 g of formaldehyde as crosslinking agent, were added to this solution under stirring. Both solutions were then poured on Petri plates and dried for 8–10 days at ambient temperature. Next, the films were transferred to an oven at 60 °C for final drying and then, aged for 1 week. As a result homogeneous and transparent membranes with a thickness of 150 μm were obtained.

2.3. Measurements

2.3.1. Cyclic voltammetry experiments in ILs

2.3.1.1. Cells and electrodes. Cyclic voltammograms were recorded in a two-compartment cell equipped with three electrodes, as described in earlier publication [14]. The working electrode with 3 mm of diameter and area of 0.07 cm^2 was fabricated from glassy carbon rods (Tokai Electrode Manufacturing Company, Tokyo, Japan, Grade GC-20) press-fitted into Teflon shrouds (Du Pont). Before use, the electrode was cleaned with an aqueous suspension of alumina particles with 0.05 μm of diameter (Buehler) on a

Master-Tex (Buehler) polishing pad. The counter electrode was a Pt spiral placed in the same compartment. The experimental reference electrode was a $\text{Ag}/\text{AgCl}/3 \text{ mol dm}^{-3} \text{ KCl}$ in water (-0.036 V vs. SCE), separated from the working electrode by a sinter and Luggin capillary. All solutions were deoxygenated with a fast stream of dry argon before each experiment.

2.3.1.2. Instrumentation. Cyclic voltammograms were recorded with an Autolab PGSTAT-12 controlled by GPES 4.9 software.

2.3.2. Polymer electrolyte characterization

2.3.2.1. Ionic conductivity. The total ionic conductivity of the samples was determined by locating an electrolyte disk between two ion-blocking gold electrodes with 10 mm of diameter (Goodfellow, >99.95%) to form a symmetrical cell. The electrode/polymer electrolyte/electrode assembly was secured in a suitable constant volume support and installed in a Büchi TO51 tube oven with a K-type thermocouple placed close to the electrolyte disk to measure the sample temperature. Before, the day of measured, the electrode/polymer electrolyte/electrode assembly, was subjected at 90 °C during 2 h. In the day after this thermal treatment, impedance measurements were carried out in a drybox with an Autolab PGSTAT-12 (Eco Chemie) equipment. The measurements were conducted during the heating cycles between 25 and 100 °C and at approximately 7 °C intervals; frequencies range from 65 kHz to 500 MHz; *ac* amplitude of 0.025 V and bias potential of 0.0 V.

2.3.2.2. Thermal analysis. Samples of dry films were subjected to thermal analysis under a flowing argon atmosphere between -60 and 200 °C and at a heating rate of 5 °C min^{-1} using a Mettler DSC 821e. Samples for thermogravimetric studies were prepared in a similar manner, transferred to open crucibles and analyzed using a Rheometric Scientific TG1000 thermobalance operating under flowing argon, between 30 and 700 °C and at a heating rate of 10 °C min^{-1} .

2.3.2.3. Electrochemical stability. The evaluation of the electrochemical stability window of the membranes was carried out under an argon atmosphere using a two-electrode cell configuration. The gold microelectrode with 25 μm of diameter was polished with a moist cloth and alumina powder (Buehler; particles with 0.05 μm of diameter) outside the drybox. The cell was assembled by locating a clean lithium disk counter electrode (Aldrich, 99.9%; 19 mm of diameter and 0.75 mm thick) on a stainless steel current collector and centering a sample of membrane on the electrode surface. THF was used to soften the electrolyte and to obtain a reproducible microelectrode/electrolyte interfacial contact. Thus, 2 μL of THF was placed on the gold microelectrode surface and next the membrane sample and the counter electrode were assembled together and supported firmly by means of a clamp. An Autolab PGSTAT-12 (Eco Chemie) was used to record voltammograms at scan rate of 30 mV s^{-1} . Measurements were performed at room temperature, within a Faraday cage and carried out in a drybox.

2.3.2.4. Electrochromic cell assembly. Electrochromic devices with glass/ITO/ WO_3 /electrolyte/ CeO_2 - TiO_2 /ITO/glass configuration were obtained by assembling two pieces of coated glasses [13]. Electrolytes in the form of hydrated membranes were deposited on glass/ITO/ WO_3 coatings and 1 cm free space was left for the electrical contact. Then, the other coated substrate was pressed onto the membrane in such a way that the two coatings faced each other inside the assembled window. A 1 cm wide Cu-conducting tape (3 M) was glued to the free edge of each substrate for electrical connection. The mounted cells were finally sealed with a protective tape (3 M).

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