

The electrochemical properties of a platinum electrode in functionalized room temperature imidazolium ionic liquids

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Abstract The electrochemical behavior of a platinum electrode in a set of 1-alkyl ether (and 1-alkyl)-3-methylimidazolium room-temperature ionic liquids (RTILs) 1–3 ($[\text{C}_x\text{O}_y\text{Mim}]^+[\text{Anion}]^-$ or $[\text{C}_x\text{Mim}]^+[\text{Anion}]^-$, where Mim = 3-methylimidazolium; C_xO_y = 1-alkyl ether; C_7O_3 = $-(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_3$; C_3O_1 = $-(\text{CH}_2)_2\text{OCH}_3$; C_x = 1-alkyl; C_{10} = $\text{C}_{10}\text{H}_{21}$; C_4 = C_4H_9 ; and $[\text{Anion}]^-$ = H_3CSO_3^- , BF_4^- , or PF_6^-) was studied by cyclic voltammetry and electrical conductivity. This complementary set of imidazolium RTILs allowed us to explore the effect of the imidazolium cation and the counter-ion, both of which affected the electrochemical window of these RTILs. Various electrochemical events with low current values were observed, which diminished the electrochemical windows. Interestingly, RTILs 2b [1-(2-methoxyethyl)-3-methylimi-

dazolium tetrafluoroborate] and 2d [1-butyl-3-methylimidazolium tetrafluoroborate] showed quasireversible charge transfer processes. The length of the functional group attached to the imidazolium cation was shown to be of great influence as larger electrochemical windows, as well as lower electrical conductivities, were obtained with the longer C_7O_3 and C_{10} functional groups. The largest electrochemical window of 2.0 V was achieved with RTIL 2c, 1-decyl-3-methylimidazolium tetrafluoroborate.

Keywords Platinum electrode · Ionic liquids · Electrochemical window · Conductivity · Cyclic voltammetry

Introduction

Ionic compounds that are liquid at elevated temperatures are fused/molten salts. Room-temperature ionic liquids (RTILs) are ionic compounds with a weak interaction between the ions, which allows them to be liquid at and below room-temperature. Imidazolium cation-based ionic liquids are an important class of RTILs, which are used in a wide variety of applications due to their attractive physical–chemical properties [1, 2]. These properties include (1) air and moisture stability, (2) nonflammability, (3) thermal stability, (4) the absence of a measurable vapor pressure (no production of atmospheric volatile organic carbons), (5) being liquid over a wide temperature range, (6) wide electrochemical windows, (7) high conductivities and ionic mobilities, (8) easy recycling, and (9) tunable miscibility with water and organic solvents. Furthermore, imidazolium RTILs are a good solvent for a wide range of organic and inorganic compounds, which makes them an attractive solvent alternative for environmentally friendly processes. As a result, imida-

Dedicated to the memory of Prof. Francisco Nart.

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zolinium RTILs have found important applications in research fields like synthetic chemistry [1, 3], catalytic processes [2, 4–7], electrochemistry [8–10], and material science [1].

The easy modification of the cation and anion in imidazolium RTILs is an advantage for the development of task-specific RTILs for catalysis, organic synthesis, nanoparticles, extraction and dissolution, etc. [11–13]. However, structural modifications affect their physical–chemical properties. As a consequence, it is of great importance to understand the relation between structural changes and properties of imidazolium RTILs. In this paper we report about the electrochemical properties of a platinum electrode in a complementary set of 1-alkyl ether [14] (and 1-alkyl)-3-methylimidazolium RTILs 1–3 (Fig. 1), as determined by cyclic voltammetry, together with their electrical conductivities. The imidazolium RTILs 1–3 were prepared, using a simple and practical method for the preparation of halide-free ionic liquids [15, 16].

Materials and methods

The deaerated RTILs 1–3 were prepared according to known procedures, and the spectral data were in agreement with the literature [14–16]. All experiments were performed under a dry argon atmosphere to avoid the presence of oxygen and air humidity. The electrochemical properties of a polycrystalline platinum electrode in RTILs 1–3 were determined at 25 °C by cyclic voltammetry using a potentiostat/galvanostat AUTOLAB PGSTAT30. A homemade glass electrochemical cell, equipped with a Pt working electrode (surface area: 0.9 cm²), a Pt counter electrode with the same surface area, and a Pt quasireference electrode, was used. Cyclic voltammetry experiments were performed under static conditions and included two consecutive cycles recorded at 0.1 V/s. Furthermore, all experiments started from an initial cathodic potential. The electrical conductivity (k_{25}) of the RTILs 1–3 was measured using a Digimed DM-31 conductivity meter equipped with a DMC 010M conductivity cell. The conductivities were measured at room-temperature, immediately after the introduction of the conductivity cell into the RTILs, and automatically standardized to 25 °C.

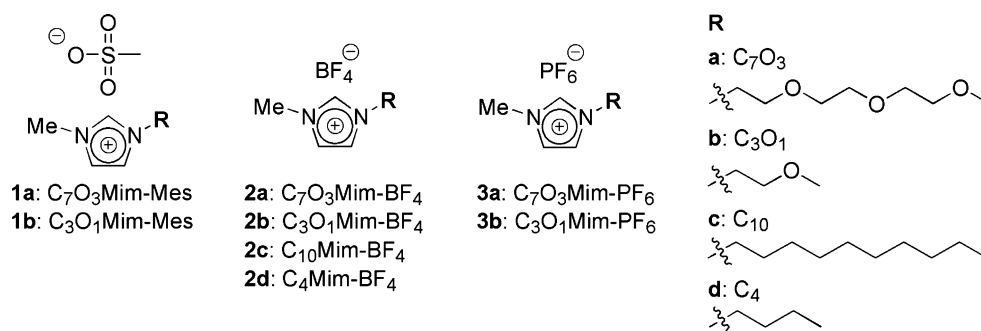
Results and discussion

Cyclic voltammetry – Analysis of the electrochemical window

The primary objective of the research reported herein was to determine the electrochemical windows of a platinum electrode in the functionalized imidazolium RTILs 1–3. A platinum electrode with a relatively large surface area of 0.9 cm² was used to increase the sensitivity of the cyclic voltammetric experiments. This should allow an accurate observation of the cathodic and anodic electrochemical processes at the platinum electrode surface, which is of decisive importance for an exact determination of the electrochemical windows.

The strategy adopted in these cyclic voltammetric experiments was to start the voltammogram from different negative potential values. As the main reason of these experiments was to find the electrochemical window where no charge transfer processes occurred, the anodic value of the potential interval was proportionally changed. Representative examples are presented in Fig. 2, showing the current \times potential curves of a platinum electrode in the methanesulfonate RTILs 1a [C₇O₃Mim-Mes] and 1b [C₃O₁Mim-Mes]. A similar electrochemical behavior was observed for the electrode in both RTILs. Initial cathodic currents were observed even at –0.5 V, and the current values depended on the cathodic potential initially applied to the electrode. These currents were most likely related to the preadsorption of species on the electrode surface due to the interaction between the electrode and the RTIL. Notably, these values decreased in the consecutive second potential sweep, which suggested that this process was associated with the electrochemical reduction of the adsorbed species formed on the electrode surface. Most likely, these charge transfer processes were related to the imidazolium electroreduction to form the corresponding carbene [17–19]. The amount of these adsorbed species increased at a higher cathodic potential. A possible explanation for the decreased current values observed in the second potential sweep could be a thwarted reorientation of the imidazolium cation at the platinum electrode

Fig. 1 Room-temperature imidazolium ionic liquids studied in this work



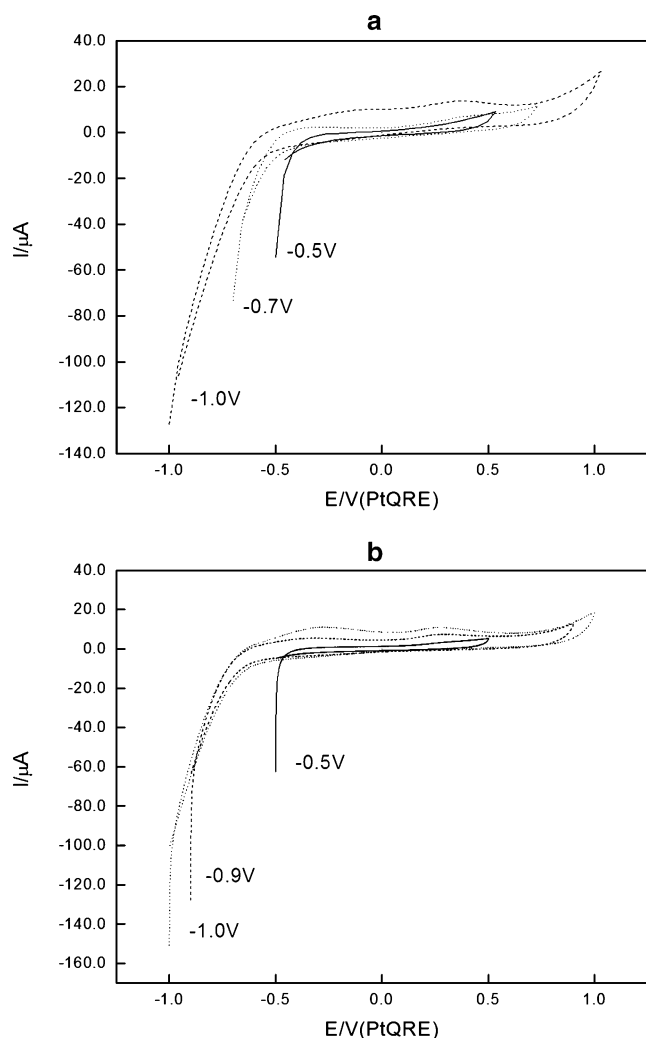


Fig. 2 Effect of the potential interval on the current \times potential curves of a platinum electrode in deaerated methanesulfonate RTILs 1a [$C_7O_3Mim-Mes$] (a) and 1b [$C_3O_1Mim-Mes$] (b), recorded at 0.1 V/s under static conditions; first potential sweep

surface [20]. Another possible explanation could be related to the amount of adsorbed species on the electrode surface, which could be coherent to the decreased current values because the time that the working electrode remained polarized at the initial potential was significantly reduced in the second cycle.

Small current values were observed at 0.5 V during the anodic potential sweep, and increased current values were observed at a higher final anodic potential. Two different anodic events were observed during the anodic potential sweep when an increased potential interval was applied to the electrode. Apparently, the imidazolium cation influenced the electrochemical properties of the electrode in these media as these two events appeared at different potentials of -0.09 and 0.35 V for 1a [$C_7O_3Mim-Mes$] and -0.29 and 0.26 V for 1b [$C_3O_1Mim-Mes$] in case a potential interval from -1.0 to 1.0 V was applied. The charge transfer processes associated to these events could

be related to an irreversible electro-oxidation of species formed at the starting potential. However, a significant increase of the first event, -0.09 V for 1a and -0.29 V for 1b, was observed during the second consecutive potential sweep. The presence of new species, formed at the anodic potential interval, could be responsible for this effect. Altogether, the cyclic voltammograms presented in Fig. 2 demonstrated the importance of applying different potential intervals for the exact determination of electrochemical windows.

Cyclic voltammetry – Effect of the imidazolium cation functional group

The cyclic voltammograms of a platinum electrode in the tetrafluoroborate RTILs 2a [$C_7O_3Mim-BF_4$], 2c [$C_{10}Mim-BF_4$], and 2d [$C_4Mim-BF_4$] recorded with a potential interval from -1.0 to 1.0 V are presented in Fig. 3. These data showed that the 1-alkyl ether and 1-alkyl functionalities of the imidazolium cation exert a pronounced effect on the electrochemical properties of imidazolium RTILs. The shortest electrochemical window of 1.23 V was observed for 2a, regarding the potential interval without charge transfer processes. Significant irreversible charge transfer processes were observed below -0.50 V and above 0.73 V. A comparison between the cyclic voltammograms of 2a and 2c allowed us to study the difference between 1-alkyl ether and 1-alkyl functionalities. The 1-alkyl ether functionality of 2a is responsible for the observed charge transfer processes as RTIL 2c showed none between -1.0 and 1.0 V. A reduction of the 1-alkyl chain-length from 1-decyl to 1-butyl resulted in a smaller electrochemical window for RTIL 2d. The electrochemical window of 2d is in agreement with previously reported data [20].

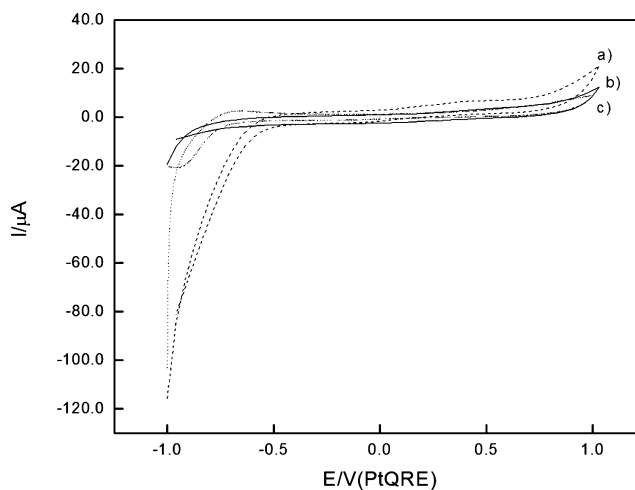


Fig. 3 Cyclic voltammograms of a platinum electrode in deaerated tetrafluoroborate RTILs 2a [$C_7O_3Mim-BF_4$] (a), 2c [$C_{10}Mim-BF_4$] (b), and 2d [$C_4Mim-BF_4$] (c), recorded at 0.1 V/s under static conditions

However, larger electrochemical windows of a platinum electrode in 2d were reported previously [21]. Most likely, this difference is related to the surface area of the platinum electrode because an ultramicroelectrode was used in earlier studies [21]. Surprisingly, RTIL 2d showed a quasireversible charge transfer process in the cathodic potential interval, which was not observed before.

The influence of the C_3O_1Mim and C_7O_3Mim cations of the methanesulfonate RTILs 1b and 1a and the hexafluorophosphate RTILs 3b and 3a on the electrochemical behavior of the platinum electrode was also studied (Fig. 4). A similar trend was observed for the methanesulfonate and hexafluorophosphate RTILs. Charge transfer processes occurred at lower potentials for the RTILs with the C_3O_1Mim cation. The same behavior was observed in Fig. 3 for the 1-alkyl functionalized tetrafluoroborate RTILs

2c and 2d. Apparently, longer 1-alkyl or 1-alkyl ether functionalities were responsible for increasing the electrochemical windows.

Cyclic voltammetry – Effect of the anion

The cyclic voltammograms of the methanesulfonate RTILs 1b and 1a, and the hexafluorophosphate RTILs 3b and 3a, presented in Fig. 4, also allowed a better understanding of the counter-ion effect and its interaction with the functional group of the imidazolium cation, especially when it is taken into account that the C_3O_1Mim or C_7O_3Mim cations were the only species adsorbed on the electrode surface at the initial negative potential. In contrast to the C_7O_3Mim cation, the hexafluorophosphate counter-ion induced pronounced changes on the current \times potential curve associated with charge transfer processes that occurred during oxidation and reduction of the C_3O_1Mim adsorbed species. This observed effect with the C_3O_1Mim cation was probably more predominant due to the shorter distance between the adsorbed species and the counter-ion in solution [22]. This hypothesis was strengthened by the previously observed hydrogen bonds between the PF_6 anion and the imidazolium ring for RTIL 1-butyl-3-methylimidazolium hexafluorophosphate [23–25]. The absence of a strong counter-ion effect with the C_7O_3Mim cation suggests that the longer functional group interacts with the anion, which increases the distance between the adsorbed imidazolium ring and the anion. This assumption is in agreement with a previous report that the adsorption process involves the coordination of the imidazolium ring and that the functional group is bent away from the electrode surface [18].

Figure 5 presents the cyclic voltammograms of the three RTILs with the C_3O_1Mim cation, 1b [$C_3O_1Mim-Mes$], 2b [$C_3O_1Mim-BF_4$], and 3b [$C_3O_1Mim-PF_6$], recorded in a

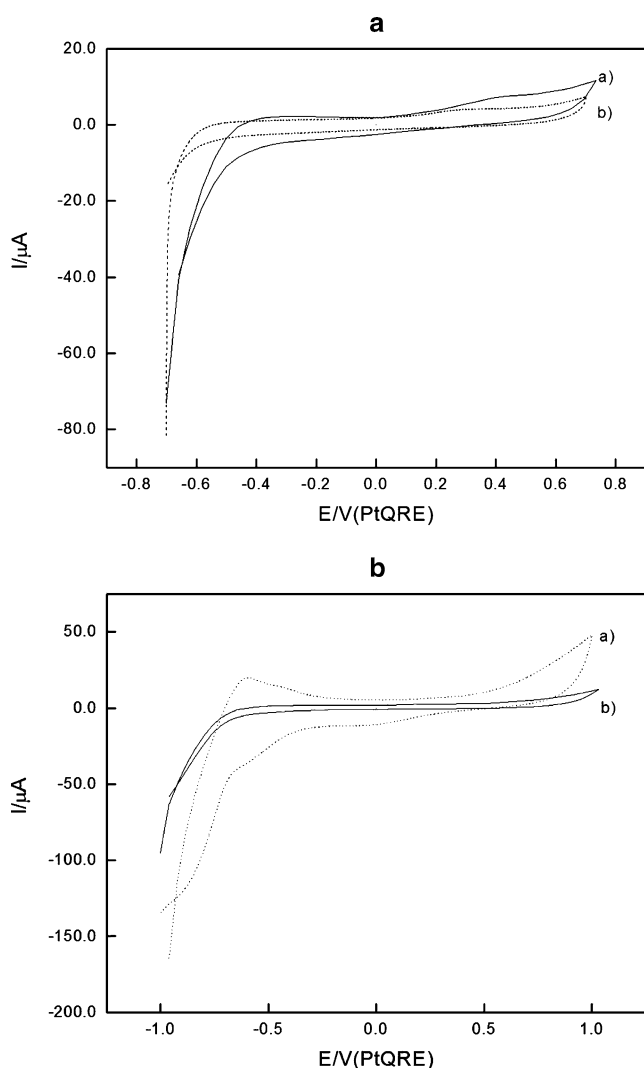


Fig. 4 Cyclic voltammograms of a platinum electrode in deaerated methanesulfonate RTILs 1b [$C_3O_1Mim-Mes$] (a) and 1a [$C_7O_3Mim-Mes$] (b) (a), and hexafluorophosphate RTILs 3b [$C_3O_1Mim-PF_6$] (a) and 3a [$C_7O_3Mim-PF_6$] (b) (b), recorded at 0.1 V/s under static conditions

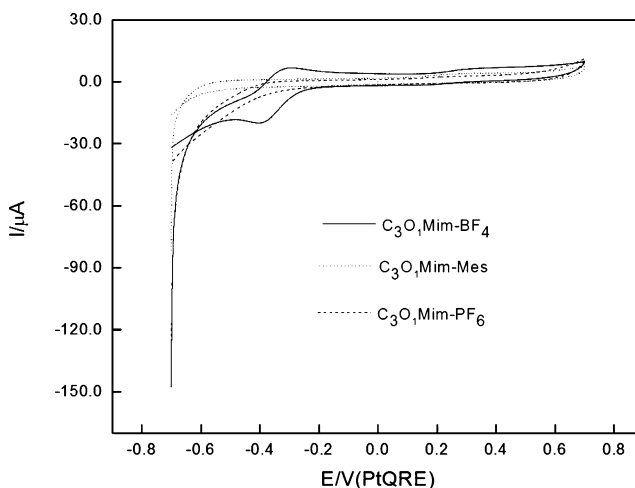


Fig. 5 Cyclic voltammograms of a platinum electrode in deaerated RTILs 1b [$C_3O_1Mim-Mes$], 2b [$C_3O_1Mim-BF_4$], and 3b [$C_3O_1Mim-PF_6$], recorded at 0.1 V/s under static conditions

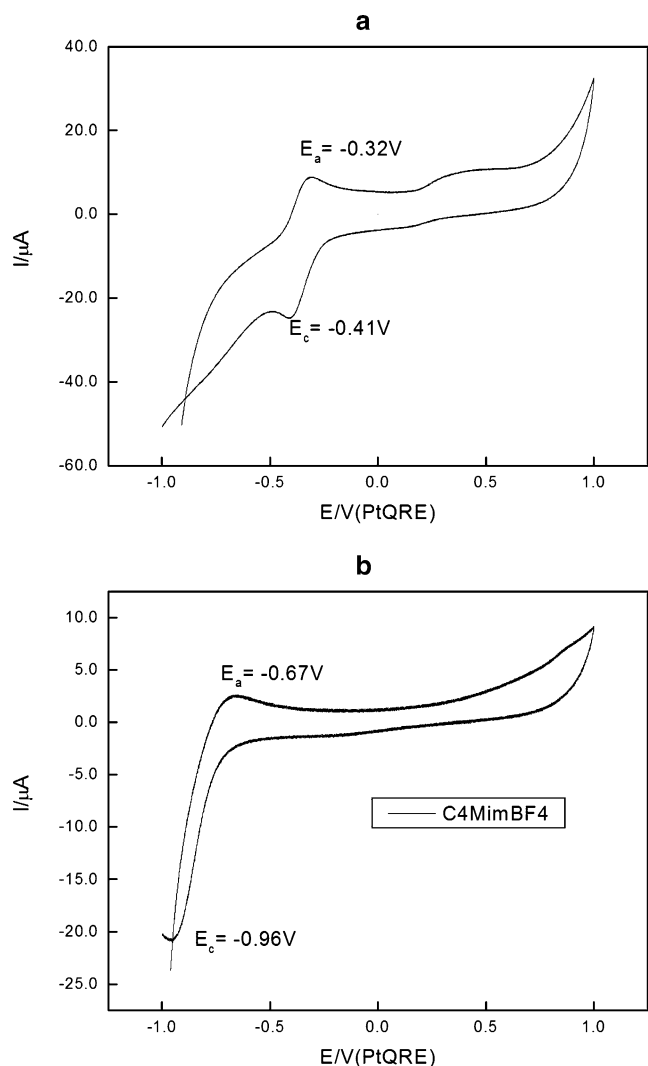


Fig. 6 Cyclic voltammograms of a platinum electrode in deaerated RTILs 2b [C₃O₁Mim-Mes] (a), and 2d [C₄Mim-BF₄] (b), recorded at 0.1 V/s under static conditions

potential interval of -0.7 to 0.7 V. Comparison of the electrochemical behavior of the platinum electrode in these RTILs showed a noticeable difference for 2b. This difference could be due to the influence of the anion adlayer on the metal electrode surface, which could affect the electro-

chemical reactions involved [22]. This electrochemical event was more pronounced when RTIL 2b was studied in a larger potential interval of -1.0 to 1.0 V (Fig. 6a).

Quasireversible charge transfer processes were only observed with the tetrafluoroborate RTILs 2b and 2d (Fig. 6). These processes could be observed by comparing the anodic process during the anodic potential sweep ($E_a = -0.32$ V for 2b and -0.67 V for 2d) with the cathodic one during the cathodic potential sweep ($E_c = -0.41$ V for 2b and -0.96 V for 2d). These quasireversible charge transfer processes remained during the second consecutive potential sweep, which suggested that the same species, present in the bulk, were responsible for this electrochemical behavior.

Cyclic voltammetry – Electrochemical windows of RTILs 1–3

The electrochemical window, the potential interval where no charge transfer processes take place, is the most important parameter with regard to possible electrochemical applications of RTILs 1–3 (Table 1). Current values above 10 μA were considered to be associated with significant charge transfer processes. This low current value was chosen to obtain reliable electrochemical windows, as any electrochemical reaction of the RTILs could interfere in their application. However, it should be kept in mind that this choice resulted in electrochemical windows considerably reduced. As it was observed in the previous sections, the electrochemical processes of the functionalized imidazolium RTILs 1–3 were influenced by both the imidazolium cation and its counter-ion. In general, the presence of a longer 1-alkyl ether or 1-alkyl functionality resulted in larger electrochemical windows (Table 1, entries 1, 3, 5, and 7 vs entries 2, 4, 6, and 8). In contrast to the 1-alkyl functionalized RTILs 2c and 2d, smaller electrochemical windows were observed for the 1-alkyl ether functionalized RTILs 2a and 2b (Table 1, entries 3–4 vs entries 5–6). Most especially, the cathodic potential limits of 2a and 2b were strongly reduced. In general, the cathodic potential region

Table 1 Electrochemical windows of a platinum electrode in RTILs 1–3 under static conditions

| Entry | Ionic liquid | Cation | Anion | Electrochemical window at 25 °C | | |
|-------|--------------|-----------------------------------|---------------------------------|---------------------------------|--------------|-------|
| | | | | Anodic (V) | Cathodic (V) | Total |
| 1 | 1a | C ₇ O ₃ Mim | H ₃ CSO ₃ | 0.70 | 0.56 | 1.26 |
| 2 | 1b | C ₃ O ₁ Mim | H ₃ CSO ₃ | 0.64 | 0.48 | 1.12 |
| 3 | 2a | C ₇ O ₃ Mim | BF ₄ | 0.73 | -0.50 | 1.23 |
| 4 | 2b | C ₃ O ₁ Mim | BF ₄ | 0.80 | -0.21 | 1.01 |
| 5 | 2c | C ₁₀ Mim | BF ₄ | 1.0 | -1.0 | 2.00 |
| 6 | 2d | C ₄ Mim | BF ₄ | 1.0 | -0.66 | 1.66 |
| 7 | 3a | C ₇ O ₃ Mim | PF ₆ | 1.0 | -0.57 | 1.57 |
| 8 | 3b | C ₃ O ₁ Mim | PF ₆ | 0.37 | -0.31 | 0.68 |

Electrochemical cell equipped with a Pt working electrode (surface area: 0.9 cm²), a Pt counter electrode with the same surface area, and a Pt quasi-reference electrode

was more sensitive towards modifications in the structure of the RTILs 1–3.

A trend for the anion effect on the electrochemical window was not observed; however, the hexafluorophosphate anion exerted a much stronger influence in comparison to the methanesulfonate and tetrafluoroborate anions (Table 1, entries 7–8 vs entries 1–4). The most limited electrochemical window was observed for RTIL 3b, mainly due to a negative hexafluorophosphate anion effect. Tetrafluoroborate RTIL 2d [$C_4Mim-BF_4$] is nowadays the standard for electrochemical applications [8–10], which is due to its known large electrochemical window [21]. Interestingly, RTIL 2c [$C_{10}Mim-BF_4$] showed a larger electrochemical window (Table 1, entry 5 vs entry 6). Furthermore, a similar electrochemical window was observed for 1-alkyl ether functionalized RTIL 3a [$C_7O_3Mim-PF_6$] as for 2d (Table 1, entry 7 vs entry 6).

Electrical conductivity

Another important electrochemical parameter that was determined for RTILs 1–3 was their electrical conductivity. Table 2 presents the electrical conductivities (k_{25}) for all RTILs, which is directly related to the functional group attached to the imidazolium ring. In all cases, independently of a 1-alkyl ether or 1-alkyl functionalization, a higher conductivity was measured for the RTILs functionalized with the shorter C_3O_1 and C_4 chains (Table 2, entries 1, 3, 5, and 7 vs entries 2, 4, 6, and 8). The presence of the tetrafluoroborate anion in the 1-alkyl ether RTILs 2a [$C_7O_3Mim-BF_4$] and 2b [$C_3O_1Mim-BF_4$] resulted in strongly enhanced electrical conductivities in comparison to their methanesulfonate and hexafluorophosphate equivalent compounds (Table 2, entries 3–4 vs entries 1–2, 7–8). A comparison between the C_7O_3Mim and the $C_{10}Mim$ cations of the tetrafluoroborate RTILs 2a and 2c showed a dramatic reduction of the conductivity for 2c (Table 2, entry 3 vs entry 5), which showed the lowest conductivity. In contrast to this, substitution of the C_3O_1 functionality with

the C_4 resulted in the largest conductivity (Table 2, entry 4 vs entry 6). In general, differences in the electrochemical properties of RTILs 1–3 could also be originated by their behavior as quasimolecular structure or as ionic species in an extended hydrogen-bonded network [23–25].

Conclusions

The electrochemical properties, including electrochemical window and electrical conductivity, of the functionalized imidazolium RTILs 1–3 were determined. Cyclic voltammetry experiments with a relatively large platinum electrode in 1–3 were allowed to detect the relevant charge transfer processes. Another important strategic parameter was shown to be the performance of the cyclic voltammetry experiments at different potential intervals, together with a second consecutive potential sweep. The first interaction at the initial cathodic potential between the electrode surface and 1–3 involved an adsorption process. This reduction process on the metal surface was ascribed to the transformation of the imidazolium cation into its corresponding carbene. In some cases, depending on the RTIL and the applied potential interval, irreversible electro-oxidation processes of species formed at the starting potential were observed during the anodic potential sweep. Interestingly, RTILs 2b and 2d showed quasireversible charge transfer processes involving the adsorbed species, which has not been previously observed.

Both the functionalized imidazolium cation and the anion of RTILs 1–3 affected the electrochemical window of the platinum electrode. Functionalization of the imidazolium cation with longer 1-alkyl or 1-alkyl ether chains resulted, in general, in larger electrochemical windows. Reduced electrochemical windows were observed for the 1-alkyl ether functionalized RTILs. In contrast to the methanesulfonate and tetrafluoroborate RTILs, a dramatic effect on the electrochemical window was observed for the hexafluorophosphate RTILs 2a and 2b. Apparently, the distance between the adsorbed species and the anion in solution is an important parameter for the anion effect, which suggests that the functional group attached to the imidazolium ring is bent away from the adsorption plane. As a consequence, 3b showed the smallest electrochemical window. Interestingly, the largest electrochemical window was achieved with 2c, which was larger than the one obtained with the well-known RTIL 2d.

RTILs with the shorter C_3O_1 and C_4 functionalities showed higher electrical conductivities. Electrical conductivities were strongly enhanced for the 1-alkyl ether functionalized tetrafluoroborate RTILs 2a and 2b. The observations reported herein are expected to facilitate the development of electrochemical applications with imidazolium RTILs.

Table 2 Electrical conductivities of the RTILs 1–3 at 25 °C

| Entry | Ionic liquid | Cation | Anion | k_{25} ($\mu S/cm$) |
|-------|--------------|-------------|------------|-------------------------|
| 1 | 1a | C_7O_3Mim | H_3CSO_3 | 356 |
| 2 | 1b | C_3O_1mim | H_3CSO_3 | 477 |
| 3 | 2a | C_7O_3Mim | BF_4 | 874 |
| 4 | 2b | C_3O_1Mim | BF_4 | 950 |
| 5 | 2c | $C_{10}Mim$ | BF_4 | 337 |
| 6 | 2d | C_4Mim | BF_4 | 1.235 ^a |
| 7 | 3a | C_7O_3Mim | PF_6 | 407 |
| 8 | 3b | C_3O_1Mim | PF_6 | 451 |

^a A value of 1.728 was reported previously for 2d, prepared from 1-butyl-3-methylimidazolium chloride [23–25]

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