

## Synthesis and characterization of the ionic liquid 1-methyl-3-(2,6-(S)-dimethyloct-2-ene)-imidazol tetrafluoroborate

Síntese e caracterização do líquido iônico 1-metil-3-(2,6-(S)-dimetiloct-2-ene)-imidazol tetrafluoroborato

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### Abstract

Ionic liquids (ILs) are good electrical conductors and organic liquid compounds at room temperature, with potential applicability in water electrolysis for H<sub>2</sub> generation. The objective of this work is to describe the synthesis, characterization and study of the feasibility of ionic liquid 1-methyl-3-(2,6-(S)-dimethyloct-2-ene)-imidazolium tetrafluoroborate (MDI-BF<sub>4</sub>) as electrolyte to produce hydrogen through electrolysis of water. The synthesized MDI-BF<sub>4</sub> was characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), mid-infrared spectroscopy with Fourier Transform by method of attenuated total reflectance (FTIR-ATR), nuclear magnetic resonance spectroscopy of hydrogen (NMR <sup>1</sup>H) and cyclic voltammetry (CV). The yield of the synthesis were calculate by the TGA and DSC. From the results: The infrared spectroscopy identified the functional groups of the compound and the B-F bond at 1053 cm<sup>-1</sup>. The NMR <sup>1</sup>H analyzed and compared with literature data confirms the structure of MDI-BF<sub>4</sub>. The yield of the synthesis of MDI-BF<sub>4</sub> which was 88.84%. The current density achieved by MDI-BF<sub>4</sub> in the voltammogram shows that the IL can conduct electrical current regardless the concentration of water, indicating that the MDI-BF<sub>4</sub> is a potential electrolyte for hydrogen production from water electrolysis.

**Keywords:** Ionic liquid; Tetrafluoroborate; 1-Methylimidazole; Reaction yield; Water; Electrolysis.

### Resumo

Líquidos iônicos (LIs) são bons condutores elétricos e compostos orgânicos líquidos em temperatura ambiente, com potencial aplicabilidade em eletrólise de água para geração de H<sub>2</sub>. O objetivo desse trabalho é descrever a síntese, caracterização e estudo da viabilidade do líquido iônico 1-metil-3-(2,6-(S)-dimetiloct-2-eno)-imidazólio tetrafluoroborato (MDI-BF<sub>4</sub>) como eletrólito para produzir hidrogênio por meio eletrólise da água. O MDI-BF<sub>4</sub>

sintetizado foi caracterizado por análise termogravimétrica (TG) e calorimetria de exploratória diferencial (DSC), espectroscopia de infravermelho médio com transformada de Fourier pelo método de refletância total atenuada (FTIR-ATR), espectroscopia de ressonância magnética nuclear de hidrogênio (NMR  $^1\text{H}$ ) e voltametria cíclica (CV). Os rendimentos da síntese foram calculados pelo TG e DSC. Dos resultados: A espectroscopia de infravermelho identificou os grupos funcionais do composto e da ligação B-F em  $1053\text{ cm}^{-1}$ . O NMR de  $^1\text{H}$  analisado e comparado com dados da literatura confirma a estrutura do MDI-BF<sub>4</sub>. O rendimento da síntese de MDI-BF<sub>4</sub> foi de 88,84%. A densidade de corrente alcançada pelo MDI-BF<sub>4</sub> no voltamograma mostra que o LI pode conduzir corrente elétrica independente da concentração de água, indicando que o MDI-BF<sub>4</sub> é um eletrólito potencial para produção de hidrogênio a partir da eletrólise da água.

**Palavras-chave:** Líquidos iônicos; Tetrafluoroborato; 1-Metilimidazol; Rendimento da reação; Água; Eletrólise.

### Resumen

Los líquidos iónicos (IL) son buenos conductores eléctricos y compuestos líquidos orgánicos a temperatura ambiente, con aplicabilidad potencial en la electrólisis del agua para la generación de H<sub>2</sub>. El propósito de este trabajo es describir la síntesis, caracterización y estudio de la viabilidad del líquido iónico 1-metil-3-(2,6-(S)-dimetiloct-2-eno)-imidazolio tetrafluoroborato (MDI-BF<sub>4</sub>) como electrolito para producir hidrógeno mediante de la electrólisis del agua. El MDI-BF<sub>4</sub> sintetizado se caracterizó por análisis termogravimétrico (TGA) y calorimetría diferencial de barrido (DSC), espectroscopia de infrarrojo medio con transformada de Fourier por método de reflectancia total atenuada (FTIR-ATR), espectroscopia de resonancia magnética nuclear de hidrógeno (RMN  $^1\text{H}$ ) y voltamperometría cíclica (CV). El rendimiento de la síntesis se calculados por TGA y DSC. De los resultados: La espectroscopía infrarroja identificó los grupos funcionales del compuesto y el enlace B-F a  $1053\text{ cm}^{-1}$ . La RMN  $^1\text{H}$  analizada y comparada con los datos de la literatura confirma la estructura de MDI-BF<sub>4</sub>. El rendimiento de la síntesis de MDI-BF<sub>4</sub> que fue del 88,84%. La densidad de corriente alcanzada por MDI-BF<sub>4</sub> en el voltamograma muestra que el IL puede conducir corriente eléctrica independientemente de la concentración de agua, lo que indica que MDI-BF<sub>4</sub> es un electrolito potencial para la producción de hidrógeno a partir de la electrólisis del agua.

**Palabras clave:** Líquido iónico; Tetrafluoroborato; 1-Metilimidazol; Rendimento de la reacción; Agua; Electrólisis.

## 1. Introdução

Ionic liquids have become increasingly popular as a reactive medium for chemical synthesis as well as they have been widely promoted as ‘green solvents’, which are considered powerful alternatives to the volatile organic compounds (VOCs) in the organic synthesis field. In addition, the task-specific ionic liquids (TSILs), in which the functional group is covalently bonded to the ionic liquid cation or anion (or both), are the last generation of ILs. The incorporation of this functionality should allow the ionic liquid to work as both medium reaction and reagent or catalyst in certain reactions and processes. Nowadays, the TSILs have been applied in chemical industries and have attracted great interest in many areas of research, specially in organic synthesis, due to economic and ecological reasons (Yue *et al.*, 2011).

Due to their extraordinary characteristics, the ionic liquids are important materials which present applications such as solvents in organic and organometallic synthesis, in catalysis, as electrolytes in electrochemistry, in fuels and photovoltaic cells, as lubricants, as stationary phase for chromatography, as matrices for mass spectrometry, as supports for enzymes and catalysts immobilization, in separation technologies, as liquid crystals, as templates for synthesis of mesoporous materials, nanomaterials and fine films, as materials for embalming and preservation of tissues (Liu & Yu, 2019; Rola *et al.*, 2019). Their great number of cations and anions allows the achievement of a wide range of physical and chemical characteristics, including volatile and nonvolatile systems. This allows the control of the reaction processing, as well as the control of the solvent-solute interactions (Zhu *et al.*, 2019).

Ionic liquids have been studied to an increasing extent at room temperature in attempt to make it environmentally ‘green’. They present low vapour pressure and limited miscibility with water and organic solvents; which indicates those liquids are, possibly, fully recyclable. The most common ionic liquids are formed by dialkylimidazolium cations and, a voluminous and hydrophobic anion (Babucci & Uzun, 2016; Baek *et al.*, 2017; Díaz-Rodríguez *et al.*, 2015; Ezzat *et al.*, 2018; Namboodiri & Varma, 2002; Orsini *et al.*, 2009; Palgunadi *et al.*, 2009; G. Wang *et al.*, 2016; Y. Wang *et al.*, 2014; Xiao *et al.*, 2010; Yan *et al.*, 2015; Zec *et al.*, 2018; Zicmanis & Antaina, 2014). These solvents are relatively inert and tolerate a large

variety of chemical substances, but they are generally good for the nucleophilic substitution reaction. In addition, the salts have a polar nature (Liang *et al.*, 2010). The present work has as objective the synthesis, characterization and study of the viability of the 1-methyl-3-(2,6-(S)-dimethyloct-2-ene)-imidazol tetrafluoroborate ionic liquid as electrolyte for the hydrogen production through water electrolysis. The reaction yield were determined by thermal methods (TGA and DSC), infrared characterization, nuclear magnetic resonance of hydrogen, and the study of the viability of the ionic liquid as electrolyte for the hydrogen production through water electrolysis by cyclic voltammetry.

## 2. Metodologia

Materials used: 8-bromo-2,6-dimethyloct-2-ene (219.16 g·mol<sup>-1</sup>, 95.0 %, Sigma Aldrich); 1-methylimidazole (82.10 g·mol<sup>-1</sup>, 99.0 %, Sigma Aldrich); acetonitrile (41.05 g·mol<sup>-1</sup>, 99.9 %, Sigma Aldrich); sodium tetrafluoroborate (109.79 g·mol<sup>-1</sup>, 98.0%, Sigma Aldrich) and acetone (58.08 g·mol<sup>-1</sup>, 99.5 %, Sigma Aldrich).

The 1-methyl-3-(2,6-(S)-dimethyloct-2-ene)-imidazolium bromide was prepared by the reaction between 8-bromo-2,6-dimethyloct-2-ene (20 mL, 96.2 mmol) and 1-methylimidazole (8.563 g, 97.17 mmol) dissolved in 40 mL of acetonitrile in a 100 mL round-bottom balloon coupled to a reflux condenser. The system ware kept under magnetic stirring and heating at 50 °C for 24 h. The resulting viscous mixture was taken to a Rotary evaporator (model 826 T), at 200 rotations per minute, 50 °C, -100 mmHg pressure for 4 h in order to remove the volatile components, with final achievement of a yellowish, viscous, concentrated liquid. The methodology of this synthesis follows the proceedings used by (Wadhawan *et al.*, 2000).

The 1-methyl-3-(2,6-(S)-dimethyloct-2-ene)-imidazolium tetrafluoroborate was obtained by the reaction between sodium tetrafluoroborate (9.943 g, 90.6 mmol) and 1-methyl-3-(2,6-(S)-dimethyloct-2-ene)-imidazolium bromide (26.966 g, 88.7 mmol), which were diluted in 40 mL of acetone. After 24 h of stirring at room temperature, the sodium bromide was removed by filtration and the solution was concentrated in a Rotary evaporator (model 826 T), at 200 rotations per minute, 50 °C, -100 mmHg pressure for 4 h, for the removal of volatile compounds.

The thermogravimetric curves were performed in a TA instruments Q600 equipment up to 900 °C for solid state samples and up to 350 °C for liquid state samples (flow rate of 100 mL·min<sup>-1</sup> of N<sub>2</sub> and heating ramp of 5 °C·min<sup>-1</sup>). The reaction yield was calculated based the thermogravimetric curves through the **Eq. (1)**.

$$R = \left( \frac{pm\ MDI-Br\ 1}{pm\ MDI-Br\ 2} \right) * 100\% \quad (1)$$

Where: R is the yield of the reaction; pm MDI-Br 1 is the mass percentage of MDI-Br and pm MDI-Br 2 is the mass percentage considering the MDI-Br and part of the reagents that did not react. The ionic liquid's mid-infrared absorption spectrum were obtained in a Spectrum 65 FT-IR spectrometer (Perkin Elmer) with scans ranging from 4000 cm<sup>-1</sup> to 650 cm<sup>-1</sup>. The spectra of nuclear magnetic resonance of hydrogen were obtained from Avance DPX-500 spectrometers (Bruker) using a 5 mm direct detection dual probe. The samples were dissolved in quotes of 0.6 mL of deuterated chloroform solvent (CDCl<sub>3</sub>) from Tedia Brazil. The chemical shifts (δ) were expressed in parts per million (ppm). The multiplicities of the hydrogen signals on the RMN <sup>1</sup>H spectrum was indicated according to the convention: s (singlet), d (duplet), t (triplet), m (multiplet).

The cyclic voltammetry proceeded in a glass cell, with -1.2 V initial potential, anodic direction, 0.1 V s<sup>-1</sup> scanning speed, 1.6 V inversion potential, where the scanning continued on the cathodic direction until it reached -1.2 V. The voltammogram was obtained with boron-doped diamond working electrode with 0.20589 cm<sup>2</sup> geometric area, Calomel reference electrode, and platinum counter electrode. Voltammograms were obtained for pure MDI-BF<sub>4</sub>, and for MDI-BF<sub>4</sub> containing 3 and 7 % of deionized water. The experiment was realized in duplicate, and a PGSTAT 302 N potenciostastgalvanostat (Autolab) was employed.

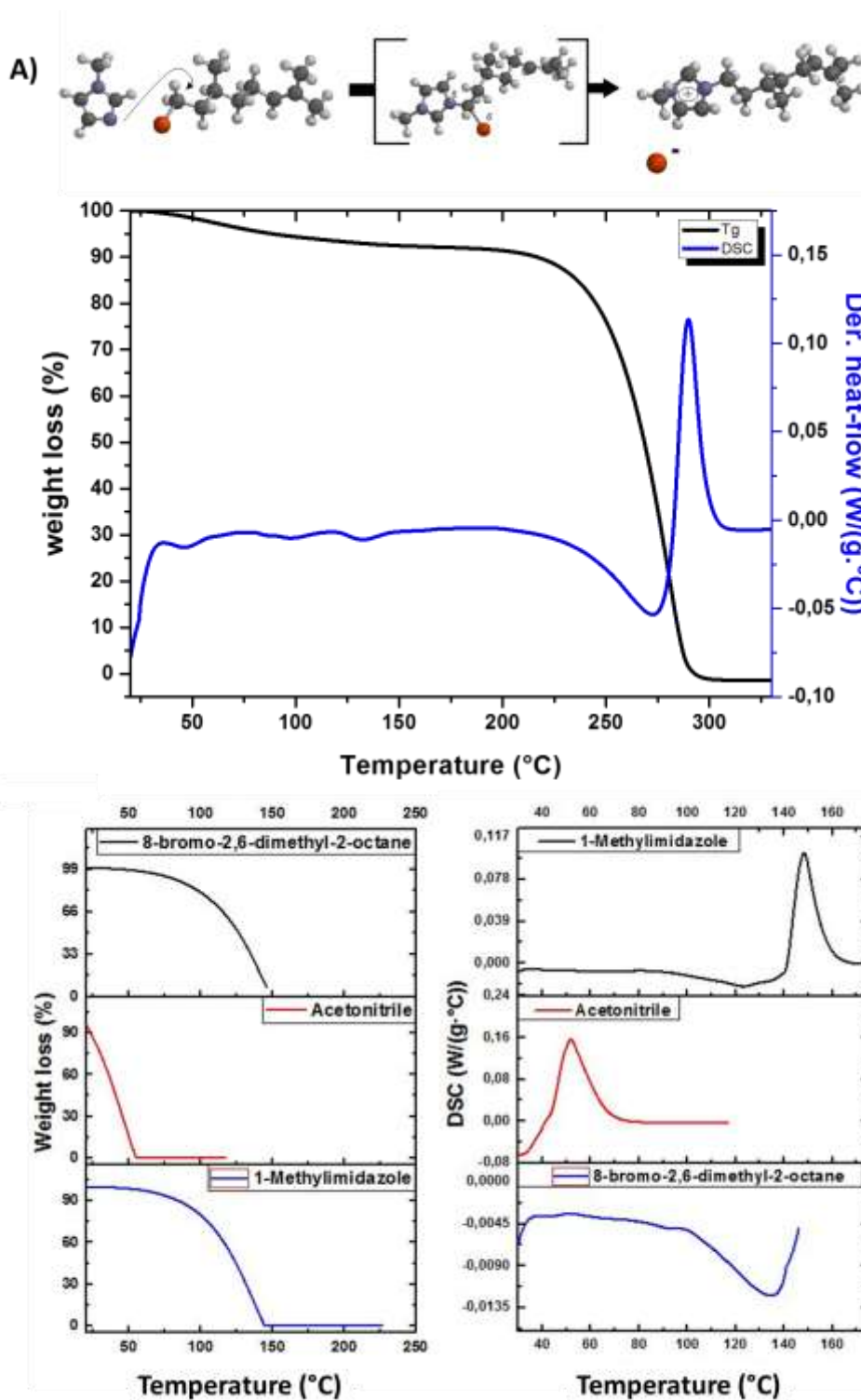
### 3. Results and Discussion

The production of MDI-Br occurs in a single step reaction as seen in Figure 1A, characterized by a bimolecular nucleophilic substitution ( $S_N2$ ) where the nitrogen of the secondary amine acts as a nucleophile attacking the carbon alpha, leading to the release of the bromide. The formation of the N-C bond occurs at the same time as the C-Br Bond cleaves. On the MDI-BF<sub>4</sub> synthesis, the reaction is also  $S_N2$ -type; however in this case, a simple exchange reaction takes place, where the organic chain (specifically the imidazole ring) presents electropositive character and the anion Br<sup>-</sup> is substituted by BF<sub>4</sub><sup>-</sup> due to its more electronegative character, forming the 1-methyl-3-(2,6-(S)-dimethyloct-2-ene)-imidazolium tetrafluoroborate.

After the synthesis, the MDI-Br was analysed by TGA and DSC techniques, in order to obtain the reaction yield. Figure 1B shows the TGA curve, which indicates only one event of mass loss, however when the DSC curve is analysed (Figure 1B), it is observed that the thermal decomposition of MDI-Br occurred in four stages. The first stage of mass loss (between 30 - 76 °C) is associated to the evaporation of acetonitrile, the solvent used on the reaction, which represents 4% of the material even after the vacuum evaporation. The second stage (between 76 - 117 °C) corresponds to the excess of 8-bromo-2,6-dimethyloct-2-ene that did not react with the 1-methylimidazole and was present in 2.40% of the mass of MDI-Br. The third stage (between 117 - 170 °C) corresponds to the evaporation of the 1-methylimidazole that did not react and was present in 1.43%. At last, the fourth stage, between 170 and 193 °C, corresponds to the 1-methyl-3-(2,6-(S)-dimethyloct-2-ene)-imidazolium bromide formed and is present in 92.15% of the mass composition of MDI-Br. The reaction yield was calculated based on the Eq. (1) which accounts only for the mass percentage of reagents and products; this calculus is done neglecting the solvent mass (R is the yield of the reaction which was 96.01 %). The value 92.15% is the mass percentage of MDI-Br (pm MDI-Br 1), 95.98% is the mass percentage considering the MDI-Br and part of the reagents that did not react (pm MDI-Br 2).

The previously described mass loss stages were defined from the study shown in Figure 1C, where it can be see the profile of thermal degradation curves of each reagent used in the synthesis of MDI-Br and of the solvent (acetonitrile). As expected, since the acetonitrile is a solvent with low boiling temperature, it evaporated completely before 60 °C. The 8-bromo-2,6-dimethyloct-2-ene fully volatilized in a temperature lower than 150 °C and the 1-methyloct-2-ene fully volatilized in a temperature inferior to 170 °C. The minimum shift of the DSC curve among Figure 1B and C is due to the intermolecular nteractions between solvent, reagents and products.

**Figure 1** - A) Reaction of production of MDI-Br. B) Thermal analysis of MDI-Br (TGA and DSC). C) Thermal analysis of the reagents (8-bromo-2,6-dimethyl-2-octane and 1-methylimidazole) for the production of MDI-Br, and of the solvent (acetonitrile) used on the synthesis.

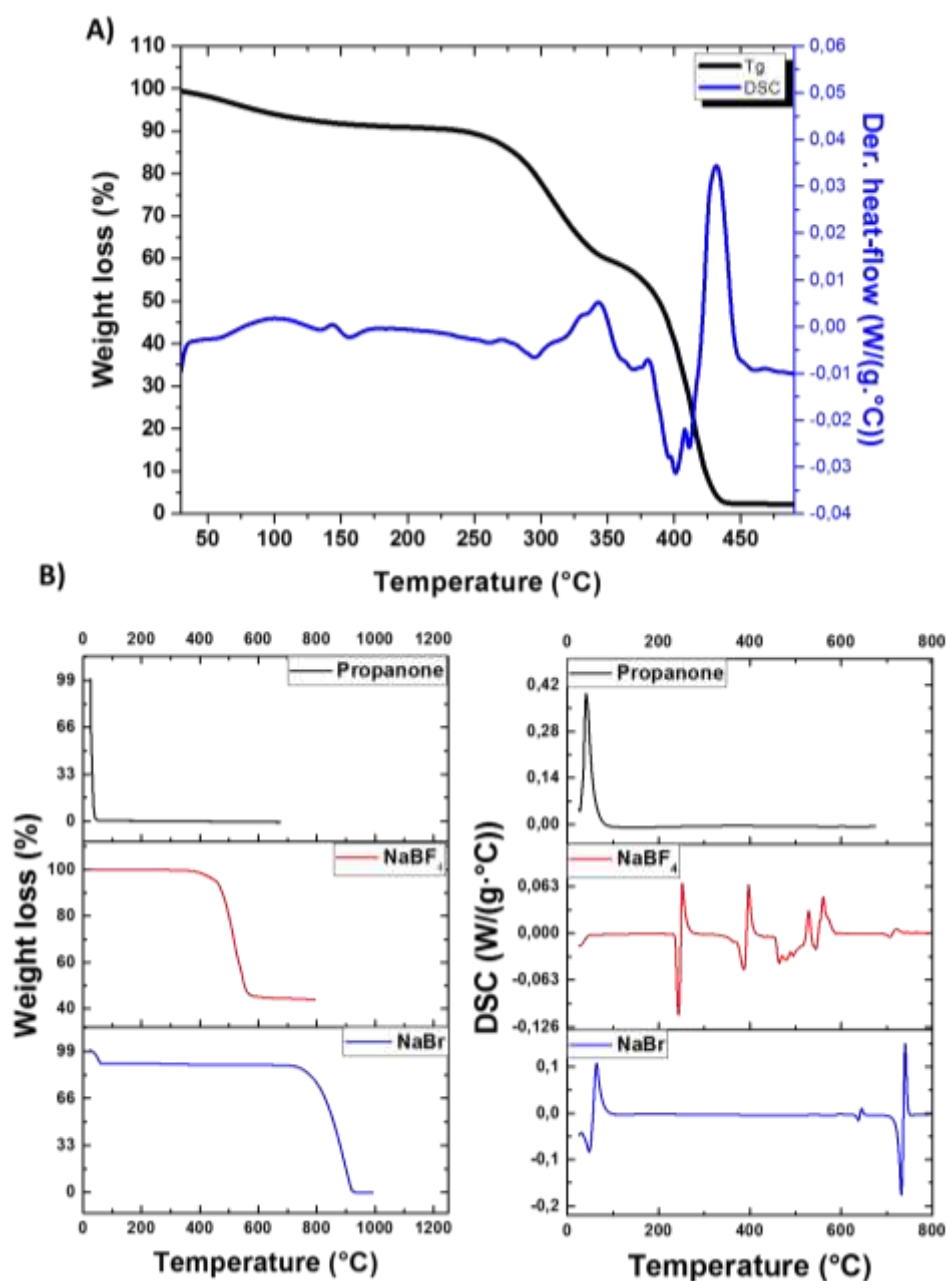


Source: Research data (2021).

The yield of the synthesis of MDI-BF<sub>4</sub> was obtained from Figure 2A, which shows its thermal decomposition curves. The event between 180 and 460 °C on the TGA profile corresponds to the percentage of MDI-BF<sub>4</sub> formed; the previous events correspond to reagents that did not react and follow the same logics applied to the yield of MDI-Br, but here the yield is

represented based on the total mass of the sample. The achieved yield was 88.84%. Figure 2B shows the profiles of thermal degradation curves of each reagent used in the synthesis of MDI-BF<sub>4</sub> and of the solvent (propanone). The first mass loss event occurred at a temperature lower than 60 °C, corresponding to the evaporation of propanone (solvent); while the two events between 125 and 175 °C refer to residues (1-methylimidazole and 8-bromo-2,6-dimethyloct-2-ene) from the synthesis of MDI-Br. The DSC curve of MDI-BF<sub>4</sub> (Figure 1B) shows no evidence of decomposition of NaBF<sub>4</sub>, indicating that virtually all the NaBF<sub>4</sub> was consumed or that part of unreacted NaBF<sub>4</sub> were retained on the filtration. The DSC curve also shows no evidence of thermal decomposition of NaBr, which only occurs at higher temperatures. However, it was observed that TGA curve of NaBr does not achieve the mass percentage of 0, revealing that part of the NaBr (subproduct of MDI-BF<sub>4</sub> synthesis) was either not well filtered, or part of it was dissociated, crossing the filter along with the desired product.

**Figure 2** - A) Thermal analysis of MDI-BF<sub>4</sub> (TGA and DSC). B) Thermal analysis of sodium bromide, sodium tetrafluoroborate and of the solvent (propanone) used on the synthesis of MDI-BF<sub>4</sub>.



Source: Research data (2021).

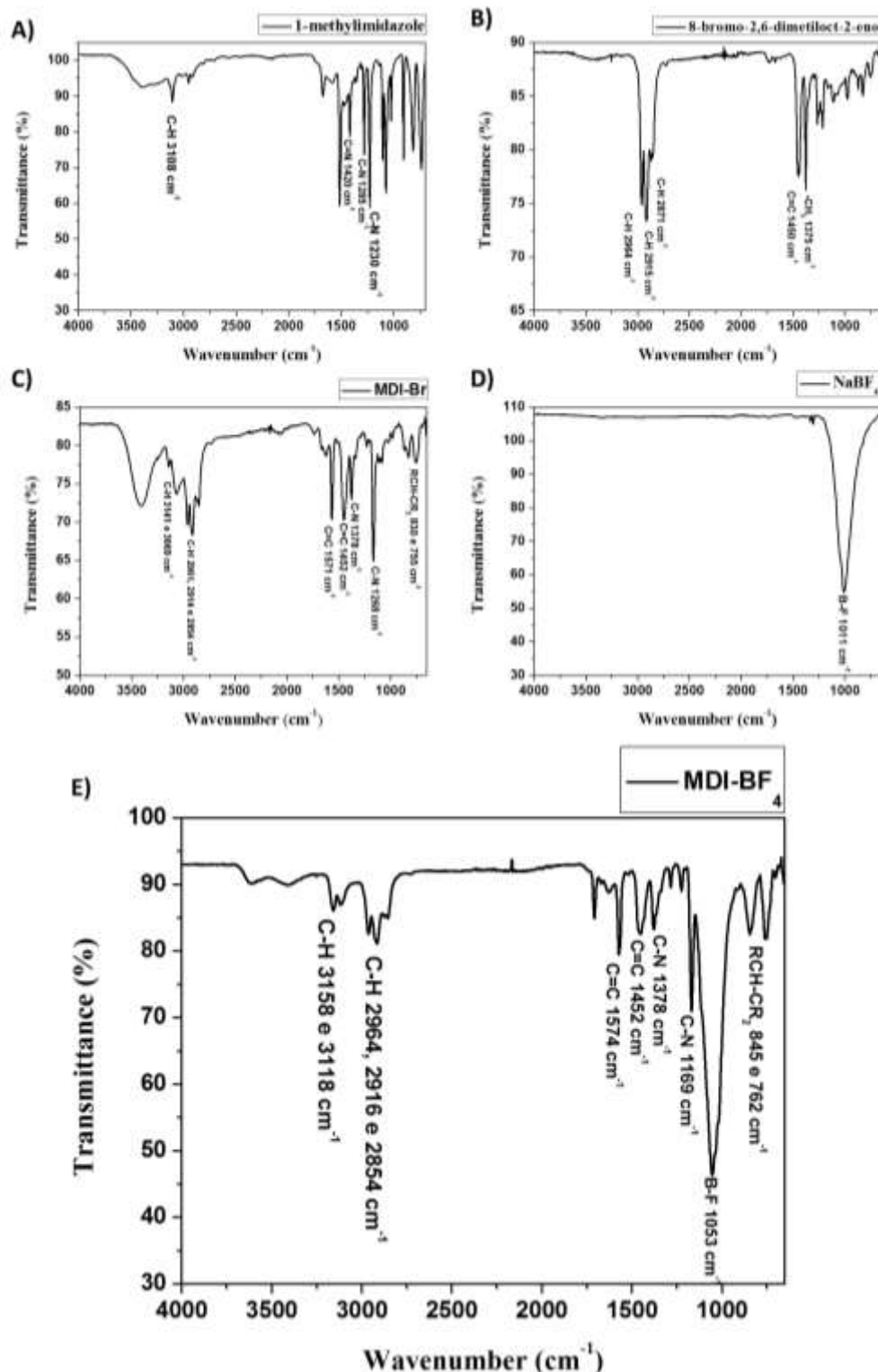


Figure 3A presents the vibrational spectrum of 1-methylimidazol. The spectrum presents bands characteristic of this compound, as the ones at 650 to 1700  $\text{cm}^{-1}$ , referents to the axial deformation vibrations of the imidazol ring's bonds. The peaks between 1200 and 1700  $\text{cm}^{-1}$  correspond to the axial deformations of the bonds C=C, C-N and C=N of the ring. The peak at 1420  $\text{cm}^{-1}$  is associated to the C=N bond; the peak at 1285  $\text{cm}^{-1}$  refers to the C-N bond of aromatics, and the peak at 1230  $\text{cm}^{-1}$  to C-N of aliphatics. At 3108  $\text{cm}^{-1}$  the C-H band of alkenes is observed. Figure 3B shows the vibrational spectrum of 8-bromo-2,6-dimethyloct-2-ene. The bands at 2964, 2915 and 2871  $\text{cm}^{-1}$  refer to the primary, secondary and tertiary carbon of the C-H bond of aliphatics, respectively. The peak at 1450  $\text{cm}^{-1}$  refers to the axial deformation of the C=C bond, and the peak at 1375  $\text{cm}^{-1}$  refers to the angular deformation of  $-\text{CH}_3$  (Small, 1992).

Figure 3C indicates that MDI-Br is successfully obtained from the proposed method, in which the peaks between 3141-3069  $\text{cm}^{-1}$  refer to the C-H bond of aromatics, and the peaks at 2961, 2914 and 2854  $\text{cm}^{-1}$  correspond to the C-H bond of aliphatics; similar values were found by (Wadhawan *et al.*, 2000). The peaks at 1571 and 1452  $\text{cm}^{-1}$  refer to the axial deformation of C=C; the peak at 1378  $\text{cm}^{-1}$  refers to the C-N bond of aromatics, and the peak at 1168  $\text{cm}^{-1}$  to the C-N bond of aliphatics; whereas the peaks at 830 and 755  $\text{cm}^{-1}$  refer to the CH out of the plane of the group  $\text{RCH}=\text{CR}_2$ . The  $\text{NaBF}_4$  used in this study was also analysed by infrared spectroscopy to find out in what region of the spectrum the interaction between fluorine and boron appears. Its spectrum is presented in Figure 3D, presenting only one peak at 1011  $\text{cm}^{-1}$ , which corresponds to the interactions of the four fluorines and the boron.

Infrared spectrum of MDI- $\text{BF}_4$  is depicted in Figure 3E and the peaks between 3158-3118  $\text{cm}^{-1}$  refer to the C-H bond of aromatics; the ones at 2964, 2916 and 2856  $\text{cm}^{-1}$  correspond to the C-H bond of aliphatics, and the peaks at 1574 and 1452  $\text{cm}^{-1}$  are related to the axial deformation of the C=C bond. Whereas, the peak at 1378  $\text{cm}^{-1}$  refers to the C-N bond of aromatics, and the peak at 1169  $\text{cm}^{-1}$  refers to the C-N of aliphatics; the peaks at 845 and 762  $\text{cm}^{-1}$  refer to the C-H out of the plane of the group  $\text{RCH}=\text{CR}_2$ , and the peak at 1053 corresponds to the B-F bond.

**Figure 3** - Mid-infrared spectra of: A) 1-methylimidazole; B) 8-bromo-2,6-dimethyloct-2-ene; C) MDI-Br; D) sodium tetrafluoroborate; E) MDI-BF<sub>4</sub>.



Source: Research data (2021).

In the RMN <sup>1</sup>H spectrum of MDI-BF<sub>4</sub> (Figure 4A), characteristic aromatic hydrogen signals of the imidazole ring appear between 7.0 and 9.0 ppm, where the singlets at 8.91, 7.42 and 7.32 ppm correspond to the hydrogens H2, H4 and H5, respectively. In the same spectrum, singlets observed at δ 3.93, 1.63 and 0.93 ppm, are characteristic of methylic hydrogen of



the lateral chain derived from the 8-bromo-2,6-dimethyloct-2-ene. The other hydrogens of this aliphatic chain appear concentrated on the region between  $\delta$  1.0 and 5.1 ppm; a triplet signal at  $\delta$  5.02 ppm is characteristic of non conjugated Double bond corresponding to H12; a multiplet signal at  $\delta$  4.18 ppm corresponds to H7; a multiplet signal at  $\delta$  1.93 ppm corresponds to H9 and H11; multiplets signals at 1.67 and 1.46 ppm corresponding to H8; and multiplets signals at 1.32 and 1.24 ppm are referent to H10. From the analysed results, as well as for comparison with literature (Liu & Yu, 2019; Wadhawan *et al.*, 2000) as shown in Table 1, it is possible to confirm the formation of the 1-methyl-3-(2,6-(S)-dimethyloct-2-ene)-imidazolium tetrafluoroborate.

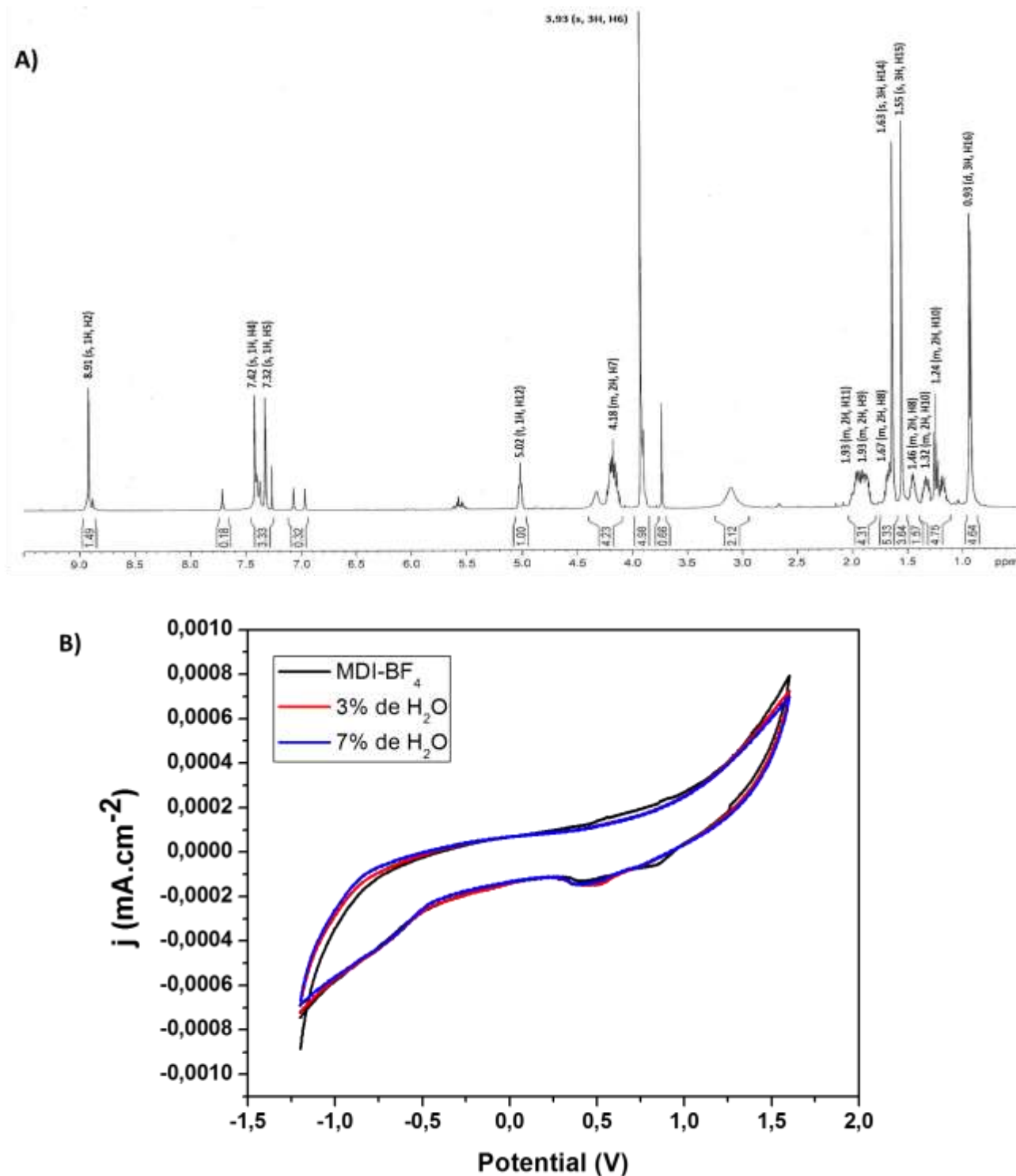
**Table 1** - RMN  $^1\text{H}$  data for the compound MDI-BF<sub>4</sub> in comparison with literature data in CDCl<sub>3</sub>.

MDI-BF <sub>4</sub>	Literature <sup>a</sup>
8.91 (s, 1H, H2)	9.09 (s, 1H, H2)
7.42 (s, 1H, H4)	7.46 (s, 1H, H4)
7.32 (s, 1H, H5)	7.36 (s, 1H, H5)
5.02 (t, 1H, H12)	5.04 (t, 1H, H12)
4.18 (m, 2H, H7)	4.19 (m, 2H, H7)
3.93 (s, 3H, H6)	3.97 (s, 3H, H6)
1.93 (m, 2H, H11)	1.96 (m, 2H, H11)
1.93 (m, 2H, H9)	1.96 (m, 1H, H9)
1.67 (m, 2H, H8)	1.71 (m, 2H, H8)
1.63 (s, 3H, H14)	1.65 (s, 3H, H14)
1.55 (s, 3H, H15)	1.58 (s, 3H, H15)
1.46 (m, 2H, H8)	1.48 (m, 2H, H8)
1.32 (m, 2H, H10)	1.36 (m, 2H, H10)
1.24 (m, 2H, H10)	1.22 (m, 2H, H10)
0.93 (d, 3H, H16)	0.95 (d, 3H, H16)

Source: adapted from <sup>a</sup>(Wadhawan *et al.*, 2000).

The cyclic voltammetry technique is used to determine the electrochemical window of stability of compounds, in other words, the potential range that could be applied without the decomposition of the IL on the surface of an electrode. In this work, the MDI-BF<sub>4</sub> was analysed pure and in aqueous solution, in order to study the influence of water addition on the IL. Figure 4B shows the cyclic voltammograms of MDI-BF<sub>4</sub> pure and with additions of 3 and 7 vol. % of deionized water. It is possible to observe that there is no relevant signal of a redox system for the purê ionic liquid MDI-BF<sub>4</sub>. However, when water was introduced in the system, the current densities observed at +1.5 V (potential near the oxidation of water molecule  $2\text{H}_2\text{O}_{(l)} \rightarrow \text{O}_{2(g)} + 4\text{H}_{(g)} + 4\text{e}^-$ ) did not rise exponentially. This happens because the concentration of water in the system does not favor the molecule oxidation at these potentials, albeit the IL was used.

**Figure 4** - A) Chemical structure of MDI-BF<sub>4</sub> and its RMN <sup>1</sup>H spectrum performed at 500 MHz in CDCl<sub>3</sub>. B) Cyclic voltammetry of the boron-doped diamond electrode on pure MDI-BF<sub>4</sub>, MDI-BF<sub>4</sub> with 3 and 7 % water, at 0.1 V s<sup>-1</sup>.



Source: Research data (2021).

When the cathodic scanings are performed, the exponential rise of the current densities at -1.2 V does not evidence a notable H<sub>2</sub>(g) production. The same behavior was observed when the water concentration in the system rose from 3% V/V to 7% V/V. From these effects, it is inferred that the IL is an electrolyte capable of conducting electrical current in a potential window of 2.4 V without structural alterations (due to the non-observation of anodic or cathodic peaks referring to the

decomposition of the IL). Likewise, the IL has a similar behavior amid different concentrations of water in the system, promoting no alteration in its voltammetric profile.

#### 4. Conclusion

From the results obtained, it was possible to conclude that: the thermogravimetric techniques (TGA/DSC) were very effective for quantification of the reagents and products present on the synthesis of MDI-Br and MDI-BF<sub>4</sub>, as well as the quantification of the solvent, which remained in low concentration even after the solution was submitted to evaporation at low pressure and at 50 °C. The thermal degradations of each component were observed thanks to the use of the DSC technique simultaneously to the TGA. From the infrared spectroscopy, it was possible to confirm some organic functions of the structure, and the presence of the tetrafluoroborate on the MDI-BF<sub>4</sub> chain after its synthesis, whereas the organic structure only could be confirmed with the RMN <sup>1</sup>H spectroscopy and comparison with the data in literature. It is concluded that 1-methyl-3-(2,6-(S)-dimethyloct-2-ene)-imidazolium tetrafluoroborate was obtained with 88.8% purity. The current density achieved by the MDI-BF<sub>4</sub> on the voltammogram (under the experimental conditions described in this work) shows that the IL can conduct electrical current, indicating that the MDI-BF<sub>4</sub> is a good electrolyte, and its behaviour does not alter with increasing water concentration. In addition, the voltammetric tests evidenced a plausible use of the IL in experiments that involve the passage of current, presenting an optimum performance for the conditions adopted in this work. Finally, the authors suggest obtaining modified electrodes with MDI-BF<sub>4</sub>, and this modification should be investigated using electrochemical techniques. In addition, it would be very interesting to repeat the synthesis using commercial citronella oil in order to carry out a comparative study between the results obtained in the present work.

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