



Synthesis and characterization of 1-(hydroxyethyl)-3-methylimidazolium sulfate and chloride ionic liquids



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ABSTRACT

We have used the imidazole as a starting compound for the preparation of a new ionic liquid 1-(hydroxyethyl)-3-methylimidazolium sulfate, with a yield of 98% in the two-steps synthesis. This new ionic liquid at room temperature exhibits a greater chemical activity. For the first step, we change the previous synthetic route using 2-chloroethanol as starting material, and with 1-methylimidazole to prepare the 1-(hydroxyethyl)-3-methylimidazolium chloride [EtOHMIM⁺][Cl⁻]. In the second stage, we have exchanged the anion Cl⁻ with HSO₄⁻. The ionic liquid shows reasonably high conductivity and thermal stability up to 340 °C. Our samples are characterized by ¹H NMR, ¹³C NMR and FT-IR. The physical characteristics of the ionic liquid, such as solvation capacity were studied using a thermo-gravimetric Analyzer (NETZSCH DSC 204 F1) in the range of 40–400 °C. The results show that the ILs may be used as polyelectrolyte for electrochemical applications.

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1. Introduction

Ionic liquids (ILs) are salts comprising ions, which exist in the liquid state at ambient temperatures. They have many unique physical and chemical properties such as negligible vapor pressure, thermal and chemical stability, high ionic conductivity and excellent solubility of many substances [1]. Several studies have been reported on the use of IL without reaction solvents [2], the separating extraction solvents [3] and electrolyte materials [4,5]. ILs properties can be modified by substitution of cations and anions with special functional groups. Functionalized ILs which are incorporated with one or more functional groups have special structures and a lot of interests in many research fields like

chemical synthesis, separation science and electrochemistry. They can be used also as doping elements in polymers [6,7].

In this work, we investigate the effect of the anions on the vibrational behavior of our samples and the changing in the thermal properties as melting, crystallization, glass and degradation temperatures by comparison between [EtOHMIM⁺][Cl⁻] and [EtOHMIM⁺][HSO₄⁻]. The last one exhibits higher characteristic temperatures.

2. Materials and methods

2.1. Reagents and materials

The reagents used in this study are: 1-methylimidazol, 2-chloroethanol, acetonitrile, diethyl ether (99% pure.) used without any further purification.

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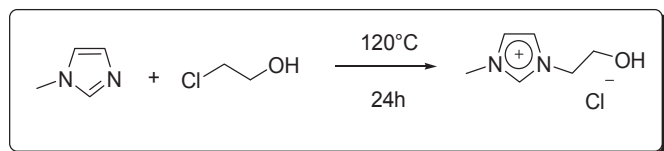


Fig. 1. Amine quaternization reaction.

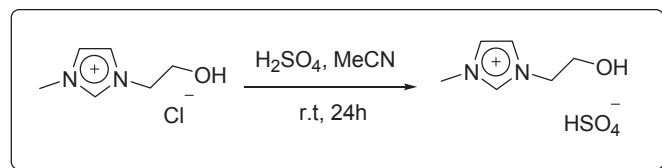


Fig. 2. Anion exchange reaction.

2.2. NMR, spectroscopy analysis

^1H and ^{13}C NMR spectra were recorded on a Bruker Biospin Avance III spectrometer equipped with a 5 mm TXI probe at 600 and 150.93 MHz, respectively. Chemical shifts (δ) are given in ppm and referenced to the internal signal solvent D_2O .

2.2.1. Synthesis and characterization of 1-(hydroxyethyl)-3-methylimidazolium chloride $[\text{EtOHMIM}^+][\text{Cl}^-]$ [8–11].

A mixture of 2-chloroethanol (0.67 mL, 10 mmol) and 1-methylimidazole (1.1 g, 10 mmol) was heated for 24 h at 120 °C. The crude product, which crystallized upon cooling, was finely crushed, washed with Et_2O (3×80 mL), and dried under reduced pressure for 10 h [10](Fig. 1).

Pale yellow powder; yield: 1.8 g (94%); mp 55–58 °C.

2.2.2. Synthesis and characterization of 1-(hydroxyethyl)-3-methylimidazolium sulfate $[\text{EtOHMIM}^+][\text{HSO}_4^-]$ [12,13].

An equimolar mixture of 1-(hydroxyethyl)-3-methylimidazolium chloride (0.01 mol/1.5256 g) and sulfuric acid H_2SO_4 (0.01 mol/0.5355 ml) dissolved in 30 ml acetonitrile was stirred vigorously at room temperature (initial liquid homogeneous medium) for 24 h (Fig. 2).

Then, the product obtained was ground, washed with diethyl ether (3×80 ml) and filtered on sintered glass of porosity $\text{N}^\circ 0.4$. The product was finally dried under reduced pressure for 10 h to remove traces of solvent.

2.3. FTIR/ATR measurements

The measurements were realized in the Walloon Agricultural Research Center (CRA-W) Belgium.

Fourier Transform mid-infrared All attenuated total reflectance (FTIR/ATR) measurements were acquired on a Bruker Vertex II-70 RAMSpectrometer (Bruker Analytical, Madison, WI) operating with a Golden Gate diamond ATR accessory TM (Specac Ltd, Slough, United Kingdom). FTIR/ATR spectra [$4000\text{--}600\text{ cm}^{-1}$] were collected with Resolution 1 cm^{-1} by co-adding 64 scans for each spectrum. The OPUS Software 6.0 for Windows was used for the management of the instrument.

2.4. DSC measurements

Characterization by DSC was carried out with a Differential calorimetry system (NETZSCH DSC 204 F1) with a speed of heating and cooling $5^\circ\text{C}/\text{min}$, by performing two heating and cooling cycles to remove traces of water and solvent in a temperature range of ($-100\text{ }^\circ\text{C}$ – $200\text{ }^\circ\text{C}$) under Argon. The experimental procedure is as follows:

- cooling from $-25\text{ }^\circ\text{C}$ to $-100\text{ }^\circ\text{C}$, leaving the sample at this temperature for 5 min
- heating from $-100\text{ }^\circ\text{C}$ to $120\text{ }^\circ\text{C}$

- cooling from $-120\text{ }^\circ\text{C}$ to $-100\text{ }^\circ\text{C}$ leaving the sample at this temperature for 5 min
- heating from $-100\text{ }^\circ\text{C}$ to $200\text{ }^\circ\text{C}$

The measures of the TGA, and the DTG analysis leaking gas during the experiment made with a NETZSCH STA 449C (TGA-DSC) ($20\text{ }^\circ\text{C}$ – $1500\text{ }^\circ\text{C}$) apparatus coupled to a mass spectrometer for analyzing the gas, with a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ in a temperature range of $20\text{ }^\circ\text{C}$ – $400\text{ }^\circ\text{C}$ under Argon.

3. Results and discussion

3.1. NMR results

3.1.1. 1-(hydroxyethyl)-3-methylimidazolium chloride $[\text{EtOHMIM}^+][\text{Cl}^-]$

NMR ^1H : (600 MHz, D_2O): $\delta = 8.78$ (s, 1H, H-2), 7.54 (s, 1H, H-4 or H-5), 7.49 (s, 1H, H-4 or H-5), 4.34 (t, 2H, $J = 4.9$ Hz, NCH_2), 3.96 (t, 2H, $J = 4.9$ Hz, CH_2O), 3.93 (s, 3H, NCH_3).

NMR ^{13}C (150.93 MHz, D_2O): $\delta = 136.4$ (C-2), 123.6, 122.4 (C-4, C-5), 59.8 (CH_2O), 51.5 (NCH_2), 35.7 (NCH_3). NMR spectra are presented on Fig. 3.

3.1.2. 1-(hydroxyethyl)-3-methylimidazolium sulfate $[\text{EtOHMIM}^+][\text{HSO}_4^-]$

NMR ^1H : (600 MHz, D_2O): $\delta = 8.78$ (s, 1H, H-2), 8.76 (s, 1H, HSO_4^-), 7.54 (s, 1H, H-4 or H-5), 7.48 (s, 1H, H-4 or H-5), 4.52 (t, 2H, $J = 5$ Hz, NCH_2), 4.33 (t, 2H, $J = 5$ Hz, CH_2OH) 3.90 (s, 3H, NCH_3).

NMR ^{13}C (150.93 MHz, D_2O): $\delta = 136.6$ (C-2), 123.6, 122.6 (C-4, C-5), 66.1 (CH_2O), 51.5 (NCH_2), 35.8 (NCH_3). NMR spectra are presented on Fig. 4.

3.2. The comparison between FTIR/ATR spectra of ionic liquids: 1-(hydroxyethyl)-3-methylimidazolium chloride $[\text{EtOHMIM}^+][\text{Cl}^-]$ and 1-(hydroxyethyl)-3-methylimidazolium sulfate $[\text{EtOHMIM}^+][\text{HSO}_4^-]$

FTIR/ATR spectra [$4000\text{--}600\text{ cm}^{-1}$] of the two ionic liquids are illustrated in Fig. 5. Both spectra were normalized on the mode at 620 cm^{-1} . The assignments of the observed modes in this spectral region are reported in Table 1. All reported peak values were based on the maximum peak height of the unfitted spectra. Curve fitting and fitted frequency values labeled * were performed as per Bresson et al. [14]. On the IR spectra (see Fig. 5), we distinguish three well defined spectral regions: $3500\text{--}2600$, $1800\text{--}1300$ and $1300\text{--}600\text{ cm}^{-1}$. For $[\text{EtOHMIM}^+][\text{Cl}^-]$, the modes in the three spectral regions seem to have a homogenous intensity, whereas for $[\text{EtOHMIM}^+][\text{HSO}_4^-]$ the modes seem more intense in the $1300\text{--}600\text{ cm}^{-1}$ spectral range.

3.2.1. Region $1300\text{--}600\text{ cm}^{-1}$

In this spectral zone (Fig. 6) where both spectra were

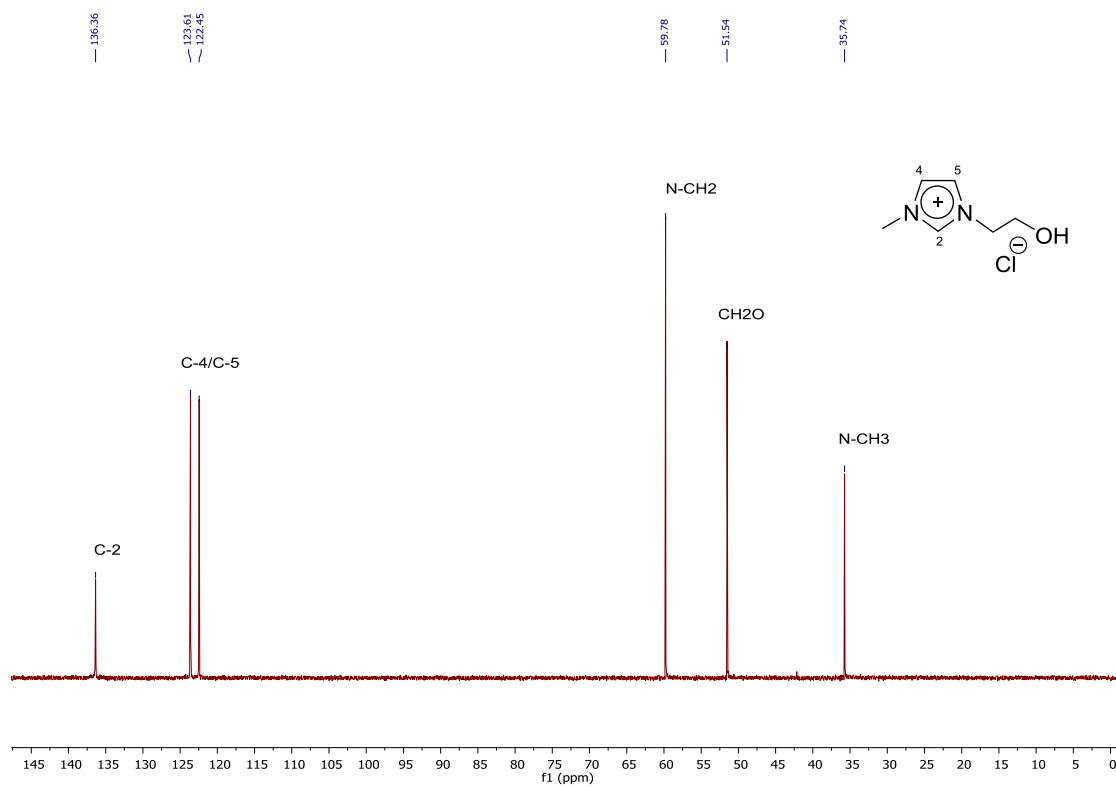
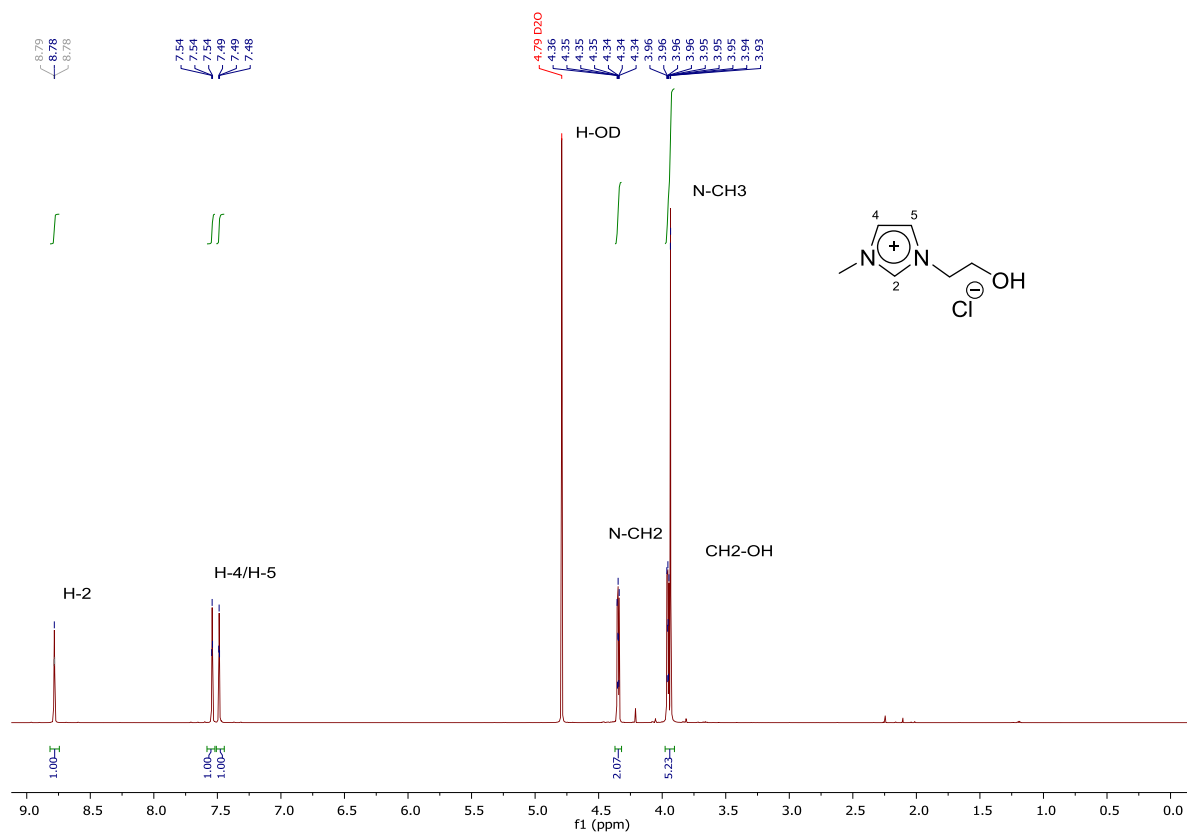


Fig. 3. ¹H NMR (600 MHz) (a) and ¹³C NMR (150.93 MHz) (b) [EtOHMIM⁺][Cl⁻].

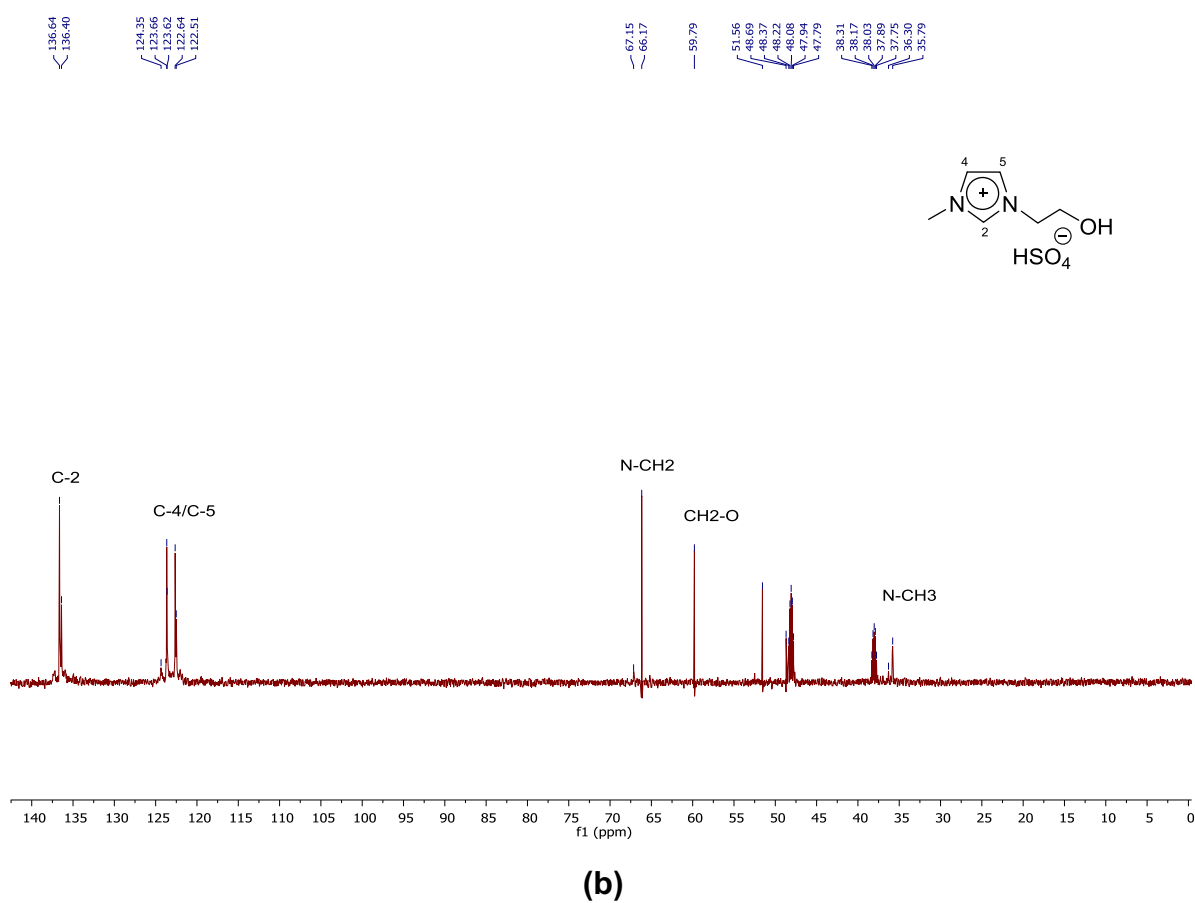
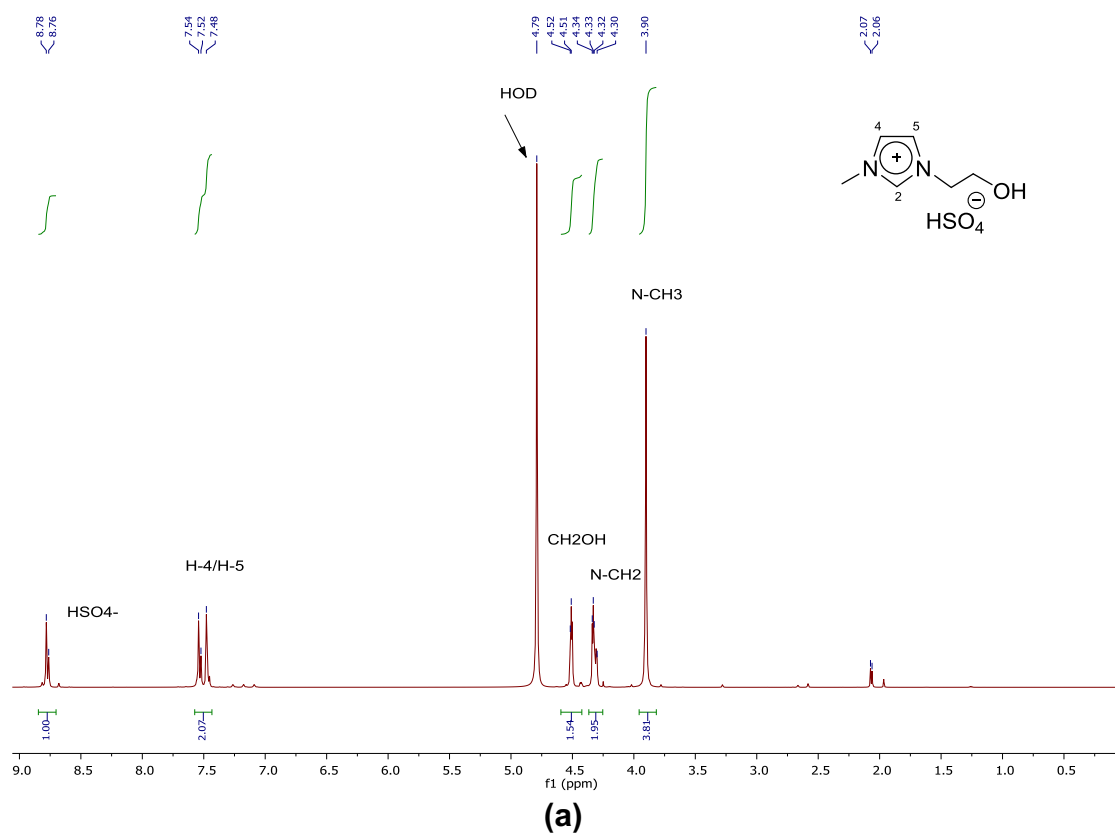


Fig. 4. ^1H NMR (600 MHz) (a) and ^{13}C NMR (150.93 MHz) (b) $[\text{EtOHMIM}^+][\text{HSO}_4^-]$.

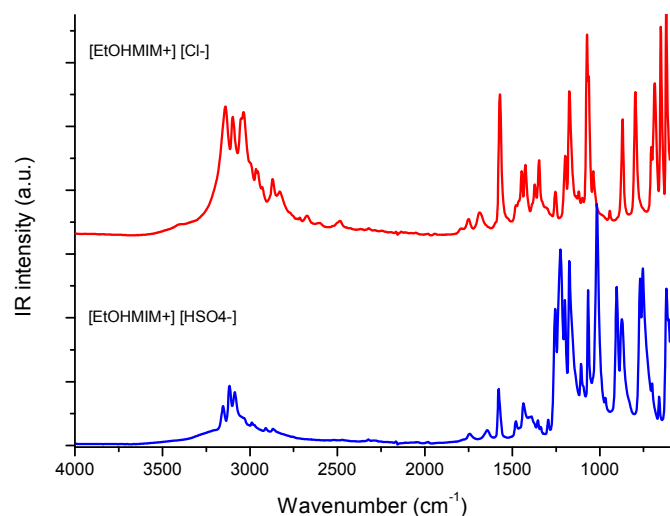


Fig. 5. FTIR/ATR spectra of [EtOHMIM⁺] [Cl⁻] and [EtOHMIM⁺] [HSO₄⁻] in the spectral range 3500–600 cm⁻¹.

normalized on the mode at 1175 cm⁻¹, we observe numerous differences of vibrational behavior according to the choice of the anion. For the Cl⁻ anion, the spectral zone 700–600 cm⁻¹ is more intense than for [EtOHMIM⁺] [HSO₄⁻] with the ascendancy of 4 modes in 620, 652, 686 and 706 cm⁻¹ while for the only HSO₄⁻ anion the mode in 620 cm⁻¹ seems to be intense. The modes at 620, 652, 686 cm⁻¹ are assigned to (N–H) wagging and CH₃(N) CN stretching whereas the mode at 706 cm⁻¹ corresponds in CH₂(N)/CH₃(N)CN bending [15,16]. Conversely in the spectral zone 950–700 cm⁻¹, the vibrational behavior for [EtOHMIM⁺] [HSO₄⁻] seems to present more modes with two doublets and shoulder (735, 754, 771 cm⁻¹ and 850, 873, 903 cm⁻¹) while for [EtOHMIM⁺] [Cl⁻] we observe only two modes in 796 and 868 cm⁻¹ assigned to ring HCCH bending and CH₂ asymmetric rocking modes respectively. The strong peak at 903 cm⁻¹ observed for [EtOHMIM⁺] [HSO₄⁻] is assigned to (N–S) stretching mode [15,16]. All assignments of the observed modes in Fig. 5 are presented in the Table 1. We notice the presence of new intense modes between both samples at 1017 and 1224 cm⁻¹ assigned to the HSO₄⁻ anion (S–O) stretching mode and the doubling of vibrational modes [17]. The presence of the HSO₄⁻ anion seems to transform a single peak in to a double one for the mode 1175 cm⁻¹ observed for the Cl⁻ anion: we notice the doublet 1156, 1175 cm⁻¹ for the HSO₄⁻ anion, assigned to ring CH₂(N)/CH₃(N)CN stretching mode [15,16]. Conversely, the doublet observed for the Cl⁻ anion at 1062 and 1074 cm⁻¹ appears as one peak for the HSO₄⁻ anion centered at 1068 cm⁻¹ assigned to (C–O) stretching mode [18]. We thus notice that this spectral zone seems very sensitive to the interactions with anions and can serve as witness of the influence of the one or the other anion in the vibrational behavior with the imidazolium.

3.2.2. Region 1800–1300 cm⁻¹

In this spectral zone (Fig. 7) where spectra were normalized on the mode at 1571 cm⁻¹ for [EtOHMIM⁺] [Cl⁻] and 1578 cm⁻¹ for [EtOHMIM⁺] [HSO₄⁻], we observe spectra with more modes for the HSO₄⁻ anion than for the Cl⁻ anion. We note that the C–C stretching mode at 1347 cm⁻¹ is transformed for the HSO₄⁻ anion to 1353 and 1336 cm⁻¹ modes [15,16]. The spectral zone of the CH₂ bending

(1500–1400) also seems to be influenced by the choice of the anion in a less important way. In the spectral zone 1800–1500 cm⁻¹, we observe a shift in frequency of the vibrational mode attributed to the ring C=C and H–C–H stretching modes. The shift is from 1571 cm⁻¹ for the anion Cl⁻ to 1578 cm⁻¹ with a shoulder at 1570 cm⁻¹ for HSO₄⁻ and conversely from 1645 cm⁻¹ for HSO₄⁻ to an unresolved doublet in 1677 and 1692 cm⁻¹ for the Cl⁻ anion [19]. We also observe the presence of overtones C–H stretching modes with a shift in frequency between both anions: 1743 cm⁻¹ for HSO₄⁻ against 1750 cm⁻¹ for Cl⁻.

3.2.3. Region 3500–2400 cm⁻¹

In this spectral region (Fig. 8) where spectra were normalized on the mode at 3098 cm⁻¹ for [EtOHMIM⁺] [Cl⁻] and 3086 cm⁻¹ for [EtOHMIM⁺] [HSO₄⁻], we observe the affected modes of alkyl stretchable region alcohol OH. We observe that these spectra each anion has its peculiarity: for the Cl⁻ anion and for HSO₄⁻ peaks with high density in the region 3200–2850 cm⁻¹, the spectral range 4000–2800 cm⁻¹ is very sensitive in FTIR/ATR depending on the choice of the anion and cation coupled and can serve as signature of a particular ionic liquid. In the case of anion 2, the (C–H) stretching modes are the most intense in this spectral range: 3038, 3055, 3098 cm⁻¹ and 3142 cm⁻¹ for the anion Cl⁻, and 3086, 3116 and 3154 cm⁻¹ for the anion HSO₄⁻ [15,16].

4. Thermal properties

The DSC thermograms for [EtOHMIM⁺] [Cl⁻] and [EtOHMIM⁺] [HSO₄⁻] are shown in Fig. 9 and the thermogravimetric analysis curves (TGA), the derivative thermogravimetric curves (DTG) and the mass spectrometry curves are shown in Fig. 10. By its turn, the thermal gravimetric parameters extracted from these curves are presented in Table 2.

4.1. DSC thermogram

While heating from lower temperature we observe a glass transitions T_g = –20 °C, then an endothermic peak onset at 64 °C was observed in the heating phase corresponding to the melting point of ([EtOHMIM⁺][Cl⁻]) (Fig. 9a), (Table 2).

For ([EtOHMIM⁺][HSO₄⁻]), we observe the same phenomenon but with different values of temperature: a glass transitions T_g = –62 °C and an endothermic peak onset at 153 °C observed in the heating phase corresponding to the melting point of ([EtOHMIM⁺][HSO₄⁻]) (Fig. 9b) (Table 2).

4.2. Thermal stability

From the TGA and DTG curves in (Fig. 10a) [EtOHMIM⁺][Cl⁻] is steady below 67 °C and the degradation began at 67 °C in two stages between 20 °C and 400 °C. The first stage begins at almost 67 °C with a mass loss of 2.30% and ends at a temperature of 253 °C corresponding to the release of OH identified gas from the mass spectrometry curve. The second stage begins at 253 °C and ends at about 334 °C with a loss of 89.46% corresponding to the release of CH₃ and OH identified gas from the mass spectrometry curve (Fig. 10b).

For [EtOHMIM⁺][HSO₄⁻] sample, the TGA and DTG thermograms (Fig. 10c) show that [EtOHMIM⁺][HSO₄⁻] is steady below 155 °C and began to degrade from 155 °C in three stages, leaving a reddish residue of 19% from the initial mass at 400 °C. The first stage begins at almost 155 °C with a mass loss of 12.82% and ends at a temperature of 274 °C corresponding to the release of H₂O identified

Table 1

Observed FTIR/ATR bands and their assignment of chloride 1-(hydroxyethyl)-3-methylimidazolium and sulfate 1-(hydroxyethyl)-3-methylimidazolium (Vw = very weak, w = weak, m = medium, s = strong, sh = shoulder, Str = stretch, d = deformation, bend = bending deformation, ω = wagging, ρ = rocking, s = symmetric, as = antisymmetric).

[EtOHMIM ⁺][Cl ⁻]	[EtOHMIM ⁺][HSO ₄ ⁻]	Assignment	Refs
	605 (m)	ω (N–H)/CH ₃ (N) CN Str	[15,16]
620 (s)	620 (s)	ω (N–H)/CH ₃ (N) CN Str	[15,16]
652 (s)	660 (w)	ω (N–H)/CH ₃ (N) CN Str	[15,16]
687 (s)		ω (C–H) + ω (N–H)	[15,16]
705 (m)	700(m)	CH ₂ (N)/CH ₃ (N)CN bend	[15,16]
	735* (sh)	ω (C–H)	[15,16]
	753 (m)	ω (C–H)	[15,16]
	771 (s)	ν (N–C)	[15,16]
797 (s)		Ring HCCH as bend	[15,16]
	850* (sh)	ρ_{as} (CH ₂)	[15,16]
868 (s)	873 (s)	ρ_{as} (CH ₂)	[15,16]
	903 (s)	ν (N–S)	[17]
942 (vw)		ρ_{as} (CH ₂)	[15,16]
	968 (vw)	ν (N–S)	[17]
	1017 (s)	S–OH	[17]
1027* (sh)		CH ₃ N Str/CH ₂ N Str	[15,16]
1038 (m)		CH ₃ N Str/CH ₂ N Str	[15,16]
1062 (m)	1068 (s)	ν (C–O)	[18]
1074 (s)		CC Str	[17]
1100 (vw)	1090* (sh)	CC Str	[17]
1119 (vw)	1108 (w)	CC Str	[15,16]
1175 (m)	1175 (m)	Ring as Str CH ₂ (N) and CH ₃ (N)CN Str/CC	[15,16]
1198 (m)	1198 (m)	Ring s CH ₂ (N) and CH ₃ (N)CN Str	[15,16]
	1224 (m)	ν (S–O)	[17]
1254 (w)	1256 (m)	Ring ip as str str	[15,16]
	1336 (m)	ν (C–C)	[15,16]
1347 (m)	1353 (m)	ν (C–C)	[15,16]
1371 (w)	1372* (sh)	δ (CH) – δ_s (CH ₃)	[18]
1388* (sh)	1390 (m)	ρ (N–H)	[15,16]
	1412* (sh)	ρ (N–H)	[15,16]
1424 (m)	1431* (sh)	ρ (N–H)	[15,16]
1446 (m)	1438 (m)	δ (CH ₂)/CCH HCH as bend	[15,16]
	1462* (sh)	δ (CH ₂)/CCH HCH as bend	[15,16]
1481 (w)	1480 (m)	δ (CH ₂)/CCH HCH as bend	[15,16]
1571 (s)	1570* (sh)	as Str CH ₂ (N)/CH ₃ (N)CN Str	[15,16]
	1578 (s)	Ring C=C str, N=C–N str	[19]
	1645 (w)	Ring C=C str, N=C–N str	[19]
1677 (w)		Ring C=C str, N=C–N str	[19]
1692 (w)		Ring C=C str, N=C–N str	[19]
1750 (w)	1742 (w)	Overtone = C–H str	[19]
2481(w)	2470 (vw)	ν (C=C)	[15,16]
2600 (vw)		ν_s (CH ₂)	[15,16]
2673 (w)		ν_s (CH ₂)	[15,16]
2714 (vw)		ν_s (CH ₂)	[15,16]
2830 (w)		ν_s (CH ₂)	[15,16]
	2842 (w)	ν_s (CH ₂)	[15,16]
2870 (m)	2865 (w)	ν_{as} (CH ₂)	[15,16]
2930 (w)	2907(m)	ν_{as} (CH ₂)	[15,16]
2954 (m)		CH ₃ (N)HCH as Str	[15,16]
2966 (m)		ν (C–H)	[15,16]
	2975 (w)	ν (C–H)	[15,16]
2991* (sh)	2990 (w)	ν (C–H)	[15,16]
3038 (m)	3030 (w)	ν (C–H)	[15,16]
3055 (m)	3048* (sh)	ν (C–H)	[15,16]
3095 (m)	3086 (m)	=C–H Str	[15,16]
3098(s)		=C–H Str	[15,16]
	3116 (m)	=C–H Str	[15,16]
3142 (m)		=C–H Str	[15,16]
	3154 (m)	=C–H Str	[15,16]
	3225* (sh)	ν (O–H)	[17,18]

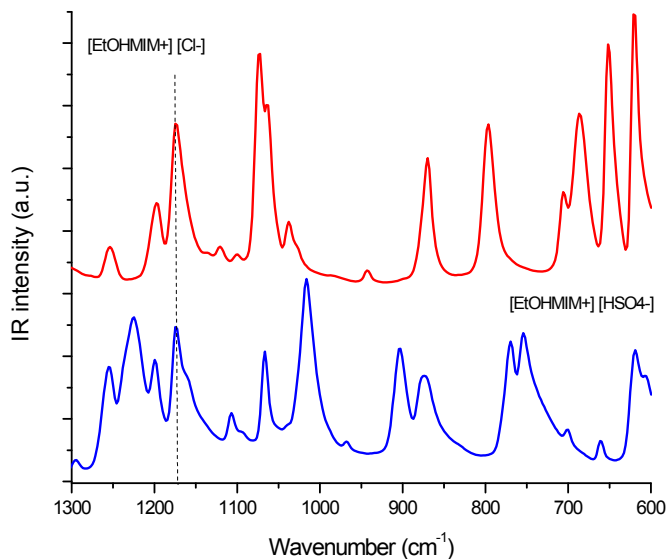


Fig. 6. FTIR/ATR spectra of [EtOHMIM⁺][Cl⁻] and [EtOHMIM⁺][HSO₄⁻] in the spectral range 1300–600 cm⁻¹.

gas from the mass spectrometry curve (Fig. 10d). The second stage begins at 274 °C and ends at about 342 °C with a loss of 6.24% corresponding to the release of CH₃ and OH identified gas from the mass spectrometry curve, and the third stage between 342 and 400 °C with a loss of 61.94%.

5. Conclusion

In this study, we synthesized a new Ionic liquid [EtOHMIM⁺][HSO₄⁻] which was characterized by RMN, FTIR/ATR and DSC. The obtained compound shows interesting thermal properties. The results of vibrational spectroscopy and DSC was compared with those obtained on the same intermediate compound [EtOHMIM⁺][Cl⁻] who differs only by the type of anion. The anion seems to play an important influence in the thermal stability of the compound as well as on its vibrational behavior.

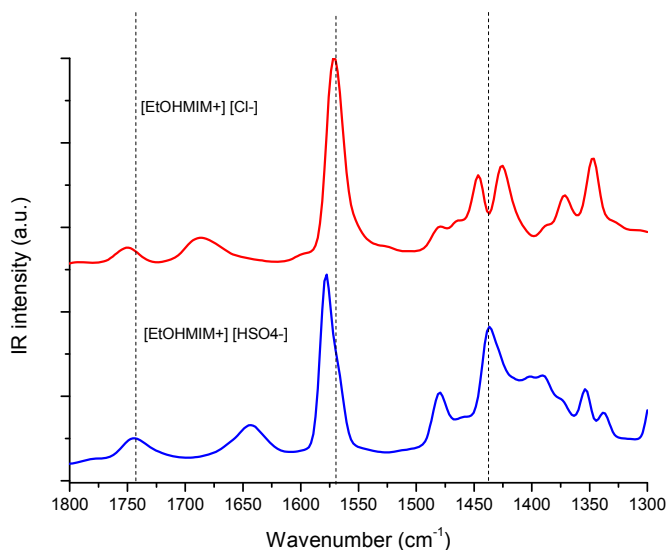


Fig. 7. FTIR/ATR spectra of [EtOHMIM⁺][Cl⁻] and [EtOHMIM⁺][HSO₄⁻] in the spectral range 1800–1300 cm⁻¹.

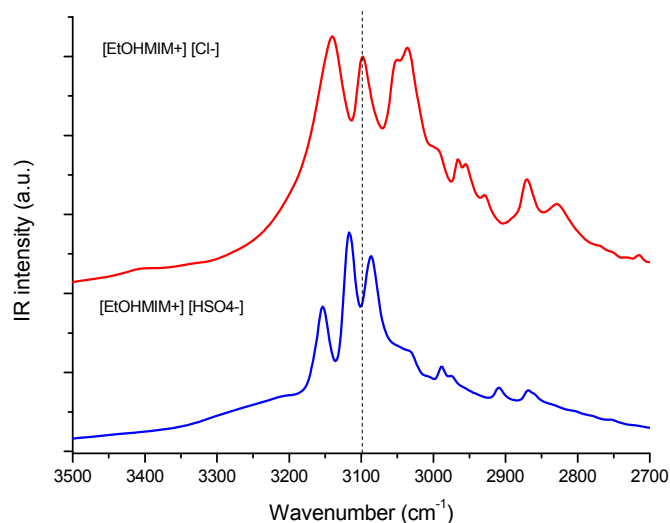


Fig. 8. FTIR/ATR spectra of [EtOHMIM⁺][Cl⁻] and [EtOHMIM⁺][HSO₄⁻] in the spectral range 3500–2400 cm⁻¹.

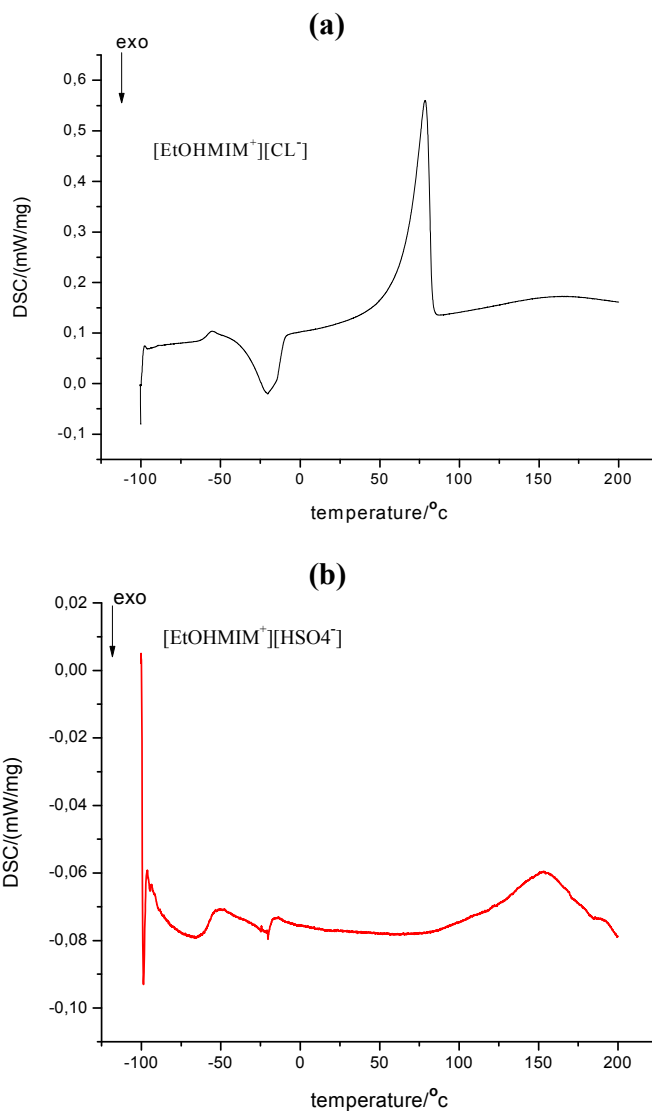


Fig. 9. DSC thermogram of ionic liquid [EtOHMIM⁺][Cl⁻] (a) and [EtOHMIM⁺][HSO₄⁻] (b) from 100 °C to 200 °C.

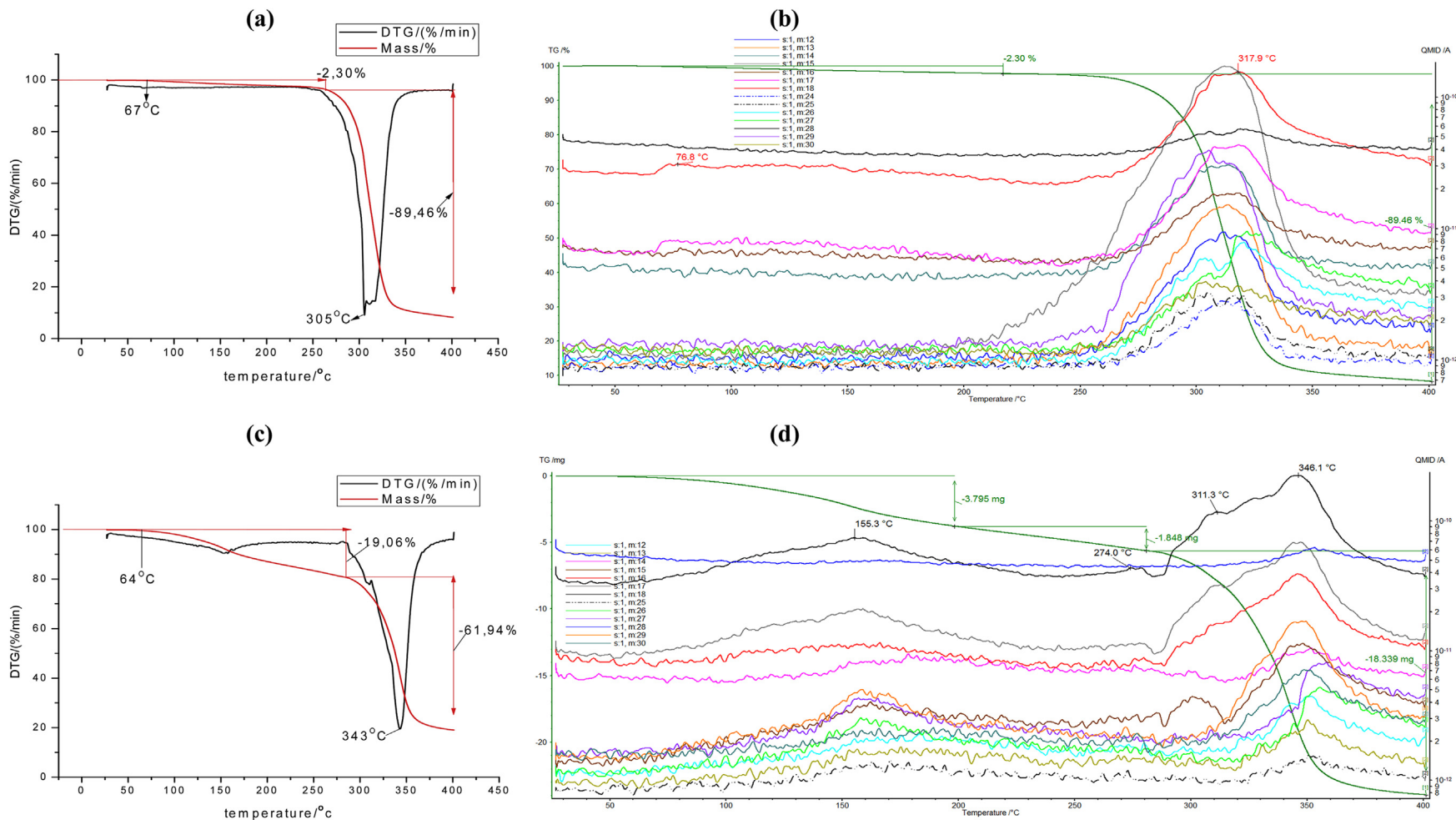


Fig. 10. TGA and DTG of ionic liquid [EtOHMIM⁺][Cl⁻] (a) and [EtOHMIM⁺][HSO₄⁻] (c) (20 °C–400 °C) and mass spectrometric diagram of gas escaped from ionic liquid [EtOHMIM⁺][Cl⁻] (b) and [EtOHMIM⁺][HSO₄⁻] (d).

Table 2
Thermal properties of [EtOHMIM⁺][Cl⁻] and [EtOHMIM⁺][HSO₄⁻].

Ionic liquids	T _g (°C)	T _f (°C)	T _d (°C)	T _{d_r} (°C)
[EtOHMIM ⁺][Cl ⁻]	-20	64	67	305
[EtOHMIM ⁺][HSO ₄ ⁻]	-62	153	155	343

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