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Synthesis, vibrational and thermal properties of new functionalized 1- (2-hydroxyethyl) -3-methylimidazolium dihydrogenophosphate ionic liquid.

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Abstract:

Very recently, the hydroxyl-functionalized ionic liquids have gained immense interest and were developed for a number of interesting applications. In this work and for the first time new hydroxyl-functionalized namely; 1-(hydroxyethyl)-3-methylimidazolium dihydrogenophosphate ionic liquid [EtOHMIM⁺][H₂PO₄⁻] was synthesized in our laboratory. The synthesis is based on an alkylation reaction of 1-methylimidazole followed by anion exchange. The obtained IL is characterized by ¹H-NMR, ¹³C-NMR spectroscopy. This experimental vibrational spectroscopy have been investigated using Infrared and Raman spectroscopy, based on the infrared (IR) and Raman spectroscopies results, complete vibrational assignments have been performed. Besides, thermal properties of this hydroxyl-functionalized IL were investigated by using following techniques, (i) Thermogravimetric Analysis (TGA) and Derivative Thermogravimetry (DTG) in the temperature range from 20 to 600 C°, (ii) differential scanning calorimetry (DSC) from -100 °C to 200 °C. The thermogravimetry analysis was coupled with mass spectrometry in order to assess the influence of anion on the measured property.

KEYWORDS: Hydroxyl-functionalized ionic liquids; dihydrogenophosphate anion; NMR spectra; IR spectra; RAMAN spectra; thermal stability.

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Introduction:

In the early 1990's, for the vast majority of chemists, the term ionic liquid was obscure and little known. Since 2000, the research in this area has been focused and greatly expanded. Indeed, their physicochemical properties are very interesting and varied, and the multiple possible applications in organic chemistry make these entities the compounds of choice as substitute solvents for catalysis [1-2] and supported synthesis [3-4]. In addition, the physical and chemical properties of the Ionic Liquids (ILs) are modifiable by varying the anion / cation combinations. This enabled the design of systems adaptable to various applications (electrochemistry, organic, inorganic and enzymatic synthesis, catalysis ...) but also to adjust the physicochemical properties of these organic salts according to needs.

In this area, several works focused on the synthesis and application of new class of ionic liquids, namely; hydroxyl functionalized ionic liquids containing, bromide, chloride, iodide, tetrafluoroborate, picrate, hexafluorophosphate, bis(trifluoromethylsulfonyl)imide, nitrate, alkyl sulfates, dicyanamide, thiocyanate, and trifluoromethanesulfate anions [5-13]. Compared to the traditional ILs, this class of ILs have received much attention in many applications, especially in the fields of catalysis [14], biotechnology [15], sonochemistry [16] and organic synthesis [17].

In this respect and at spectroscopic point of view, there are extensive works published in this area (see Ref. [18] and references therein). However, compared to the hydroxyl functionalized ionic liquids already synthesized and published and to the best of our knowledge, there are no reports in the literature dealing the synthesis, thermal and vibrational spectroscopy of 1-(hydroxyethyl)-3-methylimidazolium dihydrogenophosphate [EtOHMIM⁺][H₂PO₄⁻]. This inorganic anion used in numerous analytical methods and is one of the anions in the dissociation equilibrium of phosphoric acid dissolved in water [19-20].

Very recently, we have investigated the vibrational and thermal properties of 1-(hydroxyethyl)-3-methylimidazolium cation coupled with sulphate and chloride anion [21] by using IR / Raman spectroscopic and thermal analysis. In this work, we thought to synthesize this functionalized ionic liquid but with dihydrogenophosphate [H₂PO₄⁻] anion there are no reports in the spectroscopic literature dealing to the vibrational spectroscopy of 1-(hydroxyethyl)-3-methylimidazolium with this anion.

On the other hand and contrary to that published with this cation, the synthesis, vibrational spectroscopy and the thermal properties of this ionic liquid coupled with dihydrogenophosphate are not covered yet by the literature. In this framework, we have set out to prepare 1-(hydroxyethyl)-3-methylimidazolium dihydrogenophosphate. This new functionalized ionic liquid has been structurally identified using Nuclear magnetic resonance (NMR). Furthermore, infrared and Raman spectroscopy have been adopted to evaluate their

vibrational spectroscopy properties. Finally; their thermal properties have been investigated by thermogravimetric analysis TGA, DTG and DSC.

In order to study the impact of the anion on the thermal and vibrational behavior, we show an example of [EtOHMIM⁺][Cl⁻] to investigate these properties by comparison between chloride and dihydrogenophosphate [EtOHMIM⁺][H₂PO₄⁻] varying in their structural characteristics.

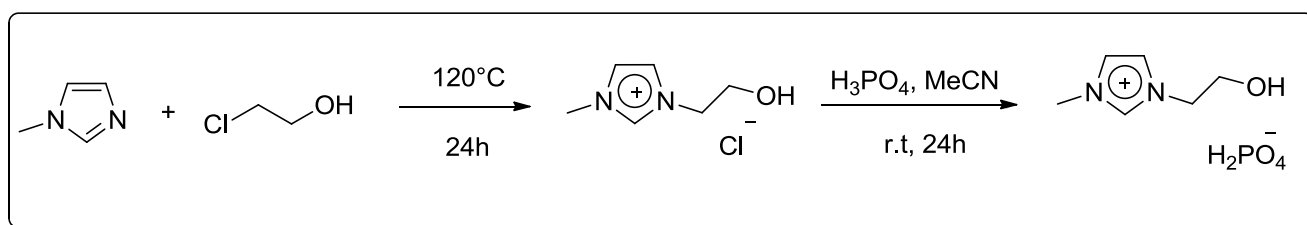
2. Experimental part:

2.1. Materials and methods:

2.1.1. Synthesis and characterization of ILs:

1-methylimidazole, 2-Chloroethanol, acetonitrile, diethyl ether is up to (99% pure) from Sigma-Aldrich as starting reagents were used in this work without any further purification.

The synthesis of 1-(hydroxyethyl)-3-methylimidazolium chloride [EtOHMIM⁺][Cl⁻] was reported in our recent study [21]. For the metathesis reaction a mixture of 1-(2-hydroxyethyl)-3-methylimidazolium chloride (5 g, 0.0252 mol) and ortho-phosphoric acid (08 ml, 0.062 mol) was carried out at room temperature for 24h with vigorous magnetic stirring in 30 ml acetonitrile. The crude was washed with diethyl ether (3 x 80 ml) after elimination of acetonitrile and then concentrated on a rotary evaporator under reduced pressure yielding a pale viscous yellow liquid. Finally, in order to obtain high purity and to remove any possible water contamination before their use, our obtained ionic liquid was dried under vacuum (10⁻³ bar). The yield of this reaction was (98%). The general procedure for the synthesis of 1-(hydroxyethyl)-3-methylimidazolium dihydrogenophosphate [EtOHMIM⁺][H₂PO₄⁻] is summarized in **Scheme 1**.



Scheme 1. Synthetic route of [EtOHMIM⁺][H₂PO₄⁻].

2.2. NMR spectroscopy analysis:

The structure and purity of our investigated functionalized ILs were confirmed by spectral analysis: ¹H and ¹³C NMR spectra were recorded on a Bruker Biospin Avance III spectrometer equipped with a 5 mm TXI probe at 600 and 300 MHz, respectively. Chemical shifts (δ) are given in ppm and referenced to the internal signal solvent D₂O and DMSO. The spectroscopic data are given below.

2.2.1. 1-(hydroxyethyl)-3-methylimidazoliumchloride [EtOHMIM⁺][Cl⁻]

¹H-NMR (600 MHz, D₂O) : δ = 9.36 (s, 1H, H-2); 9.08 (sl, 1H, OH); 7.82 (s, 1H, H-4 or H-5); 7.79 (s, 1H, H-4 or H-5); 4.25 (t, 2H, NCH₂); 3.88 (s, 3H, NCH₃); 3.69 (t, 2H, CH₂OH) (see Figure.1.a). ¹³C-NMR (600 MHz, D₂O): δ = 137.33 (C-2); 123.70 and 123.10 (C-4 and C-5); 59.71 (NCH₂); 51.94 (CH₂O); 36.12 (NCH₃) (see Figure.1.b).

2.2.2. 1-(hydroxyethyl)-3-methylimidazolium dihydrogenophosphate [EtOHMIM⁺][H₂PO₄⁻]

¹H-NMR (300 MHz, DMSO): δ = 9.21 (s, 1H, H-2); 7.75 (s, 1H, H-4 or H-5); 7.71 (s, 1H, H-4 or H-5); 6.70 (sl, 1H, OH); 4.23 (t, 2H, NCH₂); 3.86 (s, 3H, NCH₃); 3.69 (t, 2H, CH₂OH) (see Figure.2.a). ¹³C-NMR (300 MHz, DMSO): δ = 137.23 (C-2); 123.7 and 123.08 (C-4 and C-5); 59.74 (NCH₂); 51.96 (CH₂O); 36.12 (NCH₃) (see Figure.2.b).

2.3. FTIR/ATR measurements

The samples measurements were performed 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 RAM Spectrometer (Bruker Analytical, Madison, WI) operating with a Golden Gate diamond ATR accessory TM (Specac Ltd, Slough, United Kingdom). FTIR/ATR spectra [4000-600 cm⁻¹] were collected with a resolution of 1cm⁻¹ by co-adding 64 scans for each spectrum. The OPUS Software 6.0 was used for the management of the instrument.

2.4. FT-Raman measurements

These measurements were also carried out in the Walloon Agricultural Research Center (CRA-W) in Belgium. The FT-Raman spectra were acquired on a Vertex 70-RAM II Bruker FT-Raman spectrometer. This instrument is equipped with a Nd:YAG laser (yttrium aluminum garnet crystal doped with triply ionized neodymium) with a wavelength of 1064 nm and a maximum power of 1.5 W. The measurement accessory is pre-aligned: only the Z-axis of the scattered light is adjusted to set the sample in the appropriate position regarding the local measurement point. The RAM II spectrometer is equipped with a liquid nitrogen cooled Gede detector. FT-Raman spectra [4000-45 cm⁻¹] were collected with a resolution of 1 cm⁻¹ by co-adding 128 scans for each spectrum at room temperature. The OPUS 6.0 software was used for the spectral acquisition, manipulation and transformation.

2.5. Thermal measurements

Thermal gravimetric (TGA) and DTG measurements were performed using a NETZSCH STA 449 C (TGA-DSC) (20 °C to 1500 °C) apparatus coupled to a mass spectrometer for analyzing the gas, with a heating rate

of 5°C/min in a temperature range of 20°C to 400 °C under Argon. The characterization by DSC was carried out with a Differential calorimetry system (NETZSCH DSC 204 F1) with a speed of heating and cooling of 5°C /min, by performing two heating and cooling cycles to remove traces of water and solvent in a temperature range of (-100°C to 200 °C) under Argon. The experimental procedure is as follows:

- Cooling from 25 °C to -100 °C, leaving the sample at this temperature for 5 minutes
- Heating from - 100 °C to 120 °C
- Cooling from 120°C to - 100 °C leaving the sample at this temperature for 5 minutes
- Heating from - 100 °C to 200 °C

3. Results and discussion

3.1. NMR spectroscopy characterization

In order to identify and confirmed the structures of obtained ILs, the ionic liquids skeletons [EtOHMIM⁺][Cl⁻] and [EtOHMIM⁺][H₂PO₄⁻] have been characterized structurally using Nuclear magnetic resonance ¹H and ¹³C-NMR spectroscopy, which confirms the absence of any impurities. The resulting spectra are presented in **Figures 1-2**, in the ¹H-NMR spectra of [EtOHMIM⁺][Cl⁻] and [EtOHMIM⁺][H₂PO₄⁻], the signals at $\delta_H = 9.36$ ppm and at $\delta_H = 9.21$ ppm corresponds to the C2-H of imidazolium ring protons, respectively. For the proton of imidazolium ring: C₄-H and C₅-H were displayed at $\delta_H = 7.82 / 7.79$ ppm for [EtOHMIM⁺][Cl⁻] and at $\delta_H = 7.75 / 7.71$ ppm for [EtOHMIM⁺][H₂PO₄⁻]. Signatures of (N-CH₂-) protons found at $\delta_H = 4.25$ ppm in [EtOHMIM⁺][Cl⁻], while it's appeared at $\delta_H = 4.23$ ppm in [EtOHMIM⁺][H₂PO₄⁻]. Besides, the characteristic peak for N-methyl protons (N-CH₃) appeared at $\delta_H = 3.88/3.86$ ppm in [EtOHMIM⁺][Cl⁻] and [EtOHMIM⁺][H₂PO₄⁻] respectively. Moreover, the resonance of the methylene protons (-CH₂-OH) is observed at $\delta_H = 3.69$ ppm for both of ILs. As shown in **Figures 1a** and **2a**, the chemical shift O-H groups was observed at 9.08 ppm for [EtOHMIM⁺][Cl⁻] and 6.70 ppm for [EtOHMIM⁺][H₂PO₄⁻]. This behavior related to the impact of electronegativity of each anion and also the charge transfer between 1-(hydroxyéthyl)-3-methylimidazolium cation and both chloride and dihydrogenophosphate anions who plays a crucial role in the interionic interactions [22-25]. Additionally; two hydrogen's atoms are attached with [PO₄⁻] their signatures can only be found in [EtOHMIM⁺][H₂PO₄⁻], this is observed in the area of the OH peak in [EtOHMIM⁺][H₂PO₄⁻] which shows a greater amplitude than that of OH in [EtOHMIM⁺][Cl⁻].

On the other hand, the ¹³C-NMR spectra of [EtOHMIM⁺][Cl⁻] and [EtOHMIM⁺][H₂PO₄⁻] show very clearly six signals between $\delta_C = 36.12$ and 137.33 ppm. Therefore, these spectral results confirm a high-purity of our investigated ILs.

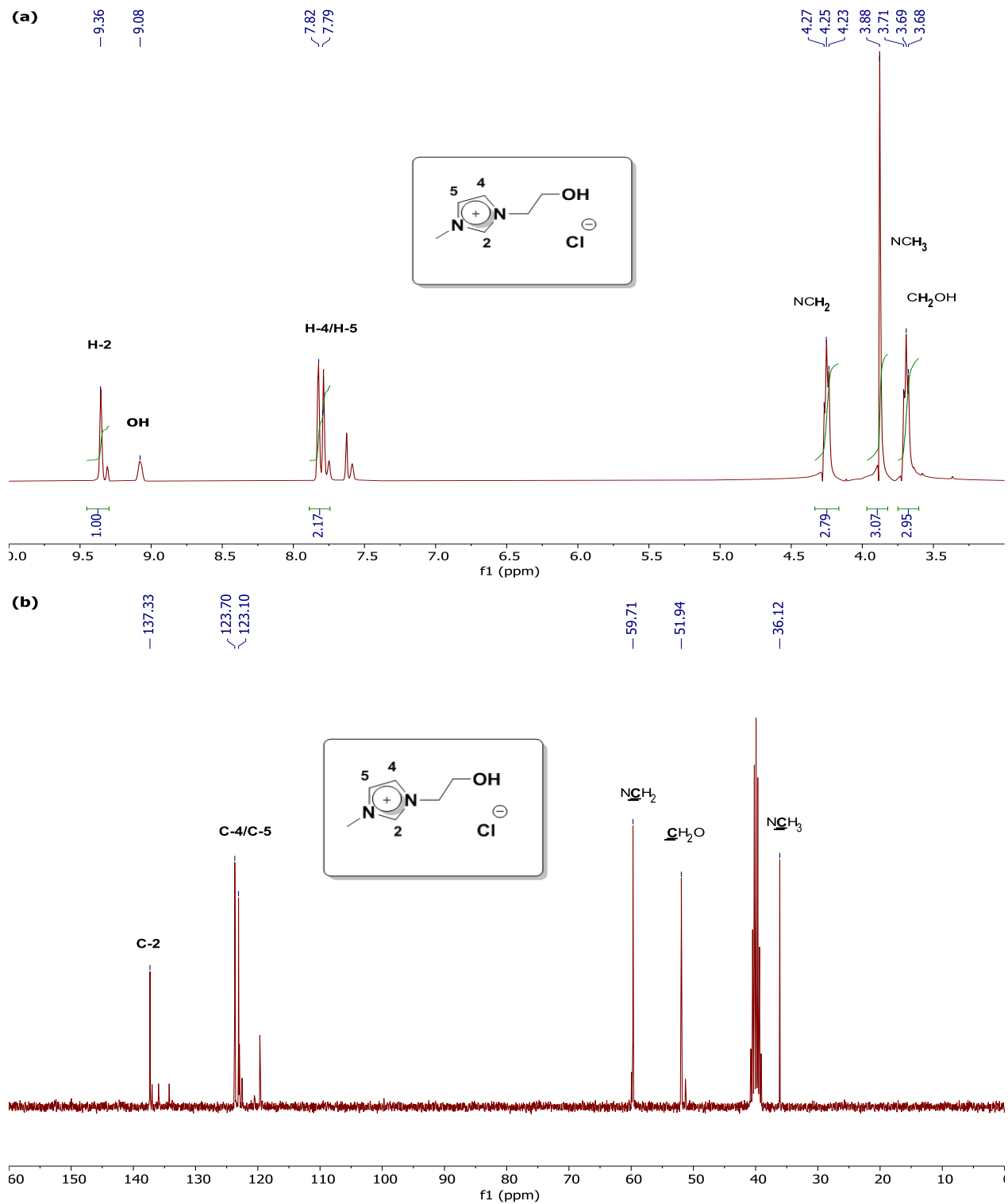


Figure.1: $^1\text{H-NMR}$ (600 MHz) (a) and $^{13}\text{C-NMR}$ (600 MHz) (b), spectra of $[\text{EtOHMIM}^+][\text{Cl}^-]$.

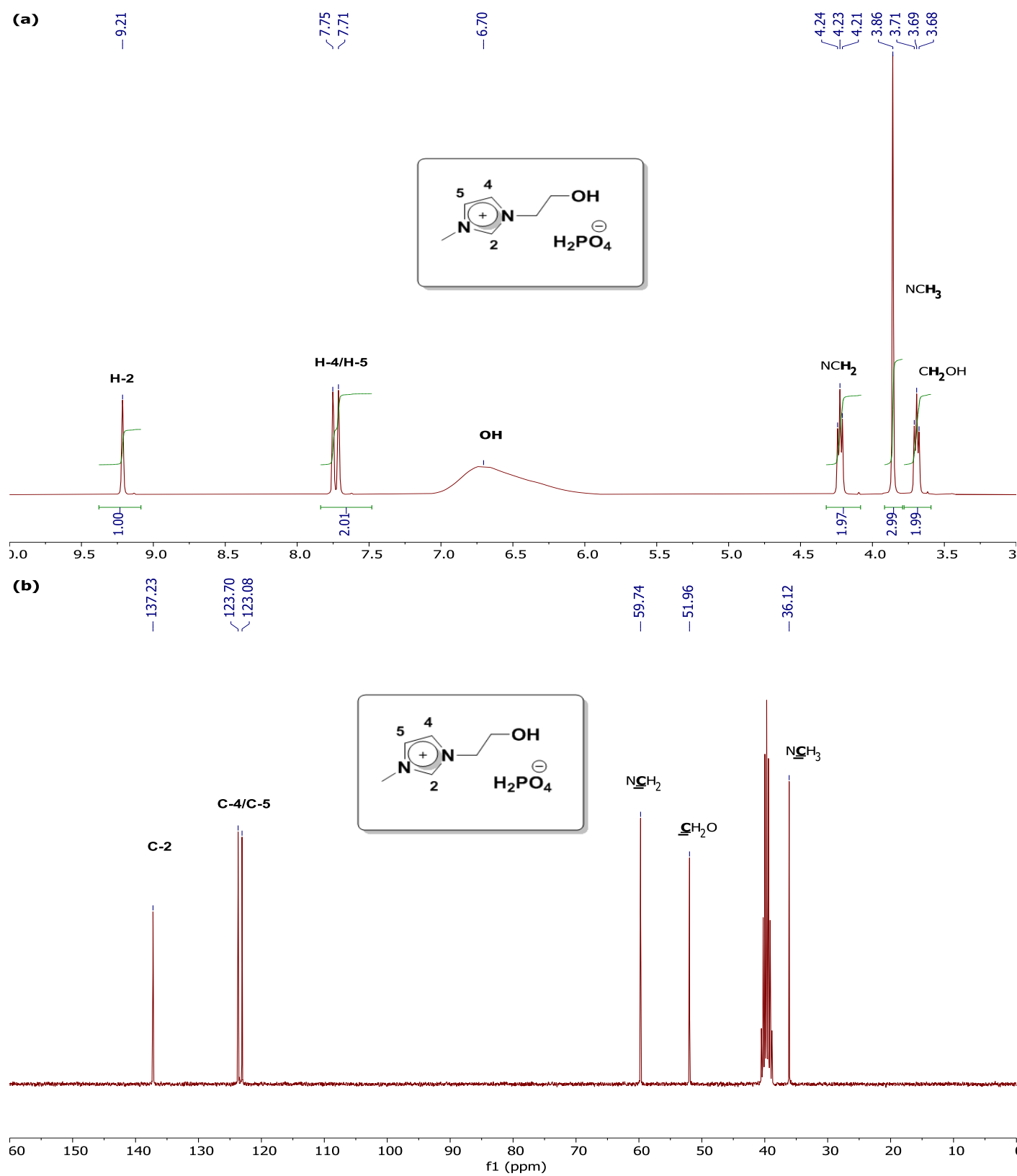


Figure 2. ^1H -NMR (300 MHz) (a) and ^{13}C -NMR (300 MHz) (b), spectra of $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$.

3.2. Experimental vibrational spectroscopy analysis

In order to evaluate the effect of anions on the vibrational spectroscopic properties, FTIR/ATR and Raman spectra of this ionic liquid compared to 1-(hydroxyethyl)-3-methylimidazolium chloride $[\text{EtOHMIM}^+][\text{Cl}^-]$ were measured and investigated in the wavenumber range $600\text{-}4000\text{ cm}^{-1}$ and from 45 to 3500 cm^{-1} ,

3.2.1. The comparison between FTIR/ATR spectra of ionic liquids: 1-(hydroxyethyl)-3-methylimidazolium chloride $[\text{EtOHMIM}^+][\text{Cl}^-]$ and 1-(hydroxyethyl)-3-methylimidazolium dihydrogenophosphate $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$.

FTIR / ATR spectra $[4000\text{-}600\text{ cm}^{-1}]$ of the two ILs are illustrated in **Figure.3**. The observed IR bands and their detailed assignments are listed in **Table 1**. We distinguish three well defined spectral regions: $3500\text{-}2700$, $1700\text{-}1300$ and $1300\text{-}600\text{ cm}^{-1}$.

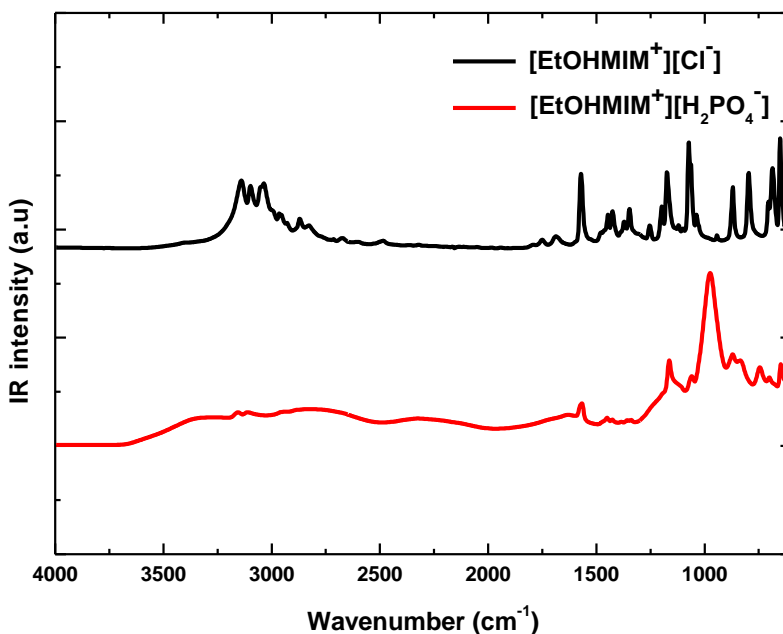


Figure.3. FTIR/ATR spectra of $[\text{EtOHMIM}^+][\text{Cl}^-]$ and $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ in the spectral range $4000\text{-}600\text{ cm}^{-1}$.

Table 1: Observed FTIR/ATR bands and their assignment of 1-(hydroxyethyl)-3-methylimidazolium with chloride and dihydrogenophosphate anions (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 ⁺]		Assignment	Refs
[Cl ⁻]	[H ₂ PO ₄ ⁻]		
621(s)	619(w)	ω (N-H), ν C=C, CH ₃ (N) CN str, τ CH(imidazolium)	[21,26,27,28]
652(s)	648(w)	ω (N-H), CH ₂ (N) str, CH ₃ (N) CN str, ν N-CH ₃ , γ (N-C)	[21,26,29,30]
687 (s)		ω (C-H), δ CC	[21,28,31]
706(m)	702(vw)	CH ₂ (N), CH ₃ (N)CN str	[18,21,22]
	746 (w)	ω (C-H), ring HCCH sym bend, CH ₃ (N) bend, CH ₂ (N) bend	[21,25,26,27]
797(s)		ring HCCH asym bend, CS str	[21,23,24]
	831(sh)	ring HCCH asym bend, NC(H)N bend, γ (C-H)	[29,32]
870 (s)	870 (w)	ρ_{as} (CH ₂), NC(H) N bend, P-OH str, ν_1 (PO ₄)	[21,26,32,33]
943 (vw)		ρ_{as} (CH ₂)	[21,34,35]
	974 (s)	(P-O) stretch, ν_3 (PO ₄)	[33,36]
1037 (m)		ring sym str, CH ₃ (N) str, CH ₂ (N) str, ν C-C	[21,37]
1063 (sh)	1060 (w)	Ring ip asym str, CC str, CH ₃ (N) twist, SNS asym str, ν (C-O), P-O str, ν_3 (PO ₄)	[21,26,33]
1074 (s)		Ring ip asym str, CC str, CH ₃ (N) twist, SNS asym str	[21,26,38]
1100 (vw)		CC str, ν (C-C)	[21,28]
1120 (vw)		δ CH, ring HCCH sym bend, CC str, ρ (CH ₃)	[21,26,29]
1175 (m)	1163 (w)	ring asym str CH ₂ (N), CH ₃ (N) CN str, CCstr, ν N-C	[26,28,29]
1198 (m)		ring s CH ₂ (N), CH ₃ (N)CN str, ν (C-C), ω (C-H), τ (C-H)	[21,26,39]
1254 (w)		ρ CH(imidazolium)	[30]
	1338 (vw)	Imidazolium ring: C-N, C=N str, CC str, CH ₂ (N) str, CH ₃ (N), ν (C-C), P=O str	[21,26,36]
1347 (m)	1360 (vw)	Imidazolium ring: C-N, C=N str, CH ₂ (N) str, CH ₃ (N) CN str, ν (C-C), ω (C-H ₂)	[21,26,29,40]
1371 (w)		δ (CH), δ_s (CH ₃)	[21]
1387 (sh)	1387 (vw)	ρ (CH ₂), ρ (CH), δ (CH ₂) [op], ω (CH), ring ip asym str, CH ₂ (N) bend, CC str, CH ₂ (N) str, CH ₃ (N) CN str, ρ (N-H)	[21,26,28]
1425 (m)	1427 (vw)	Imidazolium ring: C-N, C=N str band, δ_s (CH ₂), C-H deformation, ρ (N-H)	[21,26,28]
1447 (m)	1450 (w)	δ (CH ₂), CCH HCH as bend, ring ip asym str, CH ₃ (N) str, δ_a (CH ₃)	[21,26,29]
1464 (sh)		δ_a (CH ₃), δ (CH ₂), CH ₃ (N) HCH sym bend, CH ₃ (N) CN str	[21,29,40]
1479 (w)		δ (CH ₂), CCH HCH as bend	[21,26]
1572 (s)	1566 (sh)	Imidazolium ring ν (N=C), ring ip sym/asym str, CH ₂ (N), CH ₃ (N) CN str	[21,26,28]
	1630 (sh)	ν (C=C)	[25]
1687 (w)		ν (C=C), ring C=C, N=C-N str	[21,25]
1751 (w)		overtone =C-H str	[21]
	2316 (vw)		
2486 (vw)		ν (C=C)	[21]
2600 (vw)		ν_s (CH ₂)	[21]
2673 (vw)		ν_s (CH ₂)	[21]

2714 (vw)		$\nu_s(\text{CH}_2)$	[21]
2830 (w)	2823(sh)	$\nu_s(\text{CH}_2)$	[21]
2870 (w)		$\nu_{as}(\text{CH}_2)$	[21,29]
2928 (w)		$\nu_{as}(\text{CH}_2)$	[21,29]
2954 (m)		$\nu_s(\text{CH}_2)$, $\text{CH}_3(\text{N})$, HCH as str	[21,29]
2966 (m)	2958 (sh)	$\text{CH}_3(\text{N})$ asym str, CH_2HCH asym str, $\nu_s(\text{CH}_2)$	[21,26,29]
2993 (sh)		$\nu_{as}(\text{CH}_2)$, $\text{CH}_3(\text{N})$ HCH asym str, $\nu(\text{C-H})$	[21,29,41]
3035 (m)		$\nu(\text{C-H})$	[21,41]
3051 (sh)		$\nu_{as}(\text{CH}_3)$, $\nu(\text{C-H})$	[21,29,41]
3097 (m)		$\nu(\text{C-H})$, = C-H Str	[21,26,29,40,41]
	3111 (w)	H-C-C-H asym str, $\text{CH}_3(\text{N})$, $\nu(\text{C-H})$, = C-H str	[21,26,28,29,41]
3140 (m)		H-C-C-H asym str, $\nu(\text{C-H})$, = C-H str	[21,26,29,41]
	3157 (w)	H-C-C-H asym str, $\nu_{as}(\text{C-H})$, $\text{CH}_3(\text{N})$, = C-H str	[21,26,29,40,41]
	3311(sh)	$\nu(\text{O-H})$	[42]

3.2.2. Region 1300–600 cm^{-1}

For the Cl^- anion, this spectral zone (**Figure.4**) is more intense than for $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$. Conversely we notice new strong intense peak in 974 cm^{-1} which is assigned to the symmetric stretching ν_3 mode of dihydrogenophosphate anion not available for $[\text{EtOHMIM}^+][\text{Cl}^-]$. The presence of this new intense is assigned to (P-O) stretching mode [33,36]. The modes at 619 , 648 and 706 cm^{-1} are assigned to (N-H) wagging and $\text{CH}_3(\text{N})\text{CN}$ stretching. The band due to (CH_2) rocking antisymmetric of the cation $[\text{EtOHMIM}^+]$ and $\text{NC}(\text{H})$ N bending occurs at 870 cm^{-1} for the two ILs and is of weak to strong intensity. Also this band can be assigned to (P-OH) stretching mode of H_2PO_4^- anion [21,26,32,33]. For $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ we observe two modes in 746 and 831 cm^{-1} assigned to ring HCCH bending while for $[\text{EtOHMIM}^+][\text{Cl}^-]$ the ring HCCH bending was observed at 797 cm^{-1} . In 1074 cm^{-1} a strong peak assigned to $\text{CH}_3(\text{N})$ twisting of $[\text{EtOHMIM}^+][\text{Cl}^-]$ with weak intensity at 1060 cm^{-1} of $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$. The modes at 1175 and 1198 cm^{-1} of $[\text{EtOHMIM}^+][\text{Cl}^-]$ are assigned to $\text{CH}_3(\text{N})\text{CN}$ stretching which is observed at 1163 cm^{-1} for $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$. The peak of $[\text{EtOHMIM}^+][\text{Cl}^-]$ centered at 1254 cm^{-1} is assigned to (C-H) rocking mode of imidazolium [27].

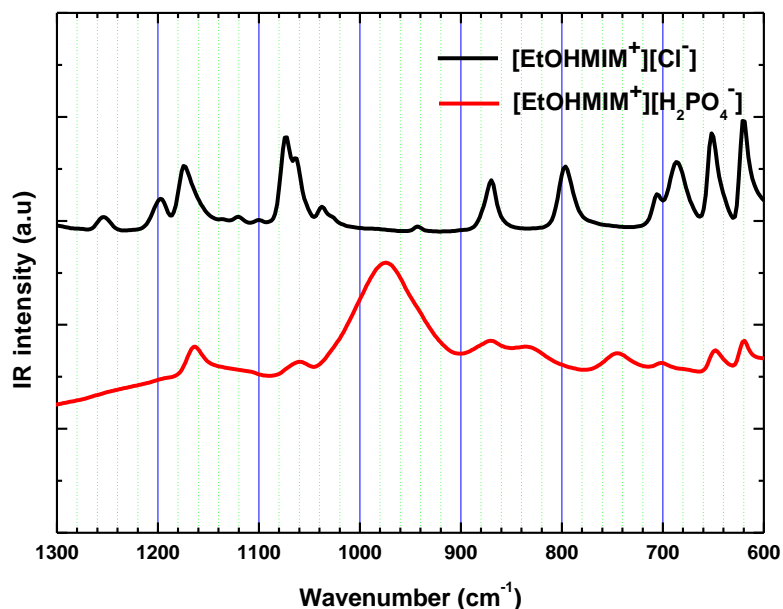


Figure.4. FTIR/ATR spectra of $[\text{EtOHMIM}^+][\text{Cl}^-]$ and $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ in the spectral range 1300–600 cm^{-1} .

3.2.3. Region 1800–1300 cm^{-1}

In this spectral zone (**Figure.5**) we observe a spectrum with high density for the Cl^- anion than for the H_2PO_4^- anion. We notice the mode in 1347 cm^{-1} for the Cl^- anion which is transformed for the H_2PO_4^- anion to 1360 and 1338 cm^{-1} modes (Imidazolium ring: C-N, C=N str, $\text{CH}_2(\text{N})$ str, $\text{CH}_3(\text{N})$ CN Str, ν (C-C)) [21,26,29,40]. We also observe in 1338 cm^{-1} the presence of the stretching mode P=O for H_2PO_4^- anion [36]. The spectral zone of the CH_2 rocking of the cation $[\text{EtOHMIM}^+]$ 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 =C-H stretching [21,32]. The shift is from 1572 cm^{-1} for the anion Cl^- to a shoulder at 1566 cm^{-1} for H_2PO_4^- and conversely from 1630 cm^{-1} for H_2PO_4^- to an doublet in 1687 and 1751 cm^{-1} for the Cl^- anion.

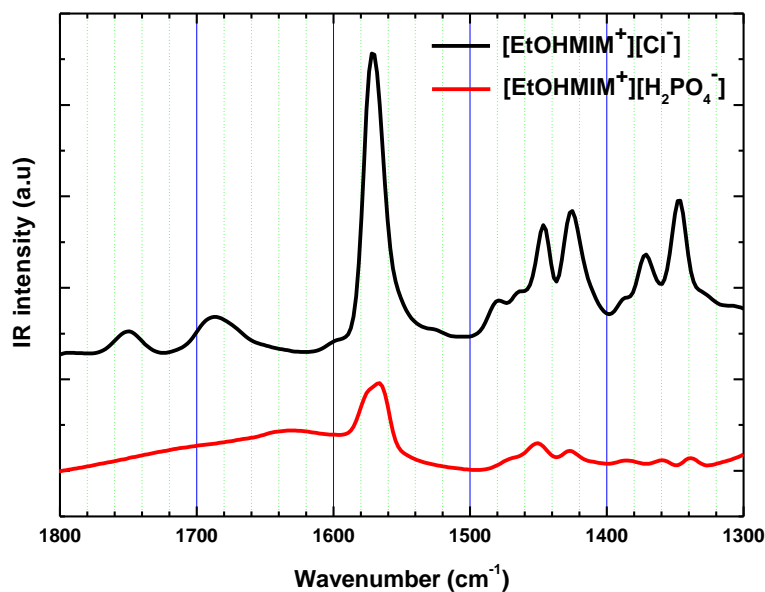


Figure.5. FTIR/ATR spectra of $[\text{EtOHMIM}^+][\text{Cl}^-]$ and $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ in the spectral range 1800–1300 cm^{-1} .

3.2.4. Region 3500–2400 cm^{-1}

In this spectral region (**Figure.6**), we observe more peaks for the Cl^- anion than for the H_2PO_4^- anion. In the spectral range 3000-2600 cm^{-1} , we observe the vibrational mode attributed to the symmetric and antisymmetric (CH_2) of the cation $[\text{EtOHMIM}^+]$ [21,29]. The C-H ring stretching occurs in the regions 3100-3000 cm^{-1} which is the characteristic region of the ready identification of the C-H stretching vibrations [41]. The vibrational mode of the (C-H) is observed in the spectral range: 2993, 3035, 3051, 3097 cm^{-1} and 3140 cm^{-1} for the anion Cl^- and at 3111 and 3157 cm^{-1} for the anion H_2PO_4^- . We notice the mode in 3140 cm^{-1} for the Cl^- anion which is transformed for the H_2PO_4^- anion to 3111 and 3157 cm^{-1} modes (H-C-C-H asym str, $\nu_{\text{as}}(\text{C-H})$, $\text{CH}_3(\text{N})$, = C-H stretching) [21,26,29,40,41]. Note that the presence of a shoulder intensity predicted at 3311 cm^{-1} can be assigned to the corresponding vibrational mode OH (alcohol function of the cation) and possibly OH of H_2PO_4^- anion [42].

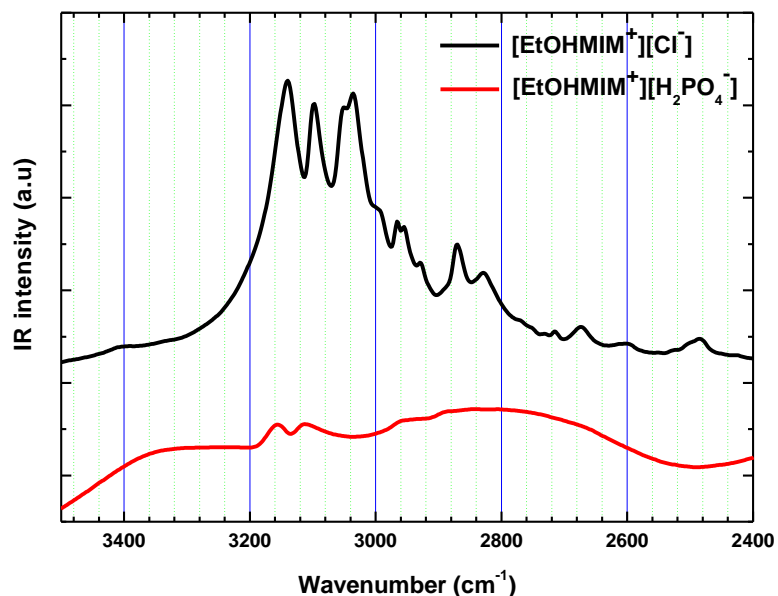


Figure.6. FTIR/ATR spectra of $[\text{EtOHMIM}^+][\text{Cl}^-]$ and $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ in the spectral range 3500–2400 cm^{-1}

3.2.5 The comparison between Raman spectra of ionic liquids: 1-(hydroxyethyl)-3-methylimidazolium chloride $[\text{EtOHMIM}^+][\text{Cl}^-]$ and 1-(hydroxyethyl)-3-methylimidazolium dihydrogenophosphate $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$.

FT-Raman spectra $[3500\text{--}45 \text{ cm}^{-1}]$ of the two ILs are illustrated in **Figure.7**. The observed Raman bands and their detailed assignments are listed in **Table 2**. We distinguish three well defined spectral regions: 3500–2700, 1700–1000 and 1000–45 cm^{-1} .

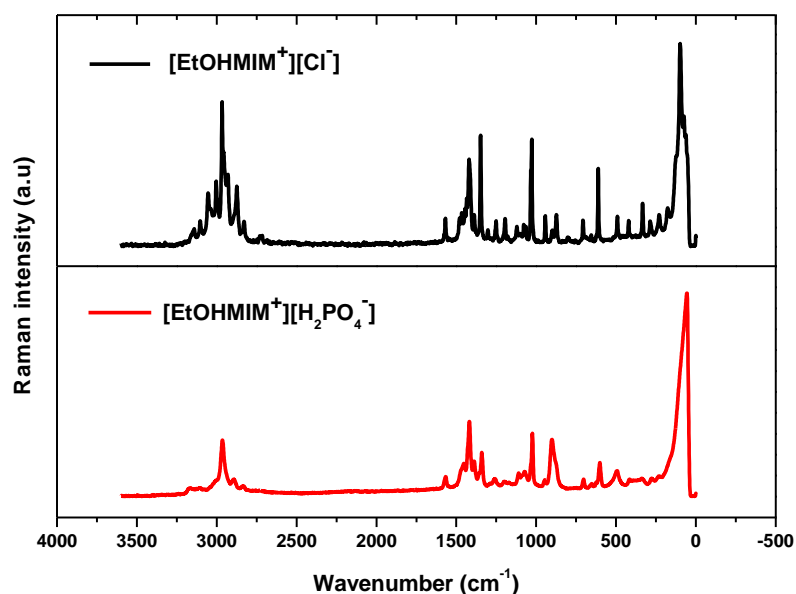


Figure.7. Raman spectra of $[\text{EtOHMIM}^+][\text{Cl}^-]$ and $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ in the spectral range 3500–45 cm^{-1} .

Table 2

Observed FT-Raman bands and their assignment of 1-(hydroxyethyl)-3-methylimidazolium with chloride and dihydrogenophosphate anions (vw = very weak, w = weak, m = medium, s = strong, sh = shoulder, str = stretch, d = deformation, bend = bending deformation, ω = wagging, ρ = rocking, τ = torsions = symmetric, as = antisymmetric).

$[\text{EtOHMIM}^+]$		Assignment	Refs
$[\text{Cl}^-]$	$[\text{H}_2\text{PO}_4^-]$		
63(sh)	56(s)	Intermolecular vibration	[18,22]
75(sh)		Intermolecular vibration	[18,22]
99(s)		Intermolecular vibration	[18,22]
124(sh)		Intermolecular vibration	[18,22]
177(w)		Intermolecular vibration, $\omega(\text{N-C}), \tau(\text{N-C}), \rho(\text{CH}_2)$	[18,22,35]
230(w)	230(vw)	$\rho(\text{CH}_2), \tau(\text{N-CH}_3)$	[25,26,27]
286(w)	276(vw)	$\text{NCH}_3, (\text{N})\text{CH}_2\text{CN bend}, \rho(\text{CH}_2), \text{CN stretch}$	[26,43]
334(w)	335(vw)	δNCH_3	[18,26]
421(w)	417(vw)	$(\text{N})\text{CH}_2\text{str}, \text{NCH}_3, \nu_2(\text{PO}_4), \text{P-O bend}$	[18,26,33]
491(w)	494(w)	$\rho(\text{CH}), \tau(\text{CH}_3), \nu_4(\text{PO}_4)$	[22,27,33]
611(m)	601(w)	$\omega(\text{N-C}), \text{NCH}_3, \text{CN stretch}, \text{P-O bend}$	[23,33,44]
655 (vw)		$\delta\text{CC}, \text{C=C-H}, (\text{N})\text{CH}_2, \text{NCH}_3, \text{CN stretch}$	[24,25,26]
707(w)	705(vw)	$\text{C=C-H}, \text{H-C-C-H}, \text{PO}_2 \text{ sym str}$	[25,26,36]

873(w)	875(sh)	$\rho(\text{CH}_2)$, NC(H)N bend, CCH bend, $\nu_1(\text{PO}_4)$, POH sym str	[26,33,45]
899(vw)	901(m)	CH def vib [op], $\nu_1(\text{PO}_4)$, P-OH str	[30,31,33]
942(w)	945(vw)	CC str, POH asym stretch,	[45,46]
1027(m)	1023(m)	$\nu(\text{C}-\text{C})$, δCC , δCH , νNCH_3	[26,47,48]
1065(w)	1072(vw)	$\nu\text{s}(\text{C}-\text{C})$, PO_2 sym stretch, P-O stretch, $\nu_3(\text{PO}_4)$	[18,33,40,45,49]
1078(w)		$\nu\text{s}(\text{C}-\text{C})$	[18,40]
1121(w)	1110(vw)	ring H-C-C-H symbend, ring ip asym str, $\rho(\text{CH}_3)$	[29,38,43]
1194(w)	1194(vw)	$\rho(\text{CH}_2)$, PO_2 sym stretch	[36,47]
1251(w)	1257(vw)	$\nu(\text{C}-\text{C})$, νNC , δNCH , ρCH_2	[27,29,37]
1303(w)		$\nu(\text{C}-\text{C})$, δCC , $\text{t}(\text{CH}_2)$ [op], $\gamma(\text{CH})$, CN ring	[27,29,30,31]
1347(m)	1340(w)	NCH_3 , (N)CH ₂ CN str, Ring ip sym str, P=O sym stretch	[18,36,43,44]
	1356(vw)	NCH_3 , (N)CH ₂ CN str, Ring ip sym str	[18,43]
1389(w)	1389(w)	Imidazolium ring: C-N, C=N stretch band	[18,26]
1420(m)	1418(m)	Imidazolium ring: C-N, C=N stretch band, (N)CH ₂ str, C-H deformation,	[25,26]
1435(w)		Imidazolium ring: C-N, C=N stretch band, δCH_2 , ring ip asym str, CC str, (N)CH ₂ str, NCH_3CN str	[25,26]
1445(w)	1453(w)	$\nu(\text{C}-\text{C})$, $\nu\text{CH}_3\text{-N-CN}$	[39,40]
1466(w)		NCH_3HCH sym bend, NCH_3CN str, δHCC , $\nu(\text{C}-\text{C})$	[37,38,39,40]
1480(w)		δCH_3 , νCN , δNCH	[39,40]
1568(w)	1567(vw)	$\nu(\text{C}-\text{C})$, $\nu(\text{N}-\text{C})$,	[47]
2829(w)	2835(vw)	$\nu\text{s}(\text{CH}_3)$, (N)CH ₂ , NCH_3 sym stretch	[25,26,44]
2874(w)	2893(vw)	$\nu\text{s}(\text{CH}_2)$, (N)CH ₂ , NCH_3 sym stretch	[25,26,29]
2930(w)		(N)CH ₂ , NCH_3 sym stretch	[25,26]
2957(sh)		$\nu\text{s}(\text{CH}_3)$, NCH_3 sym stretch	[25,47]
2966(m)	2964(m)	NCH_3 asym stretch, $\nu_{\text{as}}(\text{CH}_3)$	[25,26,29]
3003(w)	3003(vw)	NCH_3 asym stretch, C-H stretch	[25,26]
3037(sh)		C-H stretch	[25,26]
3054(w)		C-H stretch	[25,26,37]
3104(w)	3105(vw)	H-C-C-H asym stretch, $\nu_{\text{as}}(\text{H-C}(2))$, (N)CH ₂	[25,26,29]
3143(vw)		H-C-C-H asym stretch, $\nu_{\text{as}}(\text{H-C}(2))$, NCH_3HCH asym str	[25,26,29]
	3170(vw)	H-C-C-H asym stretch, $\nu_{\text{as}}(\text{H-C}(4))$, $\nu_{\text{as}}(\text{H-C}(5))$	[25,26]

3.2.6. Region 1000–45 cm⁻¹

In this region (**Figure.8**), we observe the characteristic modes of H_2PO_4^- anion. The bands appearing in the zone 200 - 50 cm⁻¹ assigned to intermolecular vibrations [18,22]. The modes between 230 and 655 cm⁻¹ are assigned to NCH_3 for both of ILs [18,25,26,43,44]. The symmetric bending mode ν_2 of dihydrogenophosphate anion is observed at 417 cm⁻¹. The bending vibration of the P-O group gives a very weak to weak band in the region 600-400 cm⁻¹ for the H_2PO_4^- anion [33]. In addition, we notice the presence of the following vibrational modes: 705, 875, 901 and 945 cm⁻¹ assigned to PO_2 symmetric stretching, POH symmetric and antisymmetric stretching respectively.

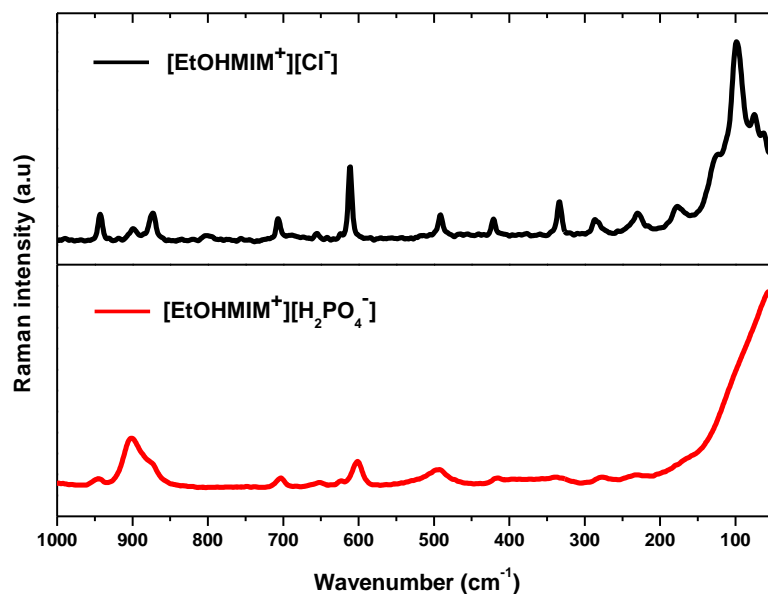


Figure.8. Raman spectra of $[\text{EtOHMIM}^+][\text{Cl}^-]$ and $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ in the spectral range $1000\text{--}45\text{ cm}^{-1}$.

3.2.7. Region $1700\text{--}1000\text{ cm}^{-1}$

In this region (**Figure.9**), both of ILs have almost similar intensities without having a big shift in frequency of the vibrational mode. In the range $1300\text{--}1000\text{ cm}^{-1}$, we observe the vibrational mode attributed to C-C of the cation and the vibrations of the H_2PO_4^- anion. Two PO_2 symmetric stretching modes are expected between 1072 and 1194 cm^{-1} , P-O stretching in 1072 cm^{-1} and P=O symmetric stretching in 1340 cm^{-1} [33,36,45,49]. The Raman modes at 1347 cm^{-1} can be assigned to (N)CH₂ CN stretching vibrations for the Cl⁻ anion which is transformed for the H_2PO_4^- anion to 1340 and 1356 cm^{-1} modes [18,43,44]. The bands appearing in the zone $1435\text{--}1389\text{ cm}^{-1}$ assigned to imidazolium ring: C-N, C=N stretching banding. For $[\text{EtOHMIM}^+][\text{Cl}^-]$ we observe four modes in 1435 , 1445 , 1466 and 1568 cm^{-1} assigned to NCH₃ CN stretching while for $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ this mode was observed at 1453 and 1567 cm^{-1} .

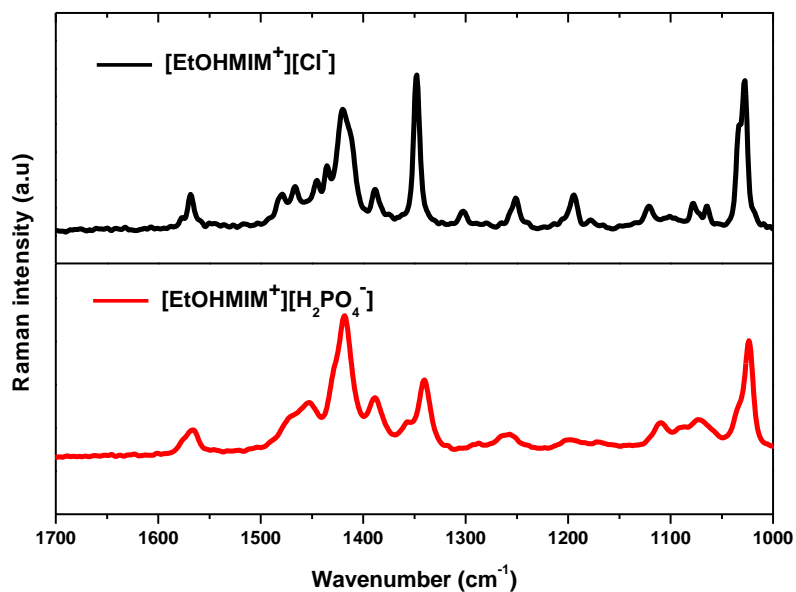


Figure.9. Raman spectra of $[\text{EtOHMIM}^+][\text{Cl}^-]$ and $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ in the spectral range $1700\text{--}1000\text{ cm}^{-1}$.

3.2.8. Region $3500\text{--}2700\text{ cm}^{-1}$

It should be noted that in this region, the only vibrational mode of the cation is observed (**Figure.10**). The bands due to the vibrations of CH_3 and symmetrical stretching NCH_3 occurs at $3000\text{--}2700\text{ cm}^{-1}$ and are of very low to medium intensity. For the $[\text{EtOHMIM}^+][\text{Cl}^-]$ the Raman modes at 3037 and 3054 cm^{-1} attributed to C-H stretching not available for $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$. The modes at 3104 and 3143 cm^{-1} of $[\text{EtOHMIM}^+][\text{Cl}^-]$ are assigned to H-C-C-H antisymmetric stretching and vibrational mode of antisymmetric (H-C(2)) which are observed at 3105 cm^{-1} for $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$. We also observe in the peak of $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ centered at 3170 cm^{-1} the presence of H-C-C-H antisymmetric stretching with vibrational mode assigned to antisymmetric (H-C(4)) and (H-C(5)) of imidazolium.

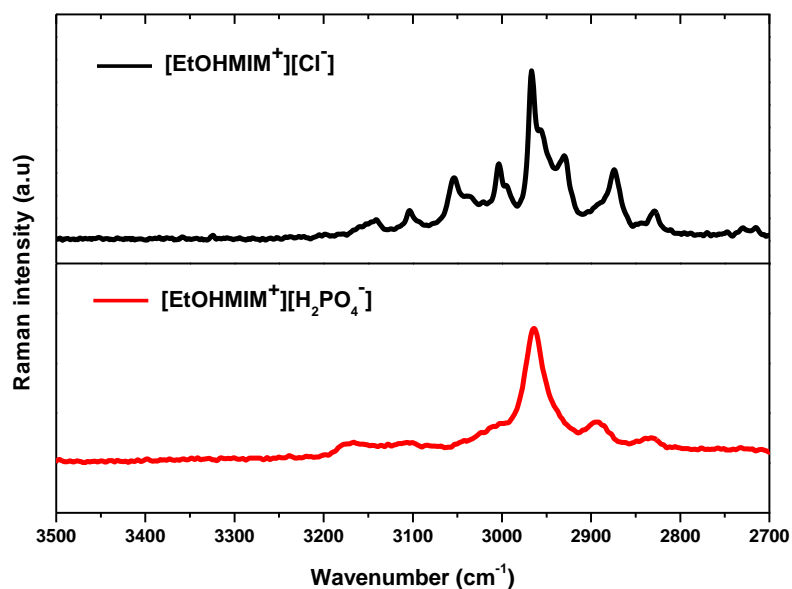


Figure.10. Raman spectra of $[\text{EtOHMIM}^+][\text{Cl}^-]$ and $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ in the spectral range $3500\text{--}2700\text{ cm}^{-1}$.

4. Thermal properties

The DSC thermograms for $[\text{EtOHMIM}^+][\text{Cl}^-]$ and $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ are shown in **Figure.11** and the thermogravimetric analysis curves (TGA) and the derivative thermogravimetric curves (DTG) are shown in **Figure.12**. The mass spectrometric diagram of gas escaped from ionic liquid $[\text{EtOHMIM}^+][\text{Cl}^-]$ and $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ are presented in **Figure.13**. The thermal gravimetric parameters extracted from these curves are presented in **Table 3**.

4.1.DSC Thermogram

Concerning $[\text{EtOHMIM}^+][\text{Cl}^-]$ we can see from **Figure.11.a** and **Table 3** that while heating from lower temperature (-100°) we observe a glass transition $T_g = -58^\circ\text{C}$, then an exothermic peak onset at -36.2°C with an enthalpy of 24.21 J/g that corresponds to the crystallization of the sample and then an endothermic peak onset at 64°C in the heating phase corresponding to the melting point of $[\text{EtOHMIM}^+][\text{Cl}^-]$ with an enthalpy of 79.44 J/g .

In the DSC curve (**Figure.11.b**), $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ has not showed a glass transition on heating scan, then an exothermic peak onset at 77°C . An endothermic peak onset at 84°C was observed in the heating phase corresponding to the melting point of $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$. We observe also another endothermic

peak at 117°C that corresponds probably to the melting point of a second morphology of the same sample[50-51]. The temperatures of decomposition and total decomposition are indicated in **Table 3**.

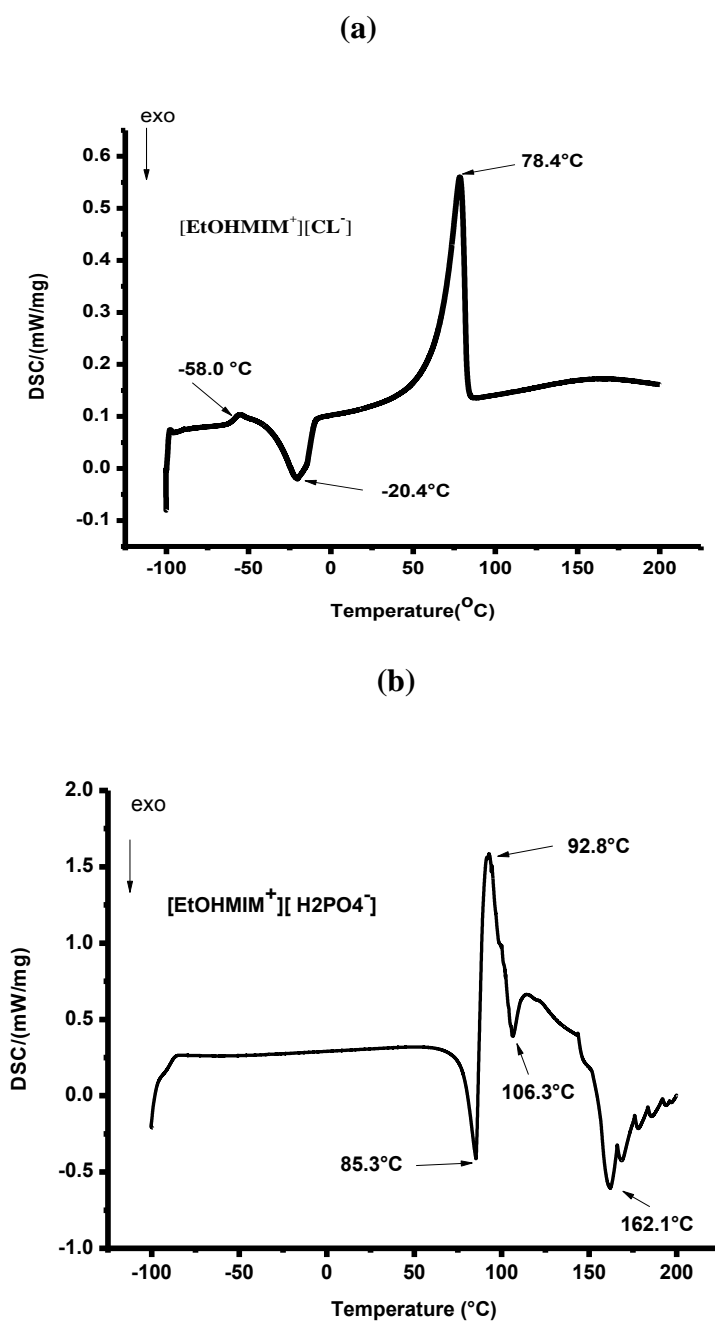


Figure.11. DSC thermograms of ionic liquids from -100 °C to 200 °C
[EtOHMIM⁺][Cl⁻] (a) and [EtOHMIM⁺][H₂PO₄⁻] (b)

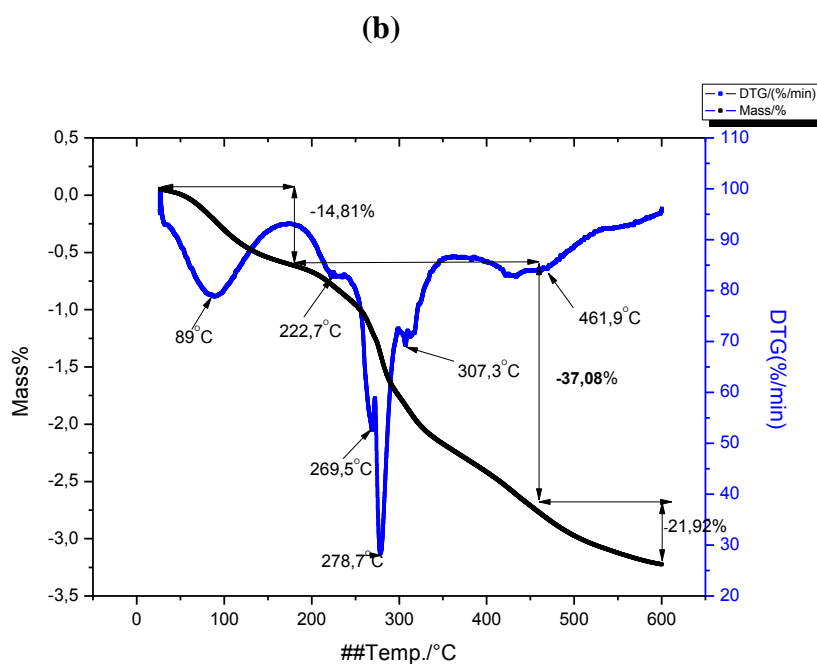
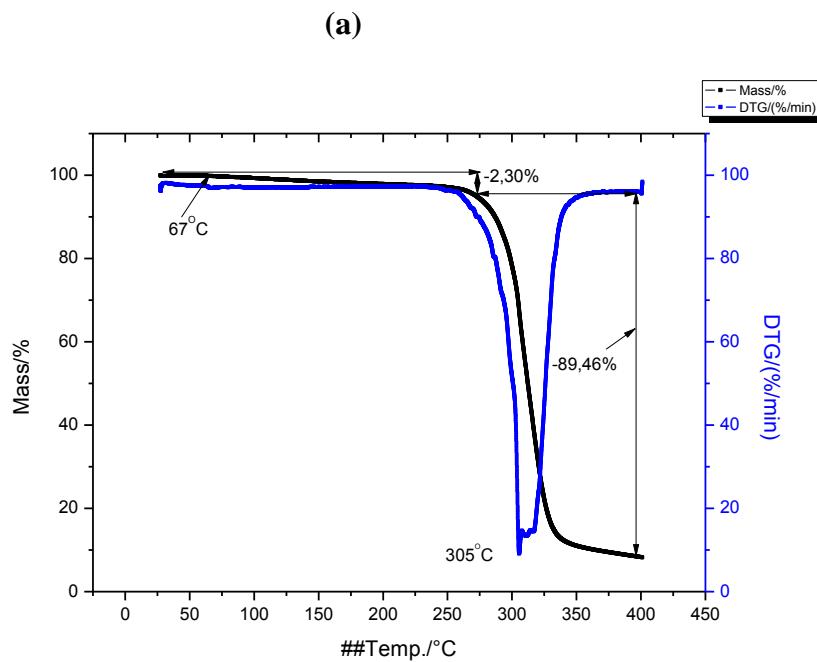
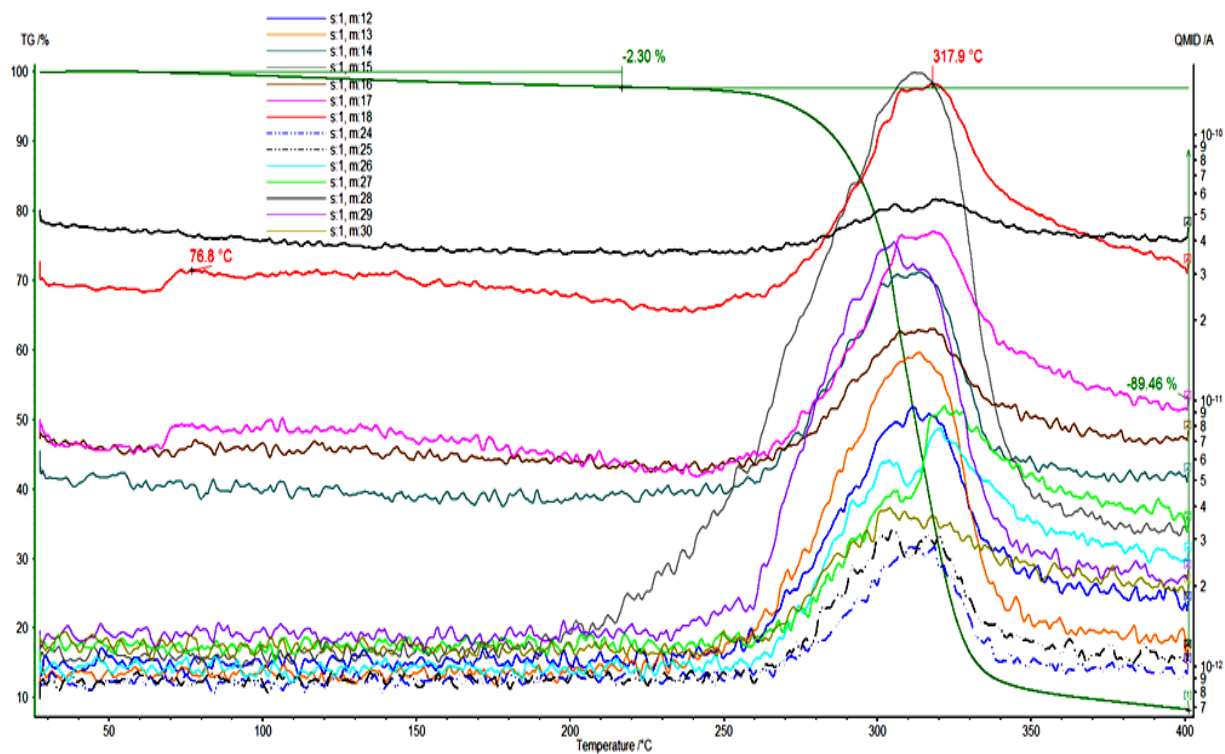


Figure.12. TGA and DTG of ionic liquids $[\text{EtOHMIM}^+][\text{Cl}^-]$ (20 °C to 400 °C) (a) and $[\text{EtOHMIM}^+][\text{H}_2\text{PO}_4^-]$ (20 °C to 600 °C)(b).

(a)



(b)

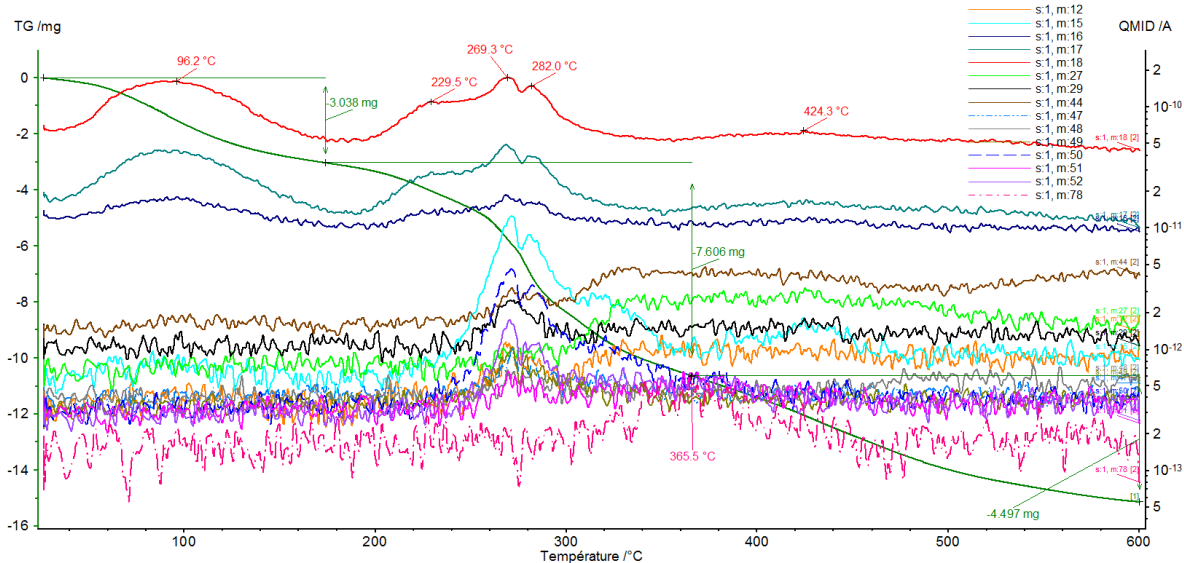


Figure.13. Mass spectrometric diagram of gas escaped from [EtOHMIM⁺][Cl⁻](20 °C to 400 °C) (a) and [EtOHMIM⁺][H₂PO₄⁻] ionic liquids(20 °C to 600 °C) (b).

Table 3 Thermal properties of [EtOHMIM⁺][Cl⁻] and [EtOHMIM⁺][H₂PO₄⁻].

Ionic Liquids	T _g (°C)	T _c (°C)	T _f (°C)	T _d (°C)	T _{d_T} (°C)
[EtOHMIM ⁺][Cl ⁻]	-58	-36.2	64	250	317
[EtOHMIM ⁺][H ₂ PO ₄ ⁻]	-	77	84	264	365

4.2. Thermal Stability

According to the TGA and DTG curves in **(Figure.12.a)**, the thermal stability of [EtOHMIM⁺][Cl⁻] covers a large domain of temperature between -100°C and 250°C. A mass loss started in two steps between 20 °C and 400°C. For the first step, a mass loss of 2.30% begins at nearly 67 °C and ends at a temperature of 253°C. This loss corresponding to the release of the H₂O gas identified from the mass spectrometry curve. The second step (from 253°C to about 334°C), a loss of 89.46%, corresponding to the release of CH₃ and OH and other fragments identified as gas from the mass spectrometry curve.

For the [EtOHMIM⁺][H₂PO₄⁻] sample, the TGA and DTG thermograms **(Figure12.b)** show that this compound is steady below 50°C and undergo change from this temperature in three steps, leaving a reddish residue of 26.19% from the initial mass at 600°C. The first step begins at almost 50°C with a mass loss of 14.81% and ends at a temperature of 200°C corresponding to the release of H₂O as a gas identified by the mass spectrometry curve. The second step begins at 200°C and ends at approximately 360°C with a loss of 37.08% corresponding to the release of H₂O, CH₃, OH and other fragments identified as gases from the mass spectrometry curve, and the third step between 360 and 600°C with a loss of 21.92%.

5. Conclusion

In this study, we synthesized a new hydroxyl-functionalized ionic liquid based on 1-(hydroxyethyl)-3-methylimidazolium dihydrogenophosphate with a yield of 98% in two-steps of synthesis where the anion Cl⁻ was exchanged by H₂PO₄⁻. ¹H and ¹³C-NMR spectroscopy measurements confirm the geometry and purity of the targeted ILs. Also, both compounds were characterized by FTIR/ATR, FT Raman and TGA / DTA/ DSC thermal measurements. The anion seems to play an important role in the thermal stability of the compound as well as on its vibrational behaviour. The results of vibrational spectroscopy and DSC are compared with those obtained on the same intermediate compound [EtOHMIM⁺][Cl⁻]. The final compound

i.e. [EtOHMIM⁺][H₂PO₄⁻] shows more interesting vibrational and thermal properties due the type of anion.

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