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*Memory*

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**Synthesis, experimental and theoretical vibrational studies  
of Chloride ionic liquids**

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# dedicate

*I dedicate this work to:*

*My father who taught me the love of science and  
Perseverance in life.*

*My mother for her tenderness and encouragement  
during  
all my life.*

*My dear brothers and sisters.*

*To all my family, to all my friends .*

*All my dear ones*

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{ Abbreviation list }

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ILs: ionic liquids

SCI: Scientific and technical journal articles

DSSCs: dye sensitized solar cells

[EMIM]Cl : 1-Ethyl-3-methylimidazolium chloride

[EtOHTHM<sup>+</sup>][Cl<sup>-</sup>]: 1-(hydroxyethyl)-3-methylthidazolium chloride

[EtOHTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>] : lehydrogenosulfate 1-(hydroxyethyl)-3-methylthidazolium

DFT: Density functional theory

# General introduction

Similar to all salts, ionic liquids consist of separate cationic and anionic species, but unlike common salts, they have a low tendency to crystallize due to their huge structure and asymmetric [1], the ionic liquids based to imidazolium It is one of the most highly synthesized ion fluids in recent years due to its distinct properties.

Furthermore, ILs is very interesting because many of their properties, such as viscosity or Melting point varied by structural changes in the cation and/or the anion can become. Their properties can thus be adapted to a given separation or Adjust solution problem, which is why they are also referred to as designer solvents [2].

This research wants to contribute to the study of ILs and their vibratory behaviour, in particular the synthesis on the basis of imidazolium , we synthesis two ILs based to imidazolium (1-(hydroxyethyl)-3-methylimidazolium chloride and lehydrogenosulfate 1-(hydroxyethyl)-3-methylimidazolium), We divided our search into four chapters.

In the first chapter, we talked about Definition of ILs and their history with the mention of the first ILs that were manufactured and with technological advances, many properties of these ILs have been discovered that go into many applications.

In chapter II we devoted this section to talking about the methods of making ILs with examples and its industry protocol.

In chapter III, we will discuss the vibratory study on ILs by FTIR/ATR spectroscopy, we will study the effect of the choice of anion on ILs behavior by comparing spectroscopy of two types of ion fluids with the same cation .

Finally, in chapter IV, entitled "Theoretical study" we will optimize the structure of two ionic's liquids and we will apply DFT theoretical and calculat using (GaussView and Gaussian) software, Results obtained from[ FTIR/ATR] spectroscopy, we will discuss and compare them with[ FTIR/ATR] spectroscopy results for Experimental studies .

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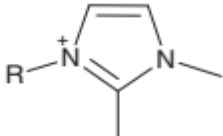
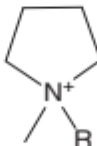
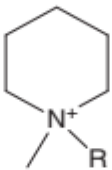


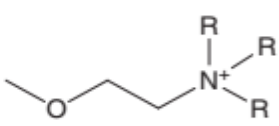
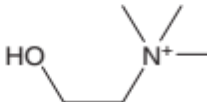
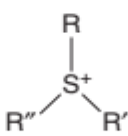
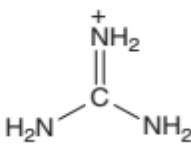
# Chapter I

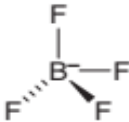

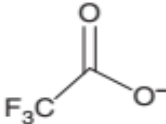
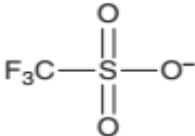
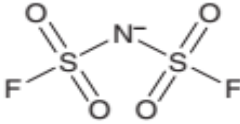
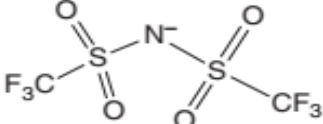
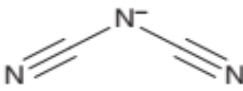
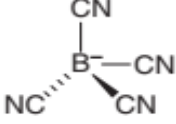
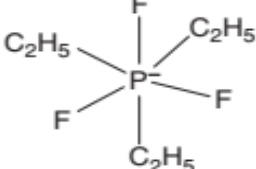
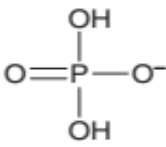
## Bibliography of ILs

## **I.1 Introduction:**

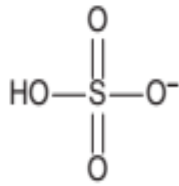
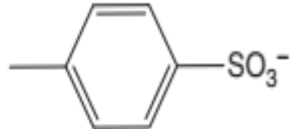
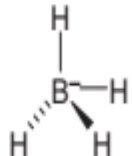
Ionic liquids (ILs) are generally defined as compounds consisting entirely of ions with melting points below 100 °C. The first IL (ethyl ammonium nitrate) was described by Paul Walden in 1914, when he had no idea that nearly a century later, IL would become a major scientific field. In fact, ILs as innovative liquids have only received widespread attention in the past 20 years. The number of SCI articles published on ILs has grown exponentially, from a few in 1996 to >5000 in 2016, outpacing the annual growth rate of other fields of popular science. This shows that more and more researchers are exploring this exciting field with great results. Multidisciplinary research on ILs is emerging, including chemistry, materials science, chemical engineering, and environmental science. More specifically, with a deeper understanding of the nature of IL, some important fundamental aspects are now different from the original concept[1].

In order to understand more about ionic liquids, we present to you a **Table 1** Glossary of structures and nomenclature abbreviations.

Quaternary cations	Abbreviation	Structure
Alkylmethylimidazolium	$[C_n\text{mim}]^+$	
Alkyldimethylimidazolium	$[C_n\text{dmim}]^+$	
Alkylmethylpyrrolidinium	$[C_n\text{mpyr}]^+$	
Alkylmethylpiperidinium	$[C_n\text{mpip}]^+$	
Ammonium	$[N_{n,n,n,n}]^+$	
Phosphonium	$[P_{n,n,n,n}]^+$	
Ether-functionalized	$[N_{R,R,R,2O1}]^+$ , etc.	
Cholinium	$[\text{Ch}]^+$	
Sulfonium	$[S_{R,R',R''}]^+$	
Guanidinium	$[\text{Gdm}]^+$	

Anions	Abbreviation	Structure
Tetrafluoroborate	$[\text{BF}_4]^-$	
Hexafluorophosphate	$[\text{PF}_6]^-$	
Trifluoroacetate	$[\text{tfa}]^-$	
Triflate	$[\text{OTf}]^-$ or $[\text{CF}_3\text{SO}_3]^-$	
Bis(fluorosulfonyl)imide <sup>a)</sup>	$[\text{fsi}]^-$ or $[\text{N}(\text{SO}_2\text{F})_2]^-$	
Bis(trifluoromethanesulfonyl)imide <sup>a)</sup>	$[\text{NTf}_2]^-$ or $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$	
Dicyanamide	$[\text{N}(\text{CN})_2]^-$ or $[\text{dca}]^-$	
Tetracyanoborate	$[\text{B}(\text{CN})_4]^-$	
Fluoroalkylphosphates	$[\text{fap}]^-$ , $[\text{efap}]^-$ , etc.	
Dihydrogenphosphate	$[\text{H}_2\text{PO}_4]^-$ or $[\text{dhp}]^-$	



Anions	Abbreviation	Structure
Hydrogen sulfate	$[\text{HSO}_4]^-$	
<i>p</i> -Toluenesulfonate or tosylate	$[\text{Tos}]^-$	
Tetrahydroborate or borohydride	$[\text{BH}_4]^-$	

**Table(1):** Glossary of structures and nomenclature abbreviations

In addition, the physical and chemical properties of ILs can be modified by changing anion/cation combinations and IL are generally considered to be solvents. This makes it possible to design systems adapted to various applications (thermal batteries, electrochemistry, and organic, inorganic and enzymatic synthesis, catalysis...), also according to need.

In this bibliographical chapter we will study ionic liquids, their physico-chemical properties and their applications in several fields and their synthesis.

## I.2. Ionic Liquids ILs:

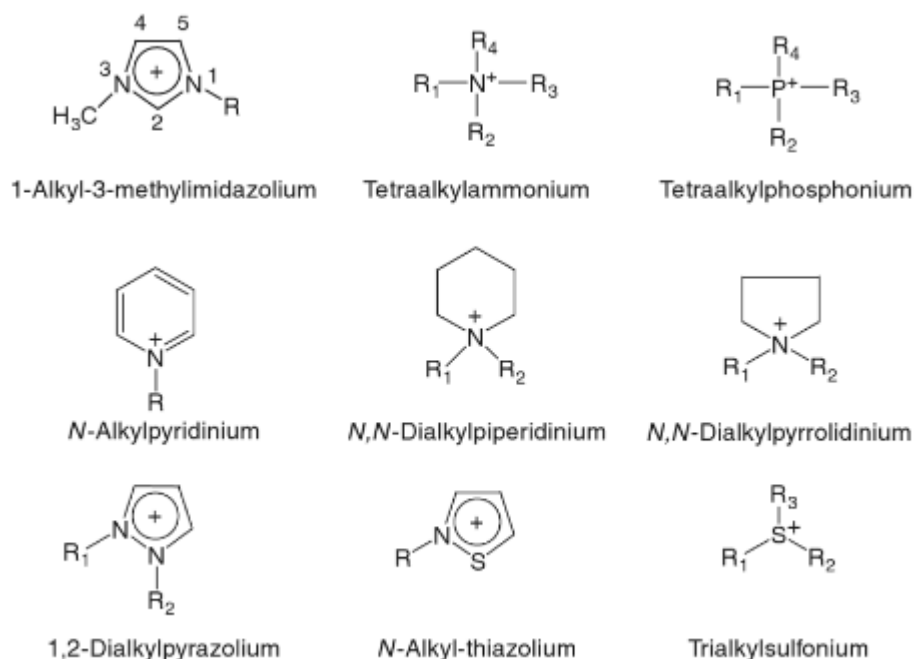
### I.2.1. Definition of an Ionic Liquid

The phrase ‘ionic liquid’ was coined only relatively recently to refer to ambient temperature liquid salts, and the definition has since been the subject of much discussion and some evolution. The most useful practical definition of an IL is ‘**A liquid comprised entirely of ions.**’[2]

Ionic liquids are composed exclusively of anions and cations. They are molecular solvents composed of neutral species such as benzene, methanol, chloroform, water etc. Usual molten salts show a high melting point (i.e., 801 °C for sodium chloride and 614 °C for lithium chloride), which greatly confine their use as solvents in most applications.[3]

Room-temperature ionic liquids are typically salts with large nitrogen or phosphorus-containing organic cations with linear alkyl chains. Much research has been devoted to imidazolium ionic

liquids, particularly those with 1-alkyl-3-methylimidazolium cations. Figure 1 shows the ring numbering system for these cations, along with the structures of other widely studied cations.



**Figure 1:** Widely studied ionic liquid cations (R, R<sub>1</sub>, R<sub>2</sub>, R, and R, are alkyl groups.)

### I.2.2. The historic:

The historic of ionic liquids came back to the second half of the nineteenth century when chemists noticed that a liquid known as « the red oil » often appeared as a separate phase during Friedel-Crafts reactions. Friedel and Crafts described their alkylation reactions in a French scientific journal in 1877. Later in 1988, gabriel reported that the protic ionic liquid ethanollammonium nitrate is the first organic salt that has a melting point of less than 100 °C .

In the end of the nineteenth century, chemists were interested in the study of other salts with low melting points. In 1934, chemists prepared a compound by adding concentrated hydrochloric acid in excess to pure pyridine. This compound was named afterwards as « pyridinium hydrochloride » and it has a melting point of 118 °C. Nowadays, it is generally accepted that the birth of room-temperature ionic liquids took place in 1914 with Walden's synthesis of ethyl ammonium nitrate. Progress was subsequently slow, with the next significant development not being reported until 1951, the explosion of interest in ionic liquids commenced in the years 1998-2000, resulting in an exponential increase in research publications on the topic during the first decade of the new millennium.[4]

### **I.3.Physicochemical Properties of ILs:**

Study and synthesis of ionic liquids is still very latest, and they reveal a wide range of properties.

The practicability of the application of ILs, especially in extraction was considerably determined by physical and chemical properties of ionic liquids such as density, viscosity, polarity... Obviously, a clear understanding about ILs' physical and chemical properties is crucial for its application in extraction.

#### **I.3.1.Density:**

The density is the most often measured and reported physical property of ILs for its importance in related applications. ILs are generally denser than organic solvents, Reported densities of ILs vary between 0.9 and 1.7 g cm<sup>-3</sup> and are little sensitive to temperature. For example, Kato and Gmehling presented data for 1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide in the range of (298.15~323.15)K, it showed variation of only 0.9% in the density.[5]

#### **I.3.2. Viscosity:**

Viscosity is another important factor of ILs in affecting its application in extraction, which is generated by the motion and molecular interaction between the molecular They called the viscosity coefficient.

Values viscosity of 1,3-dialkylimidazolium salts at room temperature range from 40 cP to 1000 cP.

For ILs, it has been shown that increasing the length of alkyl chains increases the viscosity through stronger van der Waals interactions.[6]

The anion structure has a far greater effect on the viscosity than similar changes to the cation. It is unknown why the viscosity is more dependent on the anion structure, but it is consistent with what has been seen for ILs.

#### **I.3.3. Solubility:**

The solubility of ionic liquids in water is an important parameter that determines the chemical's environmental impact and fate.

The solubility of ionic liquids in water is of great consideration. The extent of solubility in water depends mostly on the degree of coordination feasible with the ions. Basic ions (NO<sub>3</sub>)<sup>-</sup> can strongly coordinate with water, while acidic ions are non-coordinating and neutral ions (BF<sub>4</sub>)<sup>-</sup> and (NTf<sub>2</sub>)<sup>-</sup> are weakly coordinated with water. The length of alkyl chains on the cation also affects the miscibility of water in an ionic liquid. A larger chains result in a more hydrophobic ionic liquid.[7]

#### 1.3.4.Melting points:

The melting points of IL solvents define the lower end of the liquids range. Compared with molecular solvents, the low vapor pressure and very wide liquids range are probably the two meaningful properties that make the ILs very attractive as solvents. Many or most ILs are prone to super cooling, which makes melting points difficult to measure. Many ILs can form glasses and ILs' glass transition temperatures are usually reported instead of melting points. The glass transitions tend to be very low (<-50 °C).[9]

Ionic Liquids	Melting point (oC)	Viscosity (mPa)	Density (gr/cm <sup>3</sup> )	Flash Point (oC)	Solubility in Water
1-Ethyl-3methylimidazolium tetrachloroaluminate (EMIM AlCl <sub>4</sub> )	9	26	1.3040	218	react with water
1-Butyl-3methylimidazolium tetrachloroaluminate (BMIM AlCl <sub>4</sub> )	-10	32	1.234	198.5	react with water
1-Butyl-3methylimidazolium Hydrogen sulphate (BMIM HSO <sub>4</sub> )	28	4320	1.2770	>249	
1-Ethyl-3methylimidazolium acetate (EMIM Asetat)	-10	93	1.027	164	infinity
1-ethyl-3methylimidazolium thiocyanate (EMIMSCN)	< -20	22	1.1140	162	infinity
Tetrafluoroborate	-82	314	1.208		
Methyl-tri-nbutylammoniummethylsulfate	62			179.5	infinity

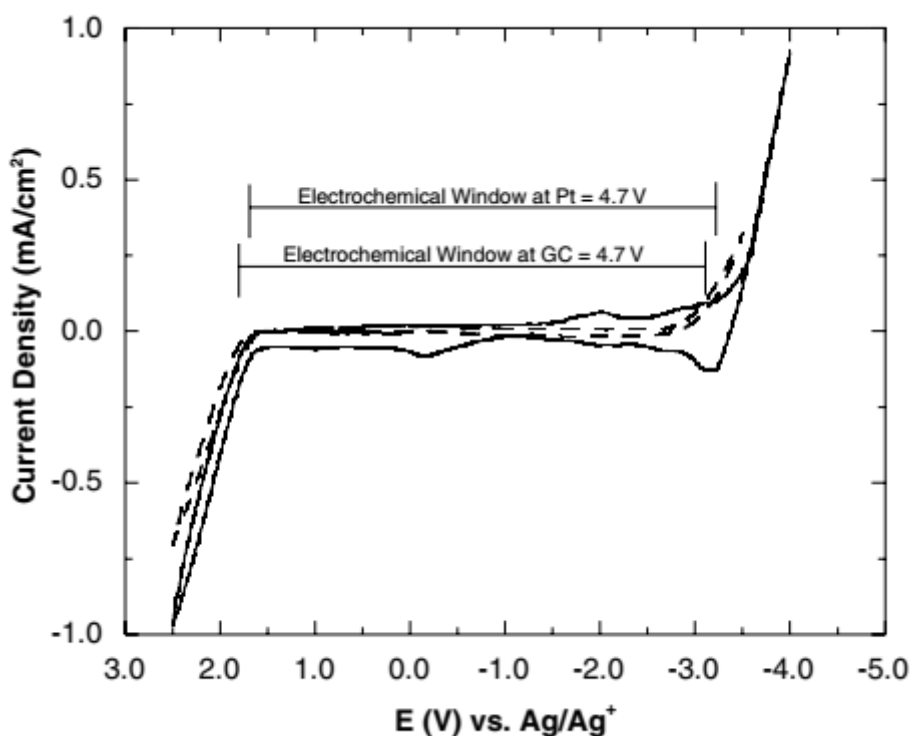
(MTBS)					
Hexafluorophosphate	-70	682	1.238		

Table 2. Types of Ionic Liquids with physical-chemical properties.[8]

## I.4. Electrochemistry Properties of ILS:

### I.4.1 Electrochemical Potential Windows

A key criterion for the selection of solvents for electrochemical studies is the electrochemical stability of the solvent ; This is most evident in the range of Above this value the solvent is electrochemically inert. This useful electrochemical potential window depends on the oxidation and reduction stability of the solvent. In the case of ionic liquids, the potential window depends mainly on Cationic reduction resistance and anionic oxidation resistance. (A sort of Notable exceptions are acidic chloroaluminate ionic liquids, where Reduction of Heptachloroaluminate  $[Al_2Cl_7]^-$  is a Cathodic-Limited Reaction Process). Furthermore, the presence of impurities can play an important role in limiting the potential window of ionic liquids.



**Figure 2:** The electrochemical window of 76–24 mol % [BMMIM][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]/Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] binary melt at: a) a platinum working electrode (solidline), and b) a glassy carbon working electrode (dashed line). Electrochemical window set at a threshold of 0.1 mA cm<sup>-2</sup>. The reference electrode was a silver wire immersed in 0.01 M AgBF<sub>4</sub> in [EMIM][BF<sub>4</sub>] in a compartment separated by a Vicor frit, and the counter-electrode was a graphite rod.

## I.4.2 Ionic Conductivity

The ionic conductivity of the solvent is critical when choosing solvent electrochemical applications. There are several DC and AC methods available for this Measurement of ionic conductivity. On the other hand, in the case of ionic liquids, The vast majority of data in the literature are collected using one of two AC techniques: the impedance bridge method or the complex impedance method both Some of these methods use simple two-electrode cells to measure impedance Ionic Liquids (Z).

where  $\omega$  is the frequency of the AC modulation. It can be seen from Equation (2) When the AC frequency increases the capacitive contribution to the impedance very small, the equation simplifies to  $Z = R$ , the resistance Ionic liquids in impedance cells. Under these conditions, the conductivity ( $\kappa$ ) of the ionic liquid may be obtained from the measured resistance by Equation(3) [9-10-11]

**Equation (3)**

$$\kappa = \frac{l}{AR}$$

## I.5. Applications of ionic liquids:

### I.5.1. Electrochemical Applications:

The inherent conductivity of ILs makes them suitable for a wide range of electrochemical applications, such as Scionix's chromium electroplating process .The system is based on cholinechloride and chromium(III)chloride in the form of a deep eutectic solvent (DES), ring safer alternative to toxic chromium(IV) salts, and avoiding embrittlement of the coating room the competing hydrogen evolution reaction observed when chromic acid-based electrolytes are used. The use of ILs results in improved current exigencies (>90%) and crack-free, corrosion resistant coatings. The IL technology is used in a variety of metal processing applications, including electroplating and electropolishing processes. IL shave also found uses in batteries due to improvements in safety (non-flammable) and increased high-voltage stability. NOHMs Technologies commercialized ILs as an electrolyte (NanoLyte) in Li-ion batteries, yielding

400% more cycle-lifetime; and Nant Energy (formerly Fluidic Energies) utilized ILs in Zn-air batteries .Another electrochemical application exploiting ILs is dye sensitized solar cells (DSSCs), comprising a semiconducting IL-based electrolyte and photo-sensitized anode, with a dye that increases the cell's sensitivity to visible light, and are a low-cost alternative to crystalline silicon cells.[12]

## I.5.2. Applications in organic synthesis and catalysis:

### I .5.2.1. Catalytic reactions:

Ion fluids were first used as a catalyst 20 years ago in the Friedel-Crafts reaction. Ionic liquids are used as a twophase catalyst or substrate to stabilize other catalysts. In the presence of ionic liquids, it is possible to reuse the catalyst. The general state of this reaction is shown in Figure 3.[13]



figure 3. Friedel-Crafts reaction[13]

### I .5.2.2. Hydrogenation :

Ionic liquids (ILs) were for the first time found to be alternatively excellent media for the heterogeneously catalyzed hydrogenation of halonitrobenzenes. The ionic liquids give rise to higher selectivity and lower dehalogenation in the hydrogenating process compared with that observed in conventional organic solvents, one of the most studied reactions in homogeneous catalysis is the catalytic reaction of hydrogenation of a carbon-carbon double bond by transition of a metal complex. However, the separation of products and reactants remains problematic. Numerous studies have shown that the use of ionic liquids improves the yields and selectivity of this type of reaction

## I .5.3 Application of Ionic Liquids in Separation and Processes:

### I .5.3.1 Liquid-liquid extraction:

One of the methods used for separation is liquid-liquid extraction. This method is widely used in industry because it is very energy efficient.

Most of the solvents used for the organic phase of chloroform are volatile solvents. Aqueous ionic liquids are a good alternative to the organic phase. Ionic liquids are mainly used in the extraction of valuable metal ions such as gold, lanthanides, and actinides or toxic metal ions of drinking water such as mercury and cadmium.

#### **I .5.4 Other application:**

##### **I .5.4.1 Gas Handling:**

ILs have several properties that make them useful in gas storage and handling applications, including low vapor pressure, steadiness at high temperatures, and solvation for a wide variety of compounds and gases. They also have weakly coordinating anions and cations which are able to stabilize polar transition states.[14]

##### **I .5.4.2.Solar Thermal Energy:**

ILs have potential as a heat transfer and storage medium in solar thermal energy systems. Concentrating solar thermal facilities such as parabolic troughs and solar power towers center the sun's energy onto a receiver which can generate temperatures of around 600 °C . This heat can then produce electricity in a steam or other cycle.

##### **I .5.4.3. Extraction of Biological Substances:**

Biological substances were different from other materials due to their unique application and potential prospects in the areas about food, health, environment and energy. The extraction of biological substances here refer in particular to the application of ILs in the extraction of the substance about protein, amino acids, enzyme, bio fuel and bio feedstock, which has many restrictions due to their unique properties and their special uses. The traditional toxic organic solvent sometimes cannot be used in the extraction of some substances when the productions are used in the areas of food or health.[15]



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# Chapter II

## Synthesis of Ionic Liquids

## 1. Introduction

Despite the ever-increasing number of papers describing ion fluid applications, their preparation and purification in recent years have taken place in an atmosphere of "need" knowledge ". Although most researchers use similar basic types of chemistry, everyone seems to have their own tricks to enhance yields and product purity [1].

This chapter is an attempt to highlight various ways of making ion liquids with mention of industry protocol and its interaction equations.

## 2. Synthesis of Ionic Liquids:

In this section we talk about the preparation and the most important methods of ILs that are involved in most of the studies of the last twenty years.

The synthesis of ionic liquids can generally be split into two methods:

- ALKYLATION
- The anion-exchange

### 2.1 ALKYLATION

The alkyl cations of many ammonium, imidazolium, pyridinium and phosphonium ionic liquids are prepared by alkylation of a suitable precursor, a nucleophile, using an alkylating agent such as a halogeno alkane or a dialkyl sulfate.[2]

For example, alkyl imidazole, which are the basic building blocks of imidazole-based ionic liquids, are easily prepared by alkylating imidazole. Similarly, halogens of alkanes are used to alkylate pyridine and to produce alkyl salts of pyrimidine.[3]

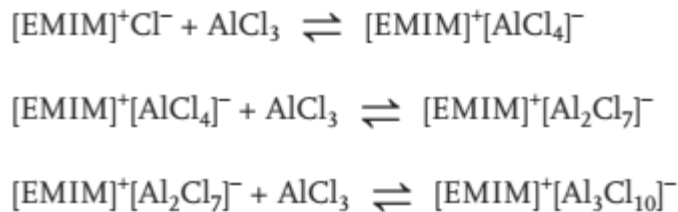
### 2.2 The anion-exchange

The anion-exchange reactions of ionic liquids can really be divided into two distinct categories: direct treatment of halide salts with Lewis acids, and the formation of ionic liquids by anion metathesis.[4]

- Lewis Acid-based Ionic Liquids
- Anion Metathesis

#### 2.2.1 Lewis Acid-based Ionic Liquids:

The formation of ionic liquids by treatment of halide salts with Lewis acids (most notably  $AlCl_3$ ) dominated the early years of this area of chemistry, and as an example we take illustrated for the reaction between  $[EMIM]Cl$  and  $AlCl_3$  by a series of equilibria as given in Equations.[5] **figure 4.**



**figure 4.:** reaction between [EMIM]Cl and AlCl<sub>3</sub>

### 2.2.2 Anion Metathesis:

The first preparation of relatively air- and water-stable ionic liquids based on 1,3-dialkyl-methylimidazolium cations was reported by Wilkes and Zaworotko in 1992 . This preparation involved a metathesis reaction between I and a range of silver salts in methanol or aqueous methanol solution. The very low solubility of silver iodide in these solvents allowed it to be separated simply by filtration, and removal of the reaction solvent allowed isolation of the ionic liquids in high yields and purities. This method remains the most efficient for the synthesis of water-miscible ionic liquids, but is obviously limited by the relatively high cost of silver salts, not to mention the large quantities of solid by-product produced.

Most notably, many of the + - based salts are solid at room temperature, facilitating purification, which may be achieved by recrystallisation. Over the past few years, an enormous variety of anion exchange reactions has been reported for the preparation of ionic liquids.[6] **table(1).**

<b>Salt</b>	<b>Anion Source</b>
[Cation][PF <sub>6</sub> ]	H <sub>2</sub> PF <sub>6</sub>
[Cation][BF <sub>4</sub> ]	HBF <sub>4</sub> , NH <sub>4</sub> BF <sub>4</sub> , NaBF <sub>4</sub>
[Cation][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]	Li[(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N]
[Cation][(CF <sub>3</sub> SO <sub>3</sub> )]	CF <sub>3</sub> SO <sub>3</sub> CH <sub>3</sub> , NH <sub>4</sub> [(CF <sub>3</sub> SO <sub>3</sub> )]
[Cation][CH <sub>3</sub> CO <sub>2</sub> ]	Ag[CH <sub>3</sub> CO <sub>2</sub> ]
[Cation][CF <sub>3</sub> CO <sub>2</sub> ]	Ag[CF <sub>3</sub> CO <sub>2</sub> ]
[Cation][CF <sub>3</sub> (CF <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> ]	K[CF <sub>3</sub> (CF <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> ]
[Cation][NO <sub>3</sub> ]	AgNO <sub>3</sub> , NaNO <sub>3</sub>
[Cation][N(CN) <sub>2</sub> ]	Ag[N(CN) <sub>2</sub> ]
[Cation][CB <sub>11</sub> H <sub>12</sub> ]	Ag[CB <sub>11</sub> H <sub>12</sub> ]
[Cation][AuCl <sub>4</sub> ]	HAuCl <sub>4</sub>

**Table(3):**Examples of ionic liquids prepared by anion metathesis.

### 3. purification of ionic liquids

#### ➤ Methods for recovery and purification of ionic liquids from solutions

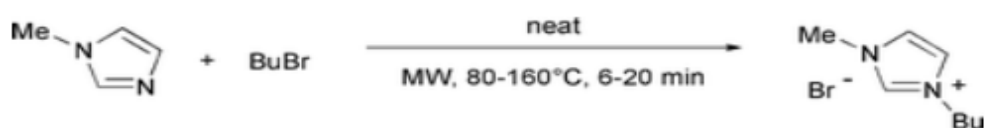
there are different methods for the recovery and purification of ionic liquids for example **(Distillation-Extraction-Adsorption-Membrane separation-aqueous two-phase extraction-Crystallization-Orefield- Combined methods)** However, due to the differences in the properties of ionic liquids, the compositions of ionic liquids solutions and the specific requirements of operational cost, each of the technologies for the recovery and purification of ionic liquids from solutions possesses its optimal application scope. Accordingly, it is necessary to know the applicable scope of each method before the process design.[7]

#### 4. Synthesis of 1-butylimidazolium hydrogensulfate ([BMIM][HSO<sub>4</sub>]):

A mixture N-butylimidazole (0.2 mol, 26 mL) and anhydrous acetonitrile (13 mL) were charged into a 250 mL round-bottom flask . Then, under cold condition and vigorous stirring, a stoichiometric amount of concentrated sulfuric acid (0.2 mol, 10.7 mL) was added drop wise and the mixture stirred for 2 h at room temperature. washed with trimethyl-1-pentene and vacuum dried for 6 h.[8]

#### 5. Synthesis of 1-butyl-3-methylimidazolium bromide ([BMIM][BR]):

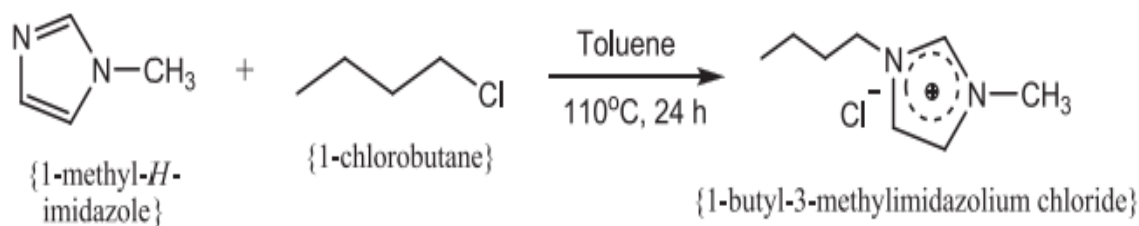
A mixture of 1-methylimidazole (1.30 g, 15.9 mmol) and butyl bromide (2.22 g, 16.2 mmol) was placed in a 10 mL. The Monowave 300 was programmed to ramp to 145 ° C using the ruby thermometer as lead sensor and applying a hold time of 20 min, after which the sample was externally cooled to 50 ° C . The resulting pale yellow viscous oil was diluted with 2 mL of MeCN and washed 3 times with EtOAc (5 mL). The lower phase was collected, the solvent removed under vacuo and dried for a further 6 h at 80 ° C under reduced pressure (2 mbar). Upon cooling to room temperature, 1-butyl-3-methylimidazolium bromide was obtained as pale yellow crystals.[9]



**Figure 5** : preparation of the ionic liquid bmimBr..[9]

## 6. Synthesis of 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) :

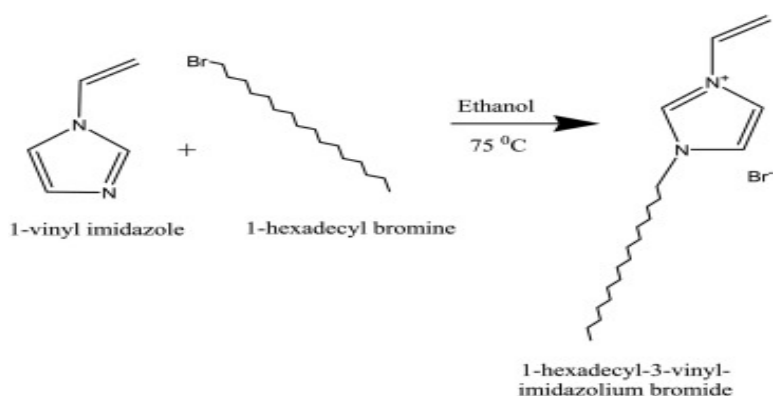
A mixture of 1-methylimidazole (25 mL, 0.31 mol) and 1-chlorobutane (36 mL, 0.35 mol) in 50 mL of toluene at 110 °C under vigorous stirring for 24 h. The resulting brown viscous oil was allowed to cool down for approximately 24 h, decanted, and then washed with acetonitrile followed by ethyl acetate.[10]



**Figure 2:** Synthesis of 1-butyl-3-methylimidazolium chloride[10]

## 7. synthesis of 1-hexadecyl-3-vinyl-imidazolium bromide ([C16Vim<sup>+</sup>][Br<sup>-</sup>]) :

A mixture of 0.8 mol of 1-vinylimidazole, 0.8 mol of 1-hexadecyl bromide and ethyl acetate was added in a dry 250 mL round-bottomed flask under nitrogen inert conditions at 343.15 K for 24 h. The resultant reaction mixture was then washed with an excess of ethyl acetate, and further vacuum dried at 313.15 K before storing in refrigerator.[11]



**Figure 6 :** synthesis of 1-hexadecyl-3-vinyl-imidazolium bromide.[11]

### 8. synthesis of bis-methyl imidazolium methyldene iodide ([M(CH<sub>2</sub>)IM<sub>2</sub><sup>+</sup>][I<sup>-</sup>]) :

In a flask, 1-methylimidazole (9.07 ml, 100 mmol) and 1,2-diiodomethane (5.07 ml, 50 mmol) were dissolved in toluene (15 ml) and the mixture was stirred at 70 °C for 5 h. The product was washed repeatedly with diethyl ether (5 × 20 ml), the product was dried under vacuum for 6 h. bis-methyl imidazolium methyldene iodide yellowish solid (13.20 g, 31.86 mmol). [12]

### 9. synthesis of 1-allyl-3-methylimidazolium bicarbonate ([amim][HCO<sub>3</sub>]) :

A mixture of 23,0 g of N-methyl-imidazolium and 25,3 g of allyl chloride was vigorously agitated in a three-necked flask.

The excess allyl chloride was removed by keeping temperature at 60–65 ° C for 6–7 h, while the surplus N-methyl-imidazolium was extracted by vacuum drying at 80C for 48 h. The synthesised viscous liquid (35,0 g), 20,0 g of sodium bicarbonate and 50,0 mL of methanol were mixed in another three-necked flask at 40 ° C for 48 h to obtain the [amim][HCO<sub>3</sub>]. The unreacted sodium bicarbonate and methanol were removed by filtering and evaporating processes. The synthesis routes to resultant [amim][HCO<sub>3</sub>] were shown in Fig. 7. [13]

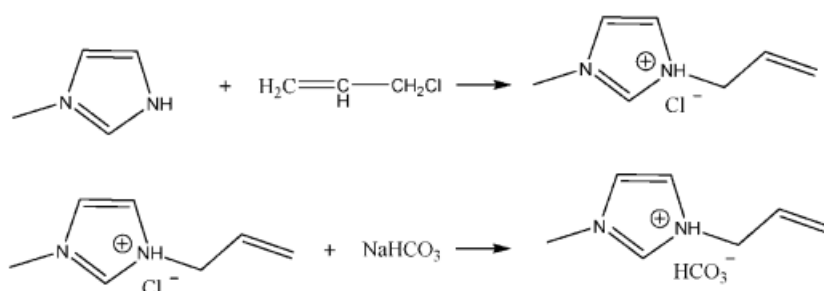
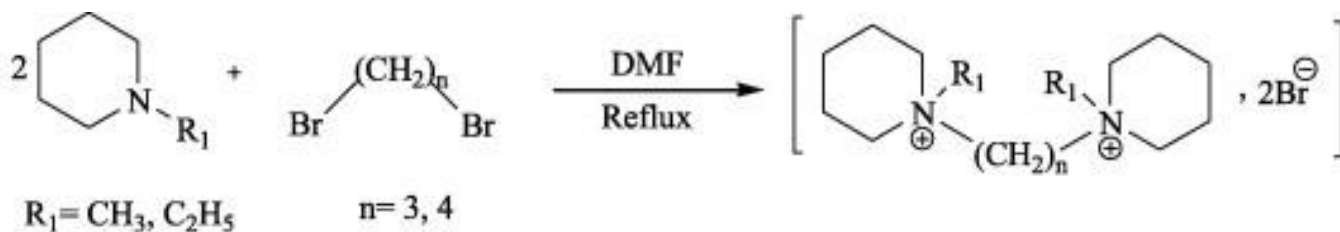


Figure 7: Synthetic routes for [amim][HCO<sub>3</sub>]. [13]

### 10. Synthesis of bis-methyl piperidinium butylidene bromide ([MBPPI<sup>+</sup>][2Br<sup>-</sup>]) :

N-methyl piperidine (12.15 mL, 100 mmol) and 1,4-dibromobutane (5.21 mL, 50 mmol) were dissolved in DMF (20 mL) before being stirred at 70 ° C for 6 h. The obtained mixture

was evaporated under vacuum and washed then with diethyl ether (100 mL) to give the bis-methyl piperidinium butylidene bromide as a yellowish solid (13.20 g, 31.86 mmol).[14]



**Figure 8** : synthesis of bis-methyl piperidinium butylidene bromide[14]

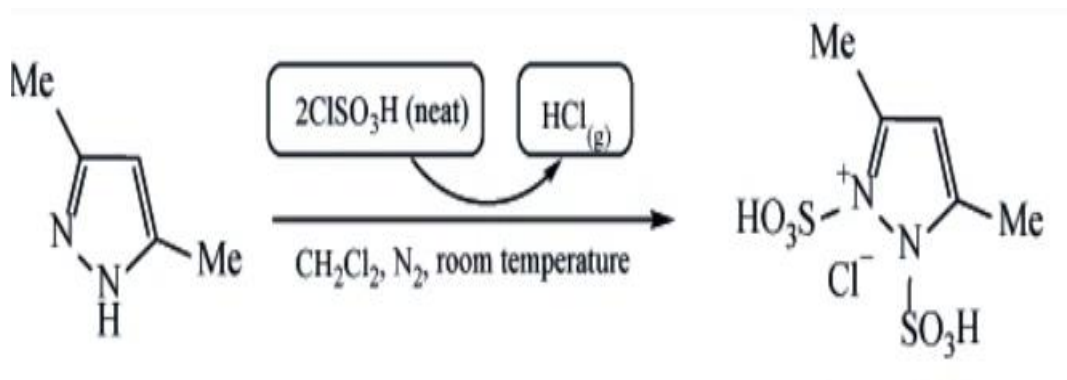
### 11. Synthesis of 1-vinyl-3-heptylimidazolium iodide ([VHpII=] [I2-]) :

N-methyl piperidine (12.15 mL, 100 mmol) and 1,4-dibromobutane (5.21 mL, 50 mmol) were dissolved in DMF (20 mL) before being stirred at 70 ° C for 6 h. The obtained mixture was evaporated under vacuum and washed then with diethyl ether (100 mL) to give the bis-methyl piperidinium butylidene bromide as a yellowish solid (13.20 g, 31.86 mmol). [15]

### 12. Synthesis of 3,5-dimethyl-1,2-disulfonic acid-1H-pyrazolium chloride ([DMDSP][Cl]) :

To a solution of 3,5-dimethyl-1H-pyrazole (10 mmol) [9] in dry CH<sub>2</sub>Cl<sub>2</sub> (25 mL), chlorosulfonic acid (20 mmol) was added dropwise over a period of 20 min at room temperature, mixture was stirred for 2 h under the atmosphere of nitrogen for driving away the produced HCl. The residue was washed with dry CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL) and dried in vacuo at 70 ° C to give the product . Pale yellow oil, yield 94%.[16]

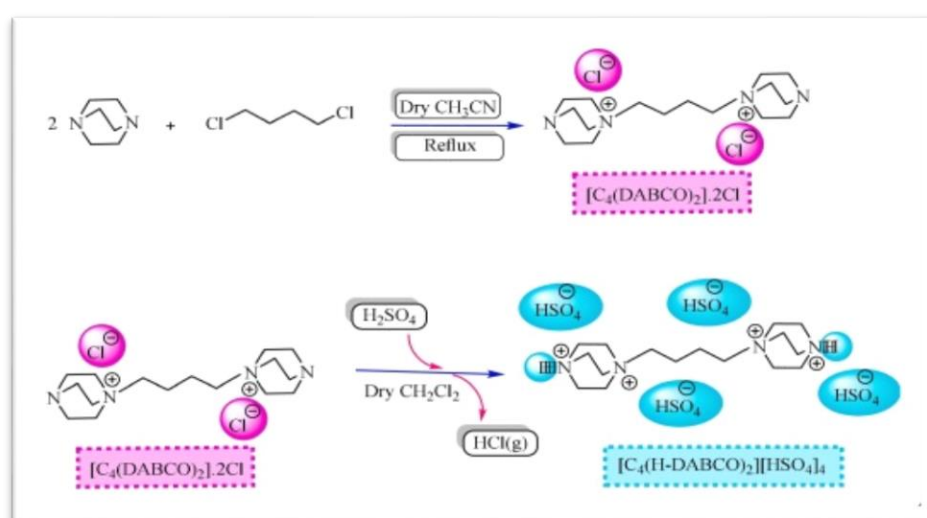




**Figure 9 :** Synthesis of disulfonic acid functionalized, [DMDSP][Cl] [16]

### 13. Synthesis of triethylaminium-N-sulfonic acid trifluoroacetate ([TEASA][TFA]) :

A solution of triethylamine (0.50 g, 5 mmol) in dichloromethane (20 mL) was added to a solution of chlorosulfonic acid (0.58 g, 5 mmol) in dry dichloromethane (20 mL) over a period of 10 min at 10 ° C. Afterward, the reaction mixture was heated to room temperature , and stirred for another 4 h. the liquid residue was triturated with t-butylmethyl ether (3 × 10 mL) and dried under powerful vacuum at 90 ° C to give [TEASA][Cl] [17]. Then, trifluoroacetic acid (0.570 g, 5 mmol) was added to [TEASA][Cl] (1.089 g, 5 mmol) over a period of 5 min at room temperature under pressure of nitrogen gas . mixture was stirred for 10 h at room temperature, and 2 h at 60 ° C under a continuous flow of nitrogen gas to give a viscous pale yellow liquid.[18]



**Figure 10 :** Synthesis of [C4(H-DABCO)2][HSO4]4. . [18]

#### 14. Synthesis and characterisation of 1-(hydroxyethyl)-3-methylimidazolium chloride ([EtOHMIM<sup>+</sup>] [Cl<sup>-</sup>]) :

An equimolar mixture of 2-chloroethanol (0.67 mL, 10 mmol) and 1-methylimidazole (1.1 g, 10 mmol) was heated at 120 °C (liquid homogeneous medium) for 24 h under vigorous magnetic stirring. After cooling to ambient temperature, the crude product (crystalline at ambient temperature) was finely crushed, washed with diethyl ether (3 × 80 ml) and then filtered on a sintered glass of porosity No 4. The product was finally dried under reduced pressure for 10 hours in order to remove traces of solvent. [19-20]

Pale beige powder; yield: 1.8 g (98%); mp 55–58 °C.

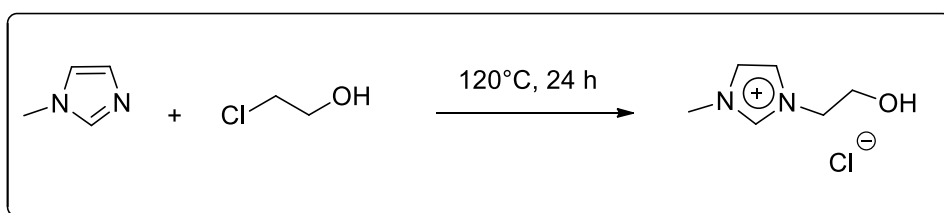


Figure 11: Amine quaternization reaction. [19-20]

#### 15. Synthesis and characterization of 1-(hydroxyéthyl)-3-methylimidazolium dihydrogénophosphate [EtOHMIM<sup>+</sup>][H<sub>2</sub>PO<sub>4</sub><sup>-</sup>] :

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 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. The product was finally dried under reduced pressure for 3 hours to remove traces of solvent. [21-24]

Pale yellow liquid; yield: (94%).

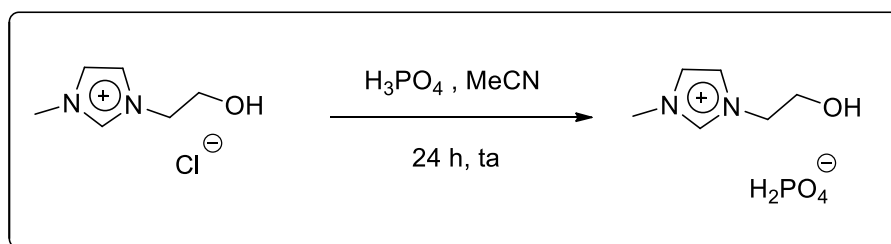


Figure 12: Anion exchange reaction. [21-24]

## Conclusion

In this chapter we saw examples of synthesis ionic liquids based in imidazolium with mention the work mode, We noted that many ionic liquids can be synthesized with characteristic properties only by changing anions.

To learn more about the effect of the selected anion, we will synthesis two ion liquids based in imidazolium and study its vibrations and this is what we will see in the next chapter.

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# Chapter III

## Experimental studies of ILs

# 1. Introduction

ILs are usually composed of large asymmetric organic cations and inorganic or organic anions. They exhibit unique properties, and they are usually used in chemical synthesis because they exhibit specific properties. ILs allow for the quick and easy transfer of electrons, which is critical in many chemical reactions [1].

In this chapter we will study two types of ILs and study specifically vibrational studies through methods of characterization

## *Part 1: the results of NMR in Experimental Study*

The NMR spectra and the results released in the PhD thesis by Mr Chaker yassine [2]

### The results of NMR

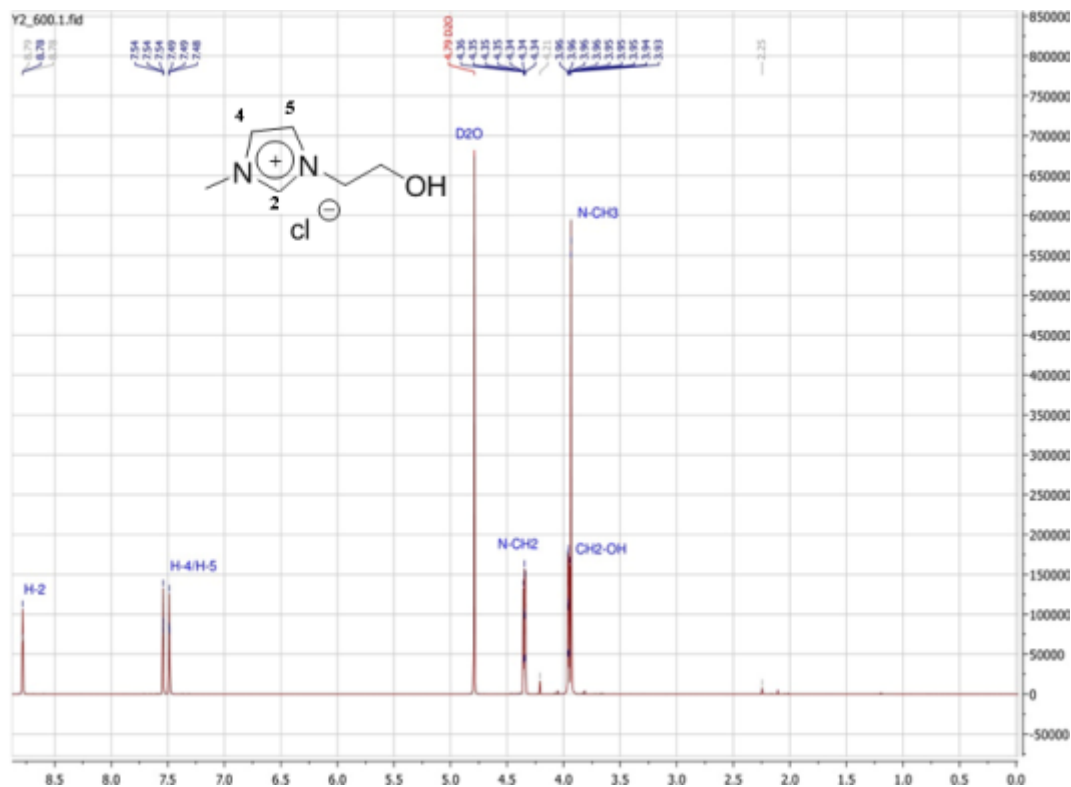
**NMR  $^1\text{H}$  (600 MHz,  $\text{D}_2\text{O}$ )** :  $\delta = 8.78$  (s, 1H, H-2); 7.54 (s, 1H, H-4 ou H-5);

7.49 (s, 1H, H-4 ou H-5); 4.34 (t, 2H,  $J = 4.9$  Hz,  $\text{NCH}_2$ ); 3.96 (t, 2H,  $J = 4.9$  Hz,  $\text{CH}_2\text{O}$ );

3.93 (s, 3H,  $\text{NCH}_3$ ). (**Fig. II. 3**). [2]

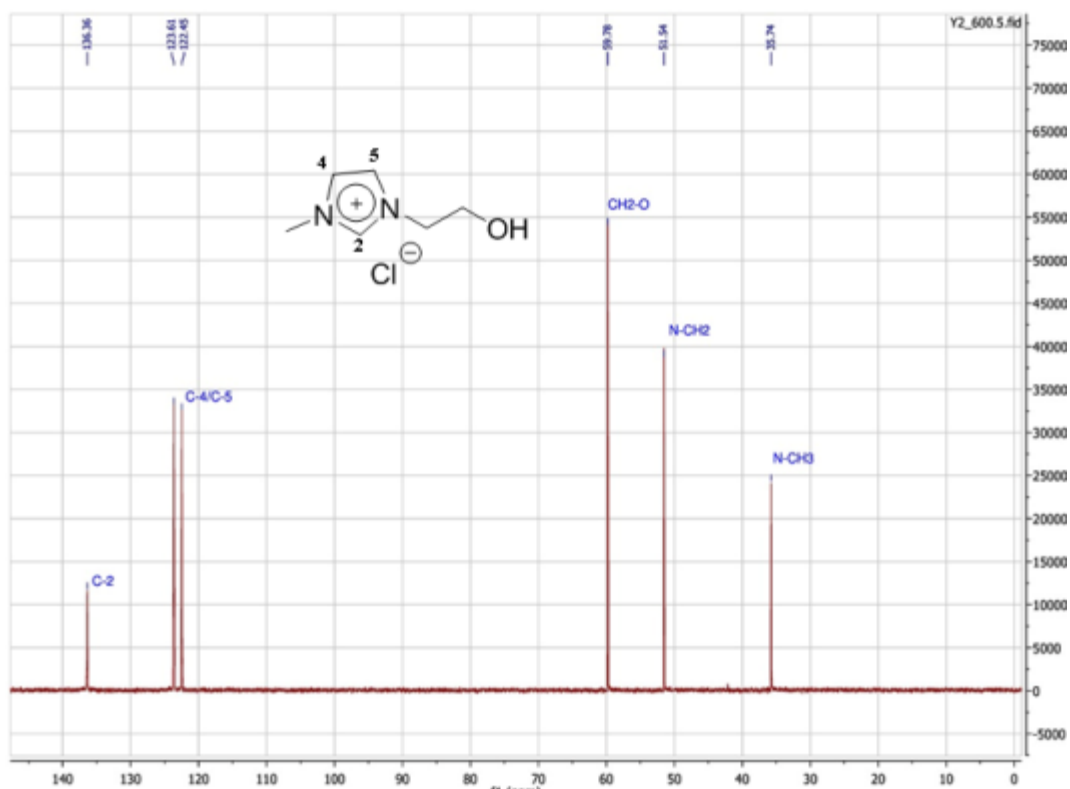
**RMN $^{13}\text{C}$**  (150.93 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 136.4$  (C-2), 123.6, 122.4 (C-4, C5), 59.8 ( $\text{CH}_2\text{O}$ ),

51.5 ( $\text{NCH}_2$ ), 35.7 ( $\text{NCH}_3$ ). (**Fig. II. 4**). [2]



**Figure 13:** NMR spectral  $^1\text{H}$  of  $[\text{EtOHMIM}^+][\text{Cl}^-]$  in  $\text{D}_2\text{O}$ [2]





**Figure14:** NMR spectral <sup>13</sup>C of [EtOHMIM<sup>+</sup>][Cl<sup>-</sup>] in D<sub>2</sub>O[3]

### The results of NMR

Details of the spectra are given below

**NMR 1H: (600 MHz, D<sub>2</sub>O) :**  $\delta$ =8.78 (s, 1H, H-2), 8.76 (s, 1H, HSO<sub>4</sub><sup>-</sup>), 7.54 (s, 1H, H-4 ou H-5), 7.48 (s, 1H, H-4 ou H-5), 4.52 (t, 2H, J=5 Hz, NCH<sub>2</sub>), 4.33 (t, 2H, J=5 Hz, CH<sub>2</sub>OH) 3.90 (s, 3H, NCH<sub>3</sub>) (**Fig. II. 8**). [3]

**NMR 13C (150.93 MHz, D<sub>2</sub>O) :**  $\delta$ =136.6 (C-2), 123.6, 122.6 (C-4, C5), 66.1 (CH<sub>2</sub>O), 51.5 (NCH<sub>2</sub>), 35.8 (NCH<sub>3</sub>) (**Fig. II. 9**) [3]



Figure15 : NMR spectral  $^1\text{H}$  of  $[\text{EtOHMIM}^+][\text{HSO}_4^-]$  in  $\text{D}_2\text{O}$ [4]

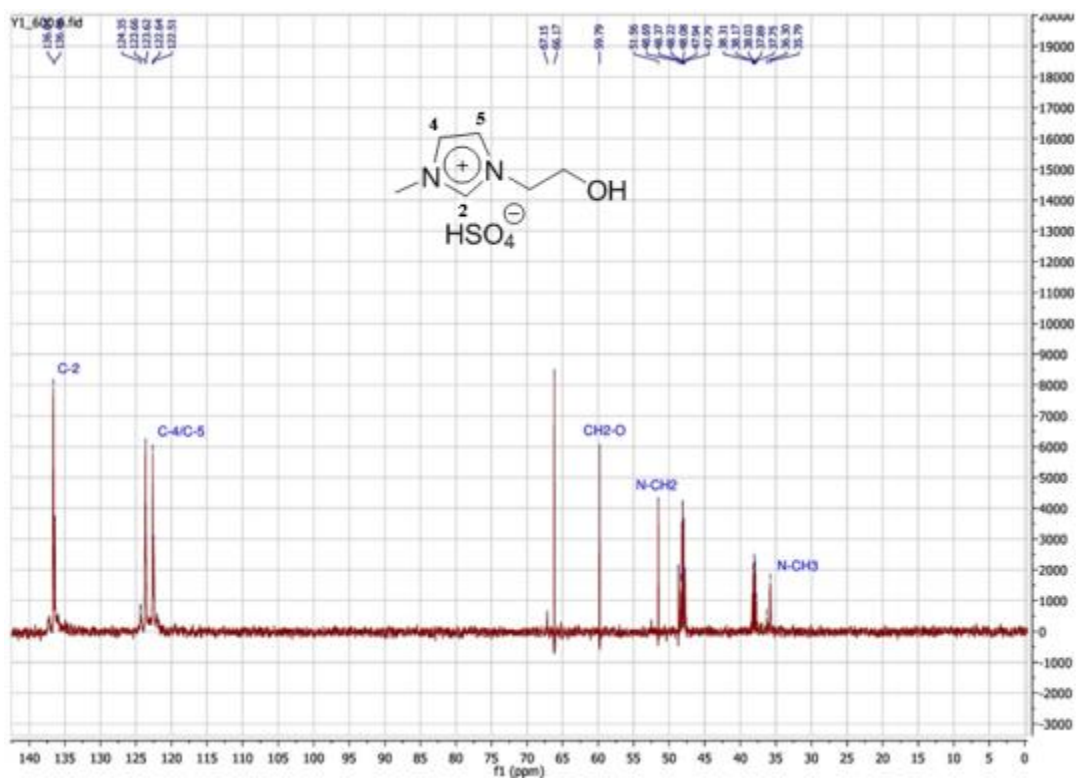


Figure16 : NMR spectral  $^{13}\text{C}$  of  $[\text{EtOHMIM}^+][\text{HSO}_4^-]$  in  $\text{D}_2\text{O}$ [4]

## 1.1 Infrared spectroscopy

### 1.2 Principles

Infrared spectroscopy (IR spectroscopy) is the spectrum of looking at the infrared portion of the electromagnetic spectrum, which is light with longer wavelengths and lower frequencies than visible light. It covers a range of techniques primarily based on absorption spectroscopy. Like all spectroscopic techniques, it can be used to identify and study chemicals [2]. Indeed, the experiment shows that certain vibration frequencies, known as 'group frequencies' [3][4], a normal mode of vibration corresponds to internal atomic motions in which all atoms move in phase with same frequency but with different amplitude. Additionally to these normal vibrations transitions corresponds to be called overtones. [5]

The infrared portion of the electromagnetic spectrum is generally divided into three regions; near-infrared, mid-infrared, and far-infrared, named for their relationship to the visible spectrum. Higher energies in the near infrared, around  $14000\text{-}4000\text{ cm}^{-1}$  ( $0.8\text{-}2.5\text{ }\mu\text{m}$  wavelength), can excite overtones or harmonic vibrations. The mid-infrared, approximately  $4000\text{-}400\text{ cm}^{-1}$  ( $2.5\text{-}25\text{ }\mu\text{m}$ ), can be used to study fundamental vibrations and related rotational vibrational structures, Far infrared, about  $400\text{-}10\text{ cm}^{-1}$  ( $25\text{-}1000\text{ }\mu\text{m}$ ), adjacent to the microwave range, low energy and useful for rotational spectroscopy. The names and classifications of these sub regions are conventional and loosely based on relative molecular or electromagnetic properties. [6]

### 1.3 Infrared range from $0.8\text{ }\mu\text{m}$ to $1000\text{ }\mu\text{m}$ divided into 3 categories:

The available infrared domains are:

Near infrared:  $0.8$  to  $2.5\text{ }\mu\text{m}$ ;  $12500\text{-}4000\text{ cm}^{-1}$

Medium infrared:  $2.5$  to  $25\text{ }\mu\text{m}$ ;  $4000\text{-}400\text{ cm}^{-1}$

Far infrared:  $25$  to  $1000\text{ }\mu\text{m}$ ;  $400\text{-}10\text{ cm}^{-1}$

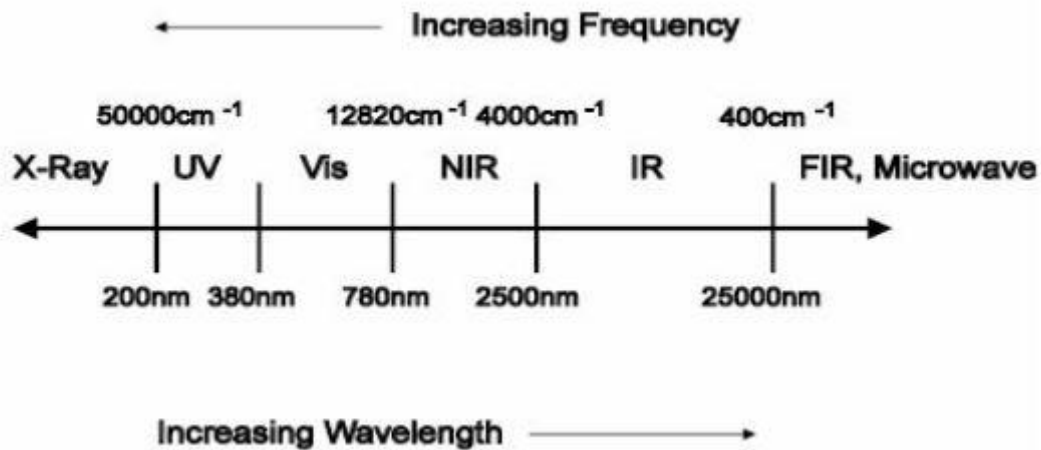


Figure13 .Range of Electromagnetic radiation [6]

### 1.4 FT-IR case

FT-IR spectrophotometers have been developed to respond to the limitations of dispersive spectrometers. The main difficulty to solve was the slowness of the acquisition. It was essential to imagine a device measuring all frequencies simultaneously. This device is the interferometer. Attenuated total reflection is commonly referred to as ATR (Attenuated Total Reflection). The principle of ATR is detailed in (Figure.14)[7]

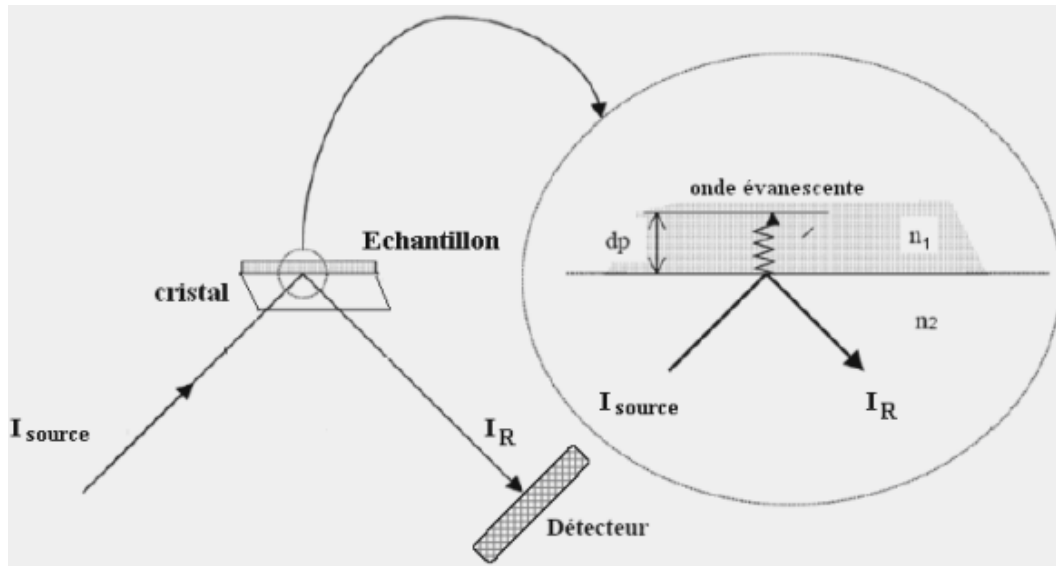
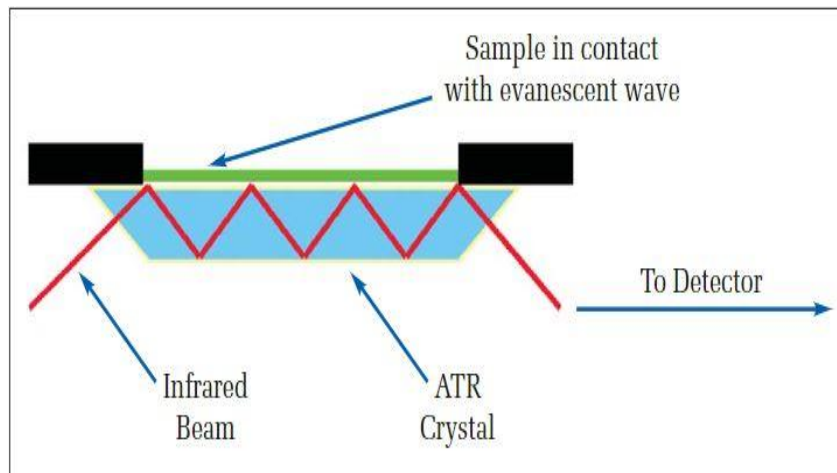


Figure 14.Principle of Total Attenuated Reflection (ATR)[7]

The Damped TIR accessory measures the changes that occur in the TIR beam when the beam is in contact with the sample (see Figure15). An infrared beam strikes an optically dense crystal with a high refractive index at a specific angle. This internal reflection creates an evanescent wave that extends from the crystal's surface into the sample in contact with the

crystal. It's easier to think of this evanescent wave as an infrared bubble sitting on the surface of a crystal. This evanescent partial wave protrudes only a few microns ( $0.5 \mu\text{-}5 \mu$ ) above the crystal surface and enters the sample. Therefore, there must be good contact between the sample and the crystal surface. In the region of the infrared spectrum where the sample absorbs energy, evanescent waves are attenuated or altered. The decaying energy of each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum.[8]



**Figure 15.A** multiple reflection ATR system[8]

### 1.5 Advantages of this technique

- Minimum sample preparation,
- Simple and quick accessory cleaning,
- Possibility to study samples directly in their natural state (without prior preparation),
- Highly reproducible technique: quantitative analysis, provided not to claim very important sensitivities,
- ATR cells capable of working in temperature or on corrosive products (acids, peroxides, etc.).

## 2. Experimental device

The measurements were carried out in the University of TISSEMSILT.

### 2.1 The experimental conditions

- Laser incident: Nd YAG (neodymium doped yttrium-aluminum garnet)
- Excitation wavelength: 1064 nm with an intensity of 300 mW
- Detector: Germanium diode
- Spectral resolution:  $1\text{cm}^{-1}$

- Number of scans: 8

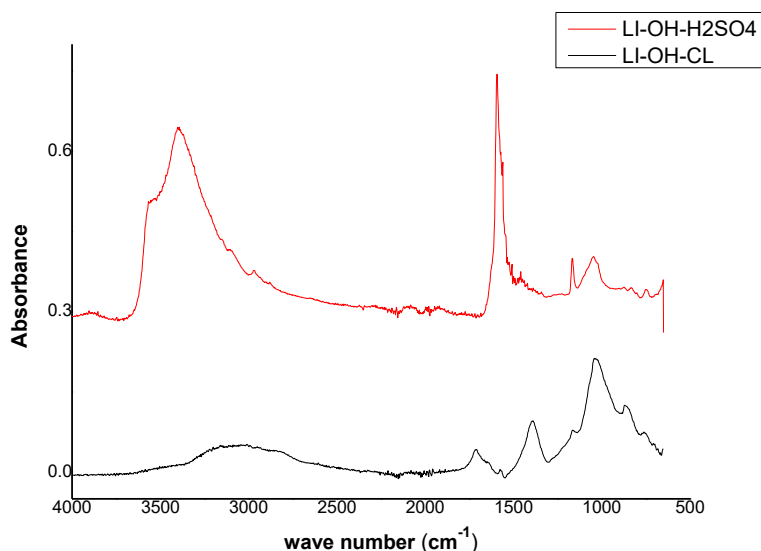


**Figure 16.** Agilent Cary 630 FTIR Spectrometer

### 3. Results and Discussion

In this section, we will present a comparison between the two new monocationic ionic liquids 1-(hydroxyethyl)-3-methylthidazolium [EtOHTHM<sup>+</sup>][Cl<sup>-</sup>] chloride and lehydrogenosulfate 1-(hydroxyethyl)-3-methylthidazolium[EtOHTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>] following two spectroscopic studies: FTIR/ATR.

FTIR/ATR spectra [4000-600 cm<sup>-1</sup>] of the ionic liquids are illustrated in (FigIII.5), The assignments of the observed modes in this spectral region are reported in (TableIII.1), On the IR spectra (see FigIII.5), we differentiate three well defined spectral regions: 3500-2600, 1800-1300 et 1300-600 cm<sup>-1</sup>, for [EtOHMIM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>] we note that there is intensity in the 1300-600 cm<sup>-1</sup> and 1800-1300 spectral range as well as for [EtOHMIM<sup>+</sup>][Cl<sup>-</sup>] in 1300-600 cm<sup>-1</sup> spectral range, whereas the modes in the two spectral regions seem to have a homogenous intensity.



**FigIII.5.** FTIR/ATR spectra of [EtOHMIM<sup>+</sup>][Cl<sup>-</sup>] and [EtOHMIM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>] in the spectral range 3500-600 cm<sup>-1</sup>.

Observed FTIR/ATR bands and their assignment for 1-(hydroxyethyl)-3-methylimidazolium chloride and 1-(hydroxyethyl)-3-methylimidazolium hydrogen sulfate samples (vw = very weak; w = weak; m = medium, s = strong; sh = shoulder; v = Str = stretch;  $\delta$  = deformation; bend = bending deformation;  $\omega$  = wagging;  $\rho$  = rocking; s = symmetric; as = antisymmetric).

[EtOHMIM <sup>+</sup> ][Cl <sup>-</sup> ]	[EtOHMIM <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ]	ASSIGNMENT	Refs
	605 (m)	$\omega$ (N-H)/CH <sub>3</sub> (N) CN Str	[9-10]
620 (s)	620 (s)	$\omega$ (N-H)/CH <sub>3</sub> (N) CN Str	[9-10]
652 (s)	660 (w)	$\omega$ (N-H)/CH <sub>3</sub> (N) CN Str	[9-10]
687 (s)		$\omega$ (C-H) + $\omega$ (N-H)	[9-10]
705 (m)	700(m)	CH <sub>2</sub> (N)/CH <sub>3</sub> (N)CN bend	[9-10]
	735* (sh)	$\omega$ (C-H)	[9-10]
	753 (m)	$\omega$ (C-H)	[9-10]
	771 (s)	v (N-C)	[9-10]
797 (s)		Ring HCCH as bend	[9-10]
	850* (sh)	$\rho_{as}$ (CH <sub>2</sub> )	[9-10]
868 (s)	873 (s)	$\rho_{as}$ (CH <sub>2</sub> )	[9-10]
	903 (s)	v (N-S)	[11]
942 (vw)		$\rho_{as}$ (CH <sub>2</sub> )	[9-10]
	968 (vw)	v (N-S)	[11]
	1017 (s)	S-OH	[11]
1027* (sh)		CH <sub>3</sub> N Str/CH <sub>2</sub> N Str	[9-10]
1038 (m)		CH <sub>3</sub> N Str/CH <sub>2</sub> N Str	[9-10]
1062 (m)	1068 (s)	v (C-O)	[12]
1074 (s)		CC Str	[11]
1100 (vw)	1090* (sh)	CC Str	[11]
1119 (vw)	1108 (w)	CC Str	[9-10]
1175 (m)	1175 (m)	Ring as Str CH <sub>2</sub> (N) and CH <sub>3</sub> (N)CN Str/CC	[9-10]
1198 (m)	1198 (m)	Ring s CH <sub>2</sub> (N) and CH <sub>3</sub> (N)CN Str	[9-10]
	1224 (m)	v (S-O)	[11]

1254 (w)	1256 (m)	Ring ip as strstr	[9-10]
	1336 (m)	v (C-C)	[9-10]
1347 (m)	1353 (m)	v (C-C)	[9-10]
1371 (w)	1372* (sh)	$\delta$ (CH) – $\delta_s$ (CH <sub>3</sub> )	[12]
1388* (sh)	1390 (m)	$\rho$ (N-H)	[9-10]
	1412* (sh)	$\rho$ (N-H)	[9-10]
1424 (m)	1431* (sh)	$\rho$ (N-H)	[9-10]
1446 (m)	1438 (m)	$\delta$ (CH <sub>2</sub> )/CCH HCH as bend	
	1462* (sh)	$\delta$ (CH <sub>2</sub> )/CCH HCH as bend	[9-10]
1481 (w)	1480 (m)	$\delta$ (CH <sub>2</sub> )/CCH HCH as bend	[9-10]
1571 (s)	1570* (sh)	as Str CH <sub>2</sub> (N)/CH <sub>3</sub> (N)CN Str	[9-10]
	1578 (s)	Ring C=C str, N=C-N str	[13]
	1645 (w)	Ring C=C str, N=C-N str	[13]
1677 (w)		Ring C=C str, N=C-N str	[13]
1692 (w)		Ring C=C str, N=C-N str	[13]
1750 (w)	1742 (w)	Overtone =C-H str	[13]
2481(w)	2470 (vw)	v (C=C)	[9-10]
2600 (vw)		$v_s$ (CH <sub>2</sub> )	[9-10]
2672 (w)		$v_s$ (CH <sub>2</sub> )	
2714 (vw)		$v_s$ (CH <sub>2</sub> )	
	2842 (vw)	$v_s$ (CH <sub>2</sub> )	[9-10]
2870 (m)	2865 (w)	$v_s$ (CH <sub>2</sub> )	[9-10]
2877 (m)		$v_{as}$ (CH <sub>2</sub> )	[9-10]
	2907(m)	$v_{as}$ (CH <sub>2</sub> )	[9-10]
2928 (w)		$v_s$ (CH <sub>3</sub> )	
2954 (m)		CH <sub>3</sub> (N)HCH as Str	[9-10]
2966 (m)		$v_{as}$ (CH <sub>3</sub> )	[9-10]
	2972 (w)	$v_{as}$ (CH <sub>3</sub> )	
2992* (sh)	2988 (w)	$v_{as}$ (CH <sub>3</sub> )	
3038 (s)		= C-H Str	
3055 (sh)	3040* (sh)	= C-H Str	[9-10]
	3086 (s)	= C-H Str	
3096 (s)	3116 (s)	Ring NC(H)NCH Str	[9-10]
3141 (s)	3154 (m)	Ring NC(H)NCHStr	[9-10]
3165 (sh)		Ring NC(H)NCH Str	[9-10]
	3250* (sh)	v (O-H)	[11-12]
3404 (w)		v (O-H)	[11-12]

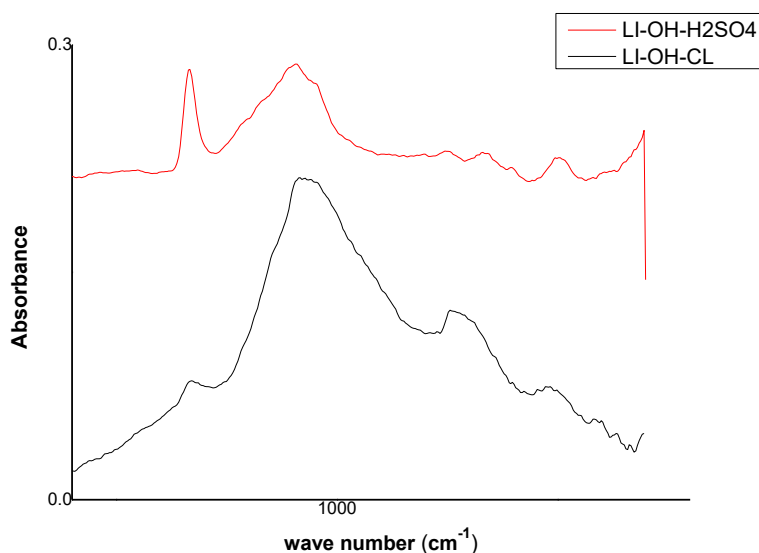
**Table III.1:** FTIR/ATR bands and their assignment for 1-(hydroxyethyl)-3-methylimidazolium chloride and 1-(hydroxyethyl)-3-methylimidazolium hydrogen sulfate

### 3.1 Region 1300-600 cm<sup>-1</sup>

In this spectral zone (**Fig III.6**), For the Cl<sup>-</sup> anion, the spectral zone 900-1138 cm<sup>-1</sup> is more intense than for [EtOHMIM+][HSO<sub>4</sub>-] with the ascendancy of 2 modes in: 1038 and 1175 cm<sup>-1</sup> are assigned to CH<sub>3</sub>N stretching /CH<sub>2</sub>N stretching and Ring antisymmetric stretching CH<sub>2</sub>(N) and CH<sub>3</sub>(N)CN stretching /CC [9-10], the strong band at 1178 cm<sup>-1</sup> observe for [EtOHMIM+][HSO<sub>4</sub>-] assigned to Ring as Str CH<sub>2</sub>(N) and CH<sub>3</sub>(N)CN Str/CC [9-10], for the [EtOHMIM+][Cl<sup>-</sup>] we observe a medium band at 1175 cm<sup>-1</sup> assigned to Ring as stretching CH<sub>2</sub>(N) and CH<sub>3</sub>(N)CN stretching /CC [9-10], in the spectral zone 620 cm<sup>-1</sup>-900 cm<sup>-1</sup> the vibrational behavior for [EtOHMIM+][HSO<sub>4</sub>-] seems to present more modes 753 cm<sup>-1</sup> medium and



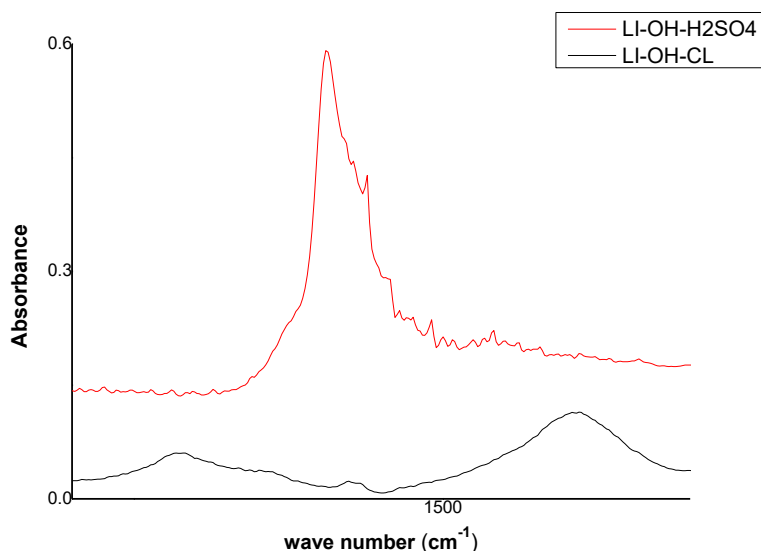
850 $\text{cm}^{-1}$  shoulder assigned to (C-H) wagging and (CH<sub>2</sub>)<sub>ant</sub> symmetric rocking [9-10], whereas [EtOHMIM+][Cl<sup>-</sup>] we observe the only mode 868 $\text{cm}^{-1}$  assigned to (CH<sub>2</sub>)<sub>ant</sub> symmetric rocking [9-10]. We thus notice that this spectral 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.



**FigIII.6.** FTIR/ATR spectra of [EtOHMIM+][Cl<sup>-</sup>] and [EtOHMIM+][HSO<sub>4</sub><sup>-</sup>] in the spectral range 1300-600  $\text{cm}^{-1}$ .

### 3.2 Region 1800-1300 $\text{cm}^{-1}$

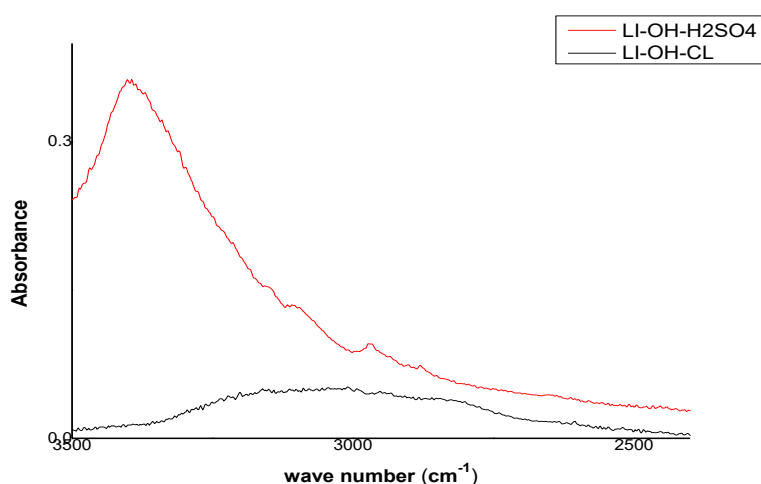
In this spectral zone (**FigIII.7**) We note that there is a very high intensity of [EtOHMIM+][HSO<sub>4</sub><sup>-</sup>], Conversely for [EtOHMIM+][Cl<sup>-</sup>] We observed medium band with the ascendancy of the modes 1388  $\text{cm}^{-1}$  and 1692 $\text{cm}^{-1}$  those modes are assigned to (N-H) rocking and Ring C=C stretching, N=C-N stretching [9-10], we observed spectra with more modes for the HSO<sub>4</sub><sup>-</sup> anion than for the Cl anion, anion HSO<sub>4</sub><sup>-</sup> for in the mode 1575 $\text{cm}^{-1}$  we distinguish a band assigned to Ring C=C stretching, N=C-N stretching [9-10].



**FigIII.7.** FTIR/ATR spectra of [EtOHMIM+][Cl<sup>-</sup>] and [EtOHMIM+][HSO<sub>4</sub><sup>-</sup>] in the spectral range 1800-1300 cm<sup>-1</sup>.

### 3.3 Region 3500-2400 cm<sup>-1</sup>

In this spectral region (**FigIII.8**) we observe intense absorption in the zone spectral 3000-3500 for [EtOHMIM+][HSO<sub>4</sub><sup>-</sup>] with the ascendancy of the mode 3250cm<sup>-1</sup> assigned to (O-H) stretching [11-12], The presence of the HSO<sub>4</sub> anion seems the influence of the O-H group in the spectral zone 3000-3500cm<sup>-1</sup> we observed two group O-H (anion and cation), Conversely for [EtOHMIM+][Cl<sup>-</sup>] we observed a weak band in the spectral zone 2900-3200cm<sup>-1</sup> assigned to = C-H Stretching [9-10] in the mode 3038cm<sup>-1</sup>.



**FigIII.8.** FTIR/ATR spectra of [EtOHMIM+][Cl<sup>-</sup>] and [EtOHMIM+][HSO<sub>4</sub><sup>-</sup>] in the spectral range 3500-2400 cm<sup>-1</sup>.

#### 4. Conclusion

In this study, we synthesized two new Ionic liquid [EtOHMIM+][Cl-] and [EtOHMIM+][HSO<sub>4</sub>-] and which was characterized by FTIR/ATR, The obtained compound shows interesting properties , It seems that anion plays an important influence in a composite structure as well as on its vibratory behavior and to confirm this we have theoretically studied using computer software and this is what we will see in the last chapter.

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- [11]:perkinelmer,« FT-IR SpectroscopyAttenuated Total Reflectance (ATR)»,in the site Rfi ([www.perkinelmer.com](http://www.perkinelmer.com)),Consulté le 15 may.2022.
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**Chapter IV:**  
**theoretical studies of Ionic**  
**liquids**

### ✓ **Introduction:**

Rapid improvement and advancement in computer science and technology, and the gradual improvement of related theories [1], gave significant impetus in the field of science, particularly in chemistry, molecular simulation using software, opened the way for comparison with vibration studies.

In this chapter, we will optimize the structure of two ionic's liquids and we will apply DFT theoretical and calculat using (GaussView and Gaussian) software and explain their results.

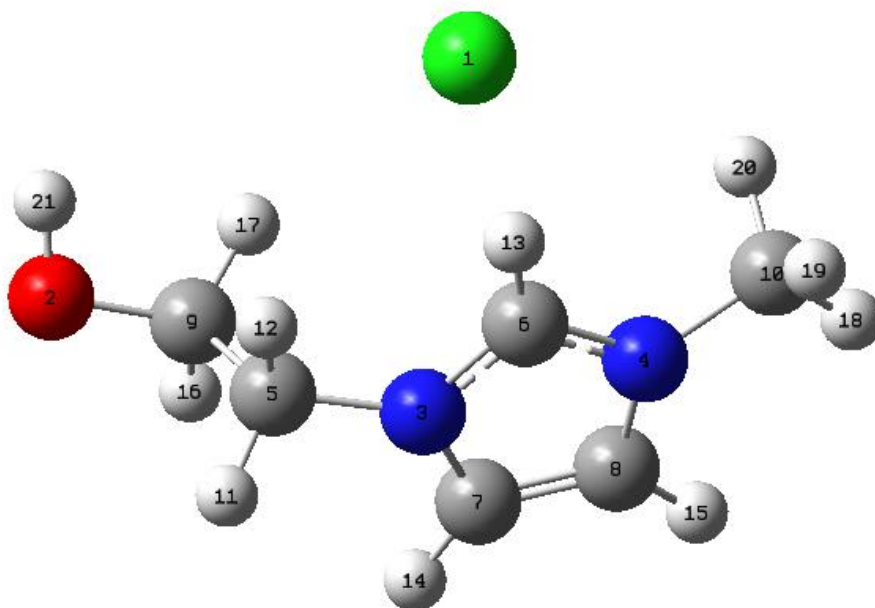
### ✓ **What is Gaussian and Gauss View ?**

**Gaussian** is a computer program used by chemists, chemical engineers, biochemists, physicists and other scientists. It utilizes fundamental laws of quantum mechanics to predict energies, molecular structures, spectroscopic data (NMR, IR, UV, etc) and much more advanced calculations [2]

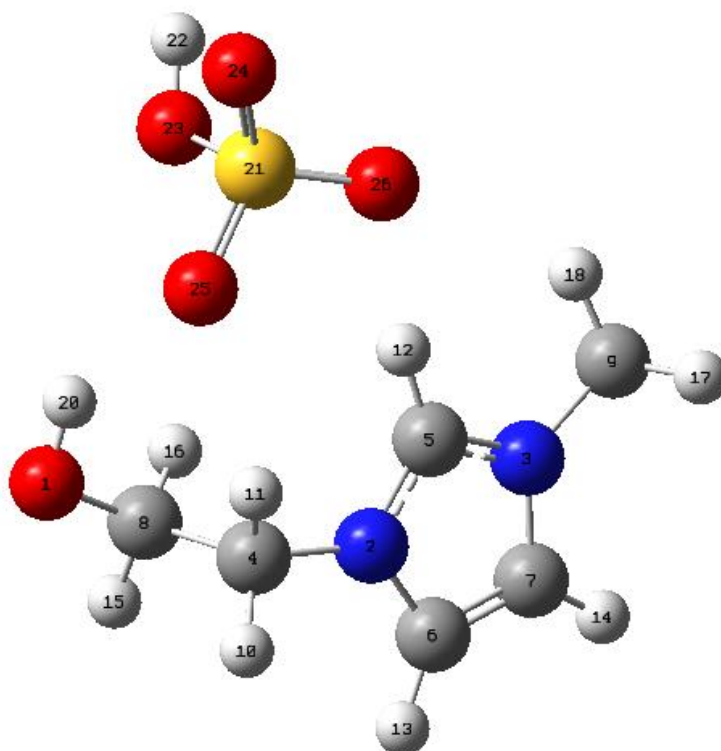
**GaussView** is a graphical user interface designed to help you prepare input for submission to Gaussian, and graphically inspect the output generated by Gaussian. GaussView does not integrate Gaussian's computing engine, but a front-end/back-end processor that supports the use of Gaussian. GaussView provides three main benefits to Gaussian users[3].

### ✓ **Advanced Calculations Using Gaussian**

1. Comprehensive Investigations of Molecules and Reactions
2. Predicting and Interpreting Spectra
3. Explore Diverse Chemical Arenas[2]



**figureIV.1.** Molecular structure of  $[\text{EtOHTHM}^+][\text{Cl}^-]$  optimized in Gaussian visualized in GaussView



**figureIV.2.** Molecular structure of  $[\text{EtOHTHM}^+][\text{HSO}_4^-]$  optimized in Gaussian visualized in GaussView

the **figureIV.1****figureIV.2** above represent the molecular structure of  $[\text{EtOHTHM}^+][\text{Cl}^-]$   $[\text{EtOHTHM}^+][\text{HSO}_4^-]$  After being improved by Gaussian, we used the DFT RB3LYP Basis Set = 6-311G (d,p) method to calculate.



in the literature (works and articles) the calculations have been calculated in the gas phase[4]and get the following results:

<p>CL            File Name = 1OHETMIM            File Type = .log            Calculation Type = FOPT            Calculation Method = RB3LYP            Basis Set = 6-311G(d,p)            Charge = 0            Spin = Singlet            E(RB3LYP) = -880.31416557 a.u.            RMS Gradient Norm = 0.00000763            a.u.            Imaginary Freq =            Dipole Moment = 9.1107 Debye            Point Group = C1            Job cpu time: 0 days 3 hours 2 minutes            51.0 seconds.</p>	<p>HSO<sub>4</sub>            File Name = 1OHETMIMHSO4            File Type = .log            Calculation Type = FOPT            Calculation Method = RB3LYP            Basis Set = 6-311G(d,p)            Charge = 0            Spin = Singlet            E(RB3LYP) = -1119.83410340 a.u.            RMS Gradient Norm = 0.00000711            a.u.            Imaginary Freq =            Dipole Moment = 13.2329 Debye            Point Group = C1            Job cpu time: 0 days 8 hours 40 minutes            2.0 seconds.</p>
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**Table4:** energy of [EtOHTHM +] [HSO<sub>4</sub><sup>-</sup>] and [EtOHTHM +] [Cl<sup>-</sup>] calculated by DFT method .

Through **figureIV.1figureIV.2** we observe deformity in cations [EtOHTHM +] [EtOHTHM +] due to electronegativity of the anions [HSO<sub>4</sub><sup>-</sup>], [Cl<sup>-</sup>] through the results (**table4**) , we found the energy of [EtOHTHM +] [HSO<sub>4</sub><sup>-</sup>] more stable than [EtOHTHM +] [Cl<sup>-</sup>].

Row	Highlight	Tag	Symbol	NA	NB	NC	Bond	Angle	Dihedral	X	Y	Z
1	No	1	O							0.6945290	-3.2045700	0.2870630
2	No	2	N	1			3.6794656			-1.9196830	-0.7048370	-0.3879910
3	No	3	N	2	1		2.1682432	138.8019346		-2.3497940	1.3704170	0.0698340
4	No	4	C	2	1	3	1.4766730	24.7165380	154.4538949	-1.1220400	-1.9179380	-0.6576480
5	No	5	C	2	1	4	1.3358412	108.8328030	-130.1725501	-1.3859140	0.5155160	-0.2864980
6	No	6	C	2	1	4	1.3827317	133.5503025	87.4817952	-3.2655880	-0.6270840	-0.0806780
7	No	7	C	6	2	1	1.3615285	107.1963057	142.7940210	-3.5393070	0.6763640	0.2019190
8	No	8	C	1	4	2	1.4009180	37.0091361	39.0609955	-0.4544840	-2.4771770	0.6235740
9	No	9	C	3	2	1	1.4667526	159.2815848	40.8243326	-2.1230440	2.8038050	0.2827810
10	No	10	H	4	2	1	1.0903028	107.8258432	146.2025148	-1.7746240	-2.6460870	-1.1400310
11	No	11	H	4	2	1	1.0875983	106.8374067	-96.1085473	-0.3298990	-1.6279610	-1.3441580
12	No	12	H	5	2	1	1.0944062	127.7500238	24.9790838	-0.3378310	0.8015060	-0.4186220
13	No	13	H	6	2	1	1.0760761	122.0491001	-37.5088173	-3.9052190	-1.4923230	-0.0938460
14	No	14	H	7	6	2	1.0760301	130.9040162	179.4206894	-4.4607000	1.1591660	0.4771970
15	No	15	H	8	1	4	1.0940337	107.8354363	120.5559090	-1.1372870	-3.1527120	1.1473510
16	No	16	H	8	1	4	1.0968231	111.8274688	-120.3512322	-0.2240660	-1.6347100	1.2870330
17	No	17	H	9	3	2	1.0904864	109.9823841	113.4881205	-2.6404560	3.3809370	-0.4842680
18	No	18	H	9	3	2	1.0893239	107.8267467	-6.4452834	-1.0503380	2.9840660	0.2241770
19	No	19	H	9	3	2	1.0899544	109.4470842	-125.6418721	-2.4884360	3.0862680	1.2700520
20	No	20	H	1	8	4	0.9745363	105.2820148	73.8145489	1.3592170	-2.5356070	0.0413000
21	No	21	S	5	2	1	3.6621370	114.9757268	12.6128725	2.2731960	0.5973300	-0.1621280
22	No	22	H	21	5	2	2.1451997	124.6024447	-106.2390332	3.4234020	1.0004390	1.6032080
23	No	23	O	21	5	2	1.6633516	106.4858103	-86.0133788	2.6960800	0.3878480	1.4328720
24	No	24	O	21	5	2	1.4585712	146.7008624	108.4147998	3.5096400	0.9291150	-0.8610950
25	No	25	O	21	5	2	1.4835476	63.6996085	9.1888015	1.6555970	-0.7122200	-0.4854910
26	No	26	O	21	5	2	1.4897058	47.7908282	178.2633098	1.2471180	1.6772970	-0.1544680

**Table5:** z matrix of [EtOHTHM+][HSO4-]

Row	Highlight	Tag	Symbol	NA	NB	NC	Bond	Angle	Dihedral	X	Y	Z
1	No	1	Cl							-0.2575890	-2.3368480	-0.2770640
2	No	2	O	1			4.5730096			3.7056870	-0.0687740	-0.0306900
3	No	3	N	1	2		3.4521570	52.8821846		0.1833500	1.0193880	0.4001660
4	No	4	N	3	1	2	2.1761455	68.4712174	173.3982121	-1.9229710	0.5193920	0.1787500
5	No	5	C	3	1	4	1.4677676	92.8455287	169.7041377	1.6055910	0.8434740	0.7173830
6	No	6	C	4	3	1	1.3388212	35.6647217	50.7237559	-0.7842990	0.1827380	0.7972420
7	No	7	C	3	1	6	1.3880945	114.2572670	-94.2533378	-0.3411530	1.8693820	-0.5637910
8	No	8	C	7	3	1	1.3565582	107.0960978	55.8219518	-1.6536070	1.5549850	-0.7011560
9	No	9	C	2	1	6	1.4205823	41.0177943	-44.6829155	2.3632470	0.1598770	-0.4351990
10	No	10	C	4	3	1	1.4636083	158.0164334	29.7479342	-3.1360340	-0.2981700	0.2258660
11	No	11	H	5	3	1	1.0916185	109.0266329	177.9136609	2.0414350	1.8169560	0.9497700
12	No	12	H	5	3	1	1.0900304	107.4042015	-64.9306095	1.6659990	0.2194970	1.6091060
13	No	13	H	6	4	3	1.0728693	125.6061718	176.4833366	-0.6786630	-0.5894020	1.5345950
14	No	14	H	7	3	1	1.0755654	122.0559662	-124.7021995	0.2579350	2.6171700	-1.0524090
15	No	15	H	8	7	3	1.0756165	130.8019829	179.8018697	-2.4138680	1.9736200	-1.3365290
16	No	16	H	9	2	1	1.0942548	107.5640908	-143.8876654	2.3889610	0.8223890	-1.3057220
17	No	17	H	9	2	1	1.0939759	112.9303596	-23.7313441	1.8371230	-0.7602260	-0.7061000
18	No	18	H	10	4	3	1.0882417	108.6255201	-159.9538837	-3.8793770	0.1445150	-0.4342410
19	No	19	H	10	4	3	1.0903708	110.1232320	80.3934002	-3.5291660	-0.3278360	1.2424660
20	No	20	H	10	4	3	1.0933080	107.6503040	-39.9419034	-2.8706200	-1.3046990	-0.1084650
21	No	21	H	2	1	6	0.9617265	66.6268417	135.9068869	3.7686330	-0.9805540	0.2686640

**Table6:** z matrix of [EtOHTHM<sup>+</sup>][Cl<sup>-</sup>]

## Part 2: The results of NMR in theoretical Study

### <sup>1</sup>H-NMR spectroscopy

Nuclear magnetic resonance (NMR) is considered a basic technique for characterizing organic materials. The <sup>1</sup>H-NMR isotropic chemical shifts for [1(2OHET)3MIM<sup>+</sup>] [Cl<sup>-</sup>] are calculated by using the GIAO (gauge-independent atomic orbital) method [78] at DFT/B3LYP/6-31G (d, p) level of theory with respect to the TMS values.

The results of NMR

Details of the spectra are given below

NMR 1H: ([EtOHMIM<sup>+</sup>][Cl<sup>-</sup>]):  $\delta = 10.20$  (s, 13H, H-1); 6.40 (s, 1H, H-14 or H-15); 3.70 (t, 2H, J = 4.9 Hz, NCH<sub>2</sub>); 5.80 (t, 2H, J = 4.9 Hz, CH<sub>2</sub>O); 4.95 (s, 3H, NCH<sub>3</sub>)

NMR 1H: ([1(2OHET)3MIM<sup>+</sup>] [HSO<sub>4</sub><sup>-</sup>]):  $\delta = 12.40$  (s, 1H, H-12), 4.20 (s, 1H, HSO<sub>4</sub><sup>-</sup>), 6.90 (s, 1H, H-13 or H-14), 4.90 (t, 2H, NCH<sub>2</sub>), 3.58 (t, 2H, CH<sub>2</sub>OH) 4.70 (s, 3H, NCH<sub>3</sub>)

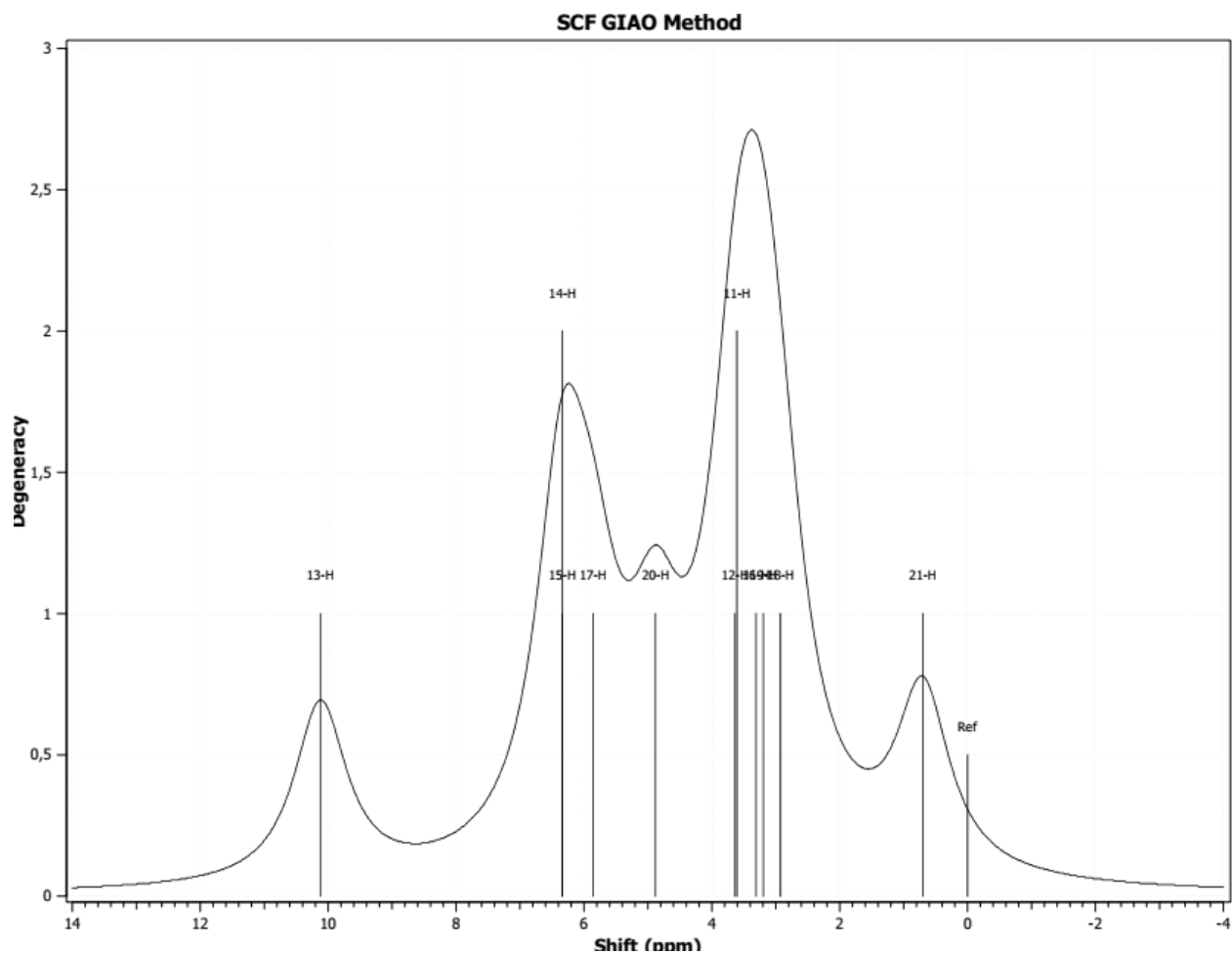
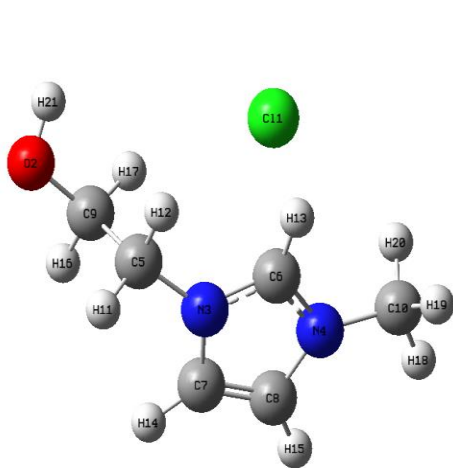
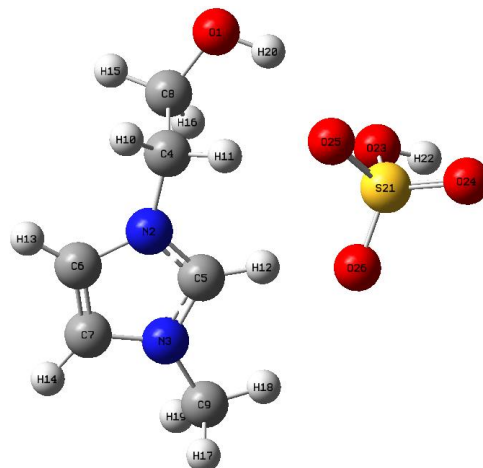


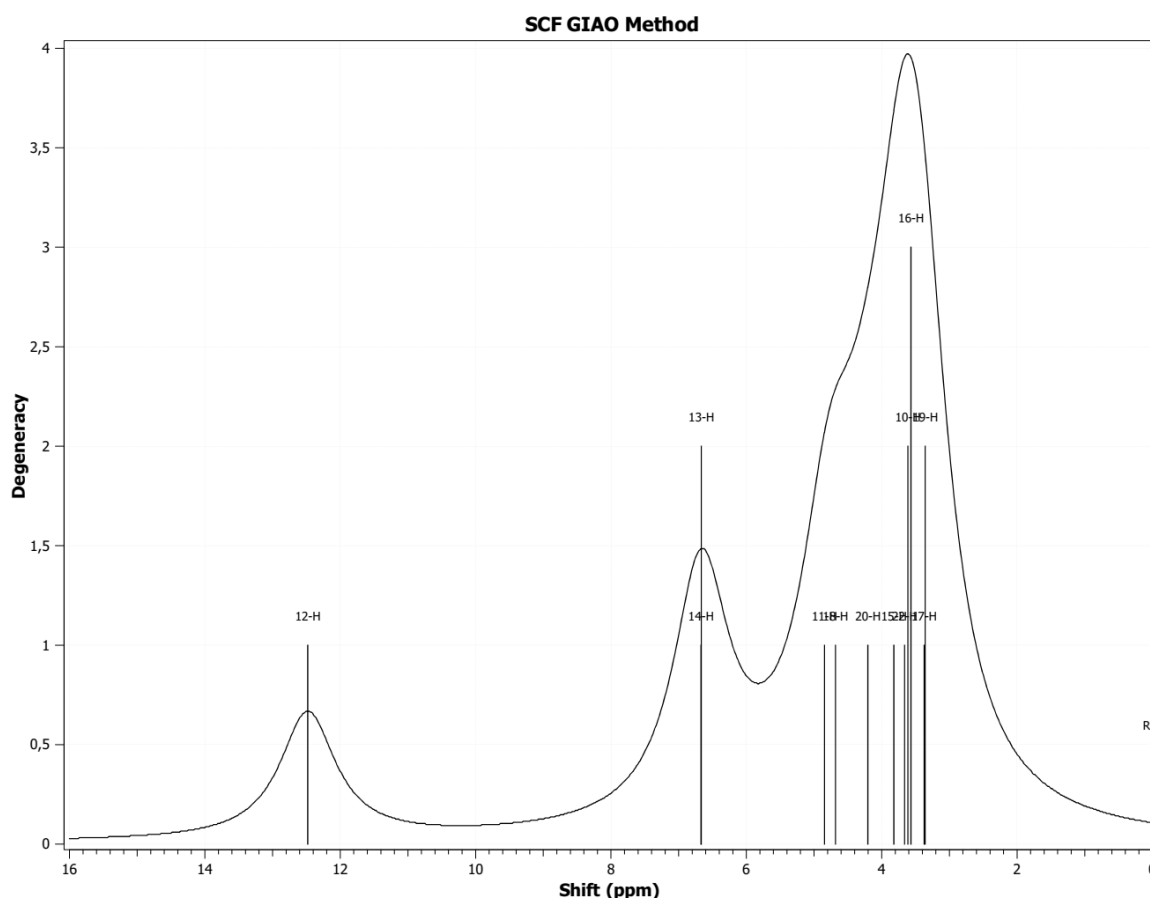
Figure IV.3: NMR spectral <sup>1</sup>H of [EtOHMIM<sup>+</sup>][Cl<sup>-</sup>]



[1(2OHET)3MIM<sup>+</sup>] [Cl<sup>-</sup>]



[1(2OHET)3MIM<sup>+</sup>] [HSO<sub>4</sub><sup>-</sup>]



**Figure IV.4** : NMR spectral <sup>1</sup>H of [EtOHMIM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>]

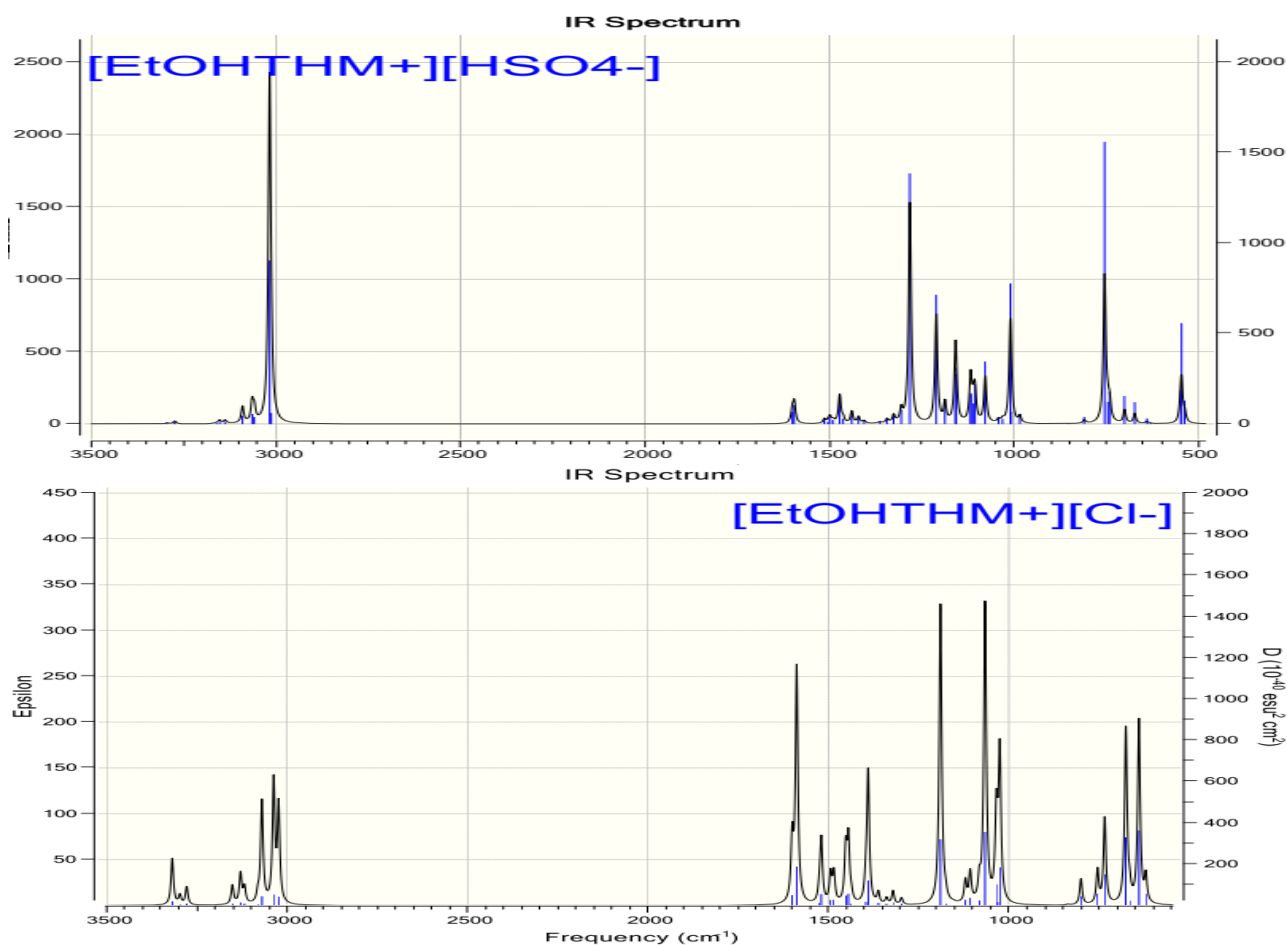
## ✓ Results and Discussion

In this section, we will present a comparison between the two new monocationic ionic liquids 1-(hydroxyethyl)-3-methylthiazolium [EtOHTHM<sup>+</sup>][Cl<sup>-</sup>] chloride and hydrogenosulfate 1-(hydroxyethyl)-3-methylthiazolium[EtOHTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>] following two spectroscopic studies: FTIR/ATR and Raman.

[EtOHMIM <sup>+</sup> ][Cl <sup>-</sup> ]	[EtOHMIM <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ]	ASSIGNEMENT
	605 (m)	$\omega$ (N-H)/CH <sub>3</sub> (N) CN Str
620 (s)	620 (s)	$\omega$ (N-H)/CH <sub>3</sub> (N) CN Str
652 (s)	660 (w)	$\omega$ (N-H)/CH <sub>3</sub> (N) CN Str
687 (s)		$\omega$ (C-H) + $\omega$ (N-H)
705 (m)	700(m)	CH <sub>2</sub> (N)/CH <sub>3</sub> (N)CN bend
868 (s)	873 (s)	$\rho$ as(CH <sub>2</sub> )
	903 (s)	$\nu$ (N-S)
942 (vw)		$\rho$ as(CH <sub>2</sub> )
	968 (vw)	$\nu$ (N-S)
	1017 (s)	S-OH
1027* (sh)		CH <sub>3</sub> N Str/CH <sub>2</sub> N Str
1038 (m)		CH <sub>3</sub> N Str/CH <sub>2</sub> N Str
1062 (m)	1068 (s)	$\nu$ (C-O)
1175 (m)	1175 (m)	Ring as Str CH <sub>2</sub> (N) and CH <sub>3</sub> (N)CN Str/CC
1198 (m)	1198 (m)	Ring s CH <sub>2</sub> (N) and CH <sub>3</sub> (N)CN Str
	1224 (m)	$\nu$ (S-O)
1254 (w)	1256 (m)	Ring ip as strstr
	1336 (m)	$\nu$ (C-C)
1347 (m)	1353 (m)	$\nu$ (C-C)
1371 (w)	1372* (sh)	$\delta$ (CH) – $\delta$ <sub>s</sub> (CH <sub>3</sub> )
1388* (sh)	1390 (m)	$\rho$ (N-H)
2966 (m)		vas(CH <sub>3</sub> )
	2972 (w)	vas(CH <sub>3</sub> )
2992* (sh)	2988 (w)	vas(CH <sub>3</sub> )
3038 (s)		= C-H Str
3055 (sh)	3040* (sh)	= C-H Str
	3086 (s)	= C-H Str
3141 (s)	3154 (m)	Ring NC(H)NCHStr
3165 (sh)		Ring NC(H)NCH Str
	3250* (sh)	$\nu$ (O-H)
3404 (w)		$\nu$ (O-H)

**Table (7)** : ASSIGNEMENT of bands of [EtOHMIM<sup>+</sup>][Cl<sup>-</sup>] and [EtOHMIM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>] in the spectral zone 600-3500 cm<sup>-1</sup>

FTIR/ATR spectra [4000-600  $\text{cm}^{-1}$ ] of the ionic liquids are illustrated in (Fig IV.3) ,The assignments of the observed modes in this spectral region are reported in(see table( 7) )On the IR spectra (see Fig IV.3), we differentiate three well defined spectral regions: 3500-2600, 1800-1300 et 1300-600  $\text{cm}^{-1}$ ,For the first regions we note that the intensity is the same for both spectrums whereas in the region 1300-1800  $\text{cm}^{-1}$  we seem a high intensity for [EtOHMIM+][Cl-] , as well as for the region 2500-3500  $\text{cm}^{-1}$  we seem a high intensity for [EtOHTHM+][HSO4-],The presence of the HSO4 anion seems the influence of the O-H group of (anion and cation) in this spectral zone.



**Fig IV.5.** FTIR/ATR spectra of [EtOHMIM+][Cl-] and [EtOHTHM+][HSO4-] in the spectral range 3500-600  $\text{cm}^{-1}$

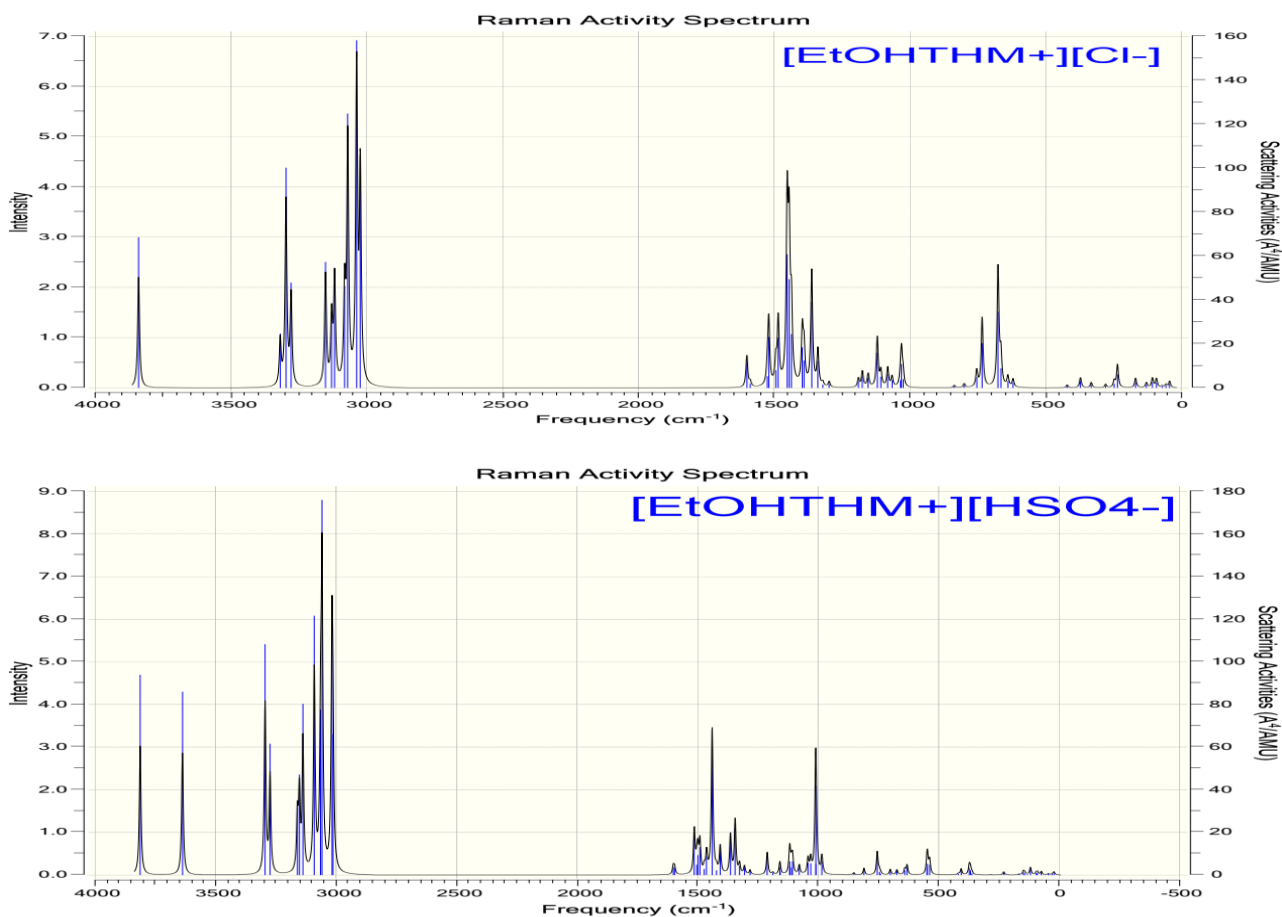


Fig IV.6. RAMAN spectra of [EtOHMIM+][Cl<sup>-</sup>] and [EtOHMIM+][HSO<sub>4</sub><sup>-</sup>] in the spectral range 3500-600 cm<sup>-1</sup>

#### 4.1 Region 1300-600 cm<sup>-1</sup>

In this spectral zone (Fig IV.7), For the Cl<sup>-</sup> anion, we observed the intensity in 600-800cm<sup>-1</sup> with the ascendancy of the modes 686 cm<sup>-1</sup> are assigned to (CH<sub>2</sub>)<sub>ant</sub> symmetric rocking[9-10], at the zone spectral 1000-1300 cm<sup>-1</sup>, we observed intense with the ascendancy of the modes :1038 and 1175 cm<sup>-1</sup> assigned to CH<sub>3</sub>N stretching /CH<sub>2</sub>N stretching and Ring antisymmetric stretchingCH<sub>2</sub>(N) and CH<sub>3</sub>(N)CN stretching /CC[9-10], for the HSO<sub>4</sub><sup>-</sup> anion, we observed two modes in spectral zone 600-900 cm<sup>-1</sup>, 753 cm<sup>-1</sup> and 850cm<sup>-1</sup> assigned to (C-H)wagging and (CH<sub>2</sub>)<sub>ant</sub> symmetric rocking[9-10], the strong band at 1178 cm<sup>-1</sup> observe for [EtOHMIM+][HSO<sub>4</sub><sup>-</sup>] assigned to Ring as Str CH<sub>2</sub>(N) and CH<sub>3</sub>(N)CN Str/CC [9-10].



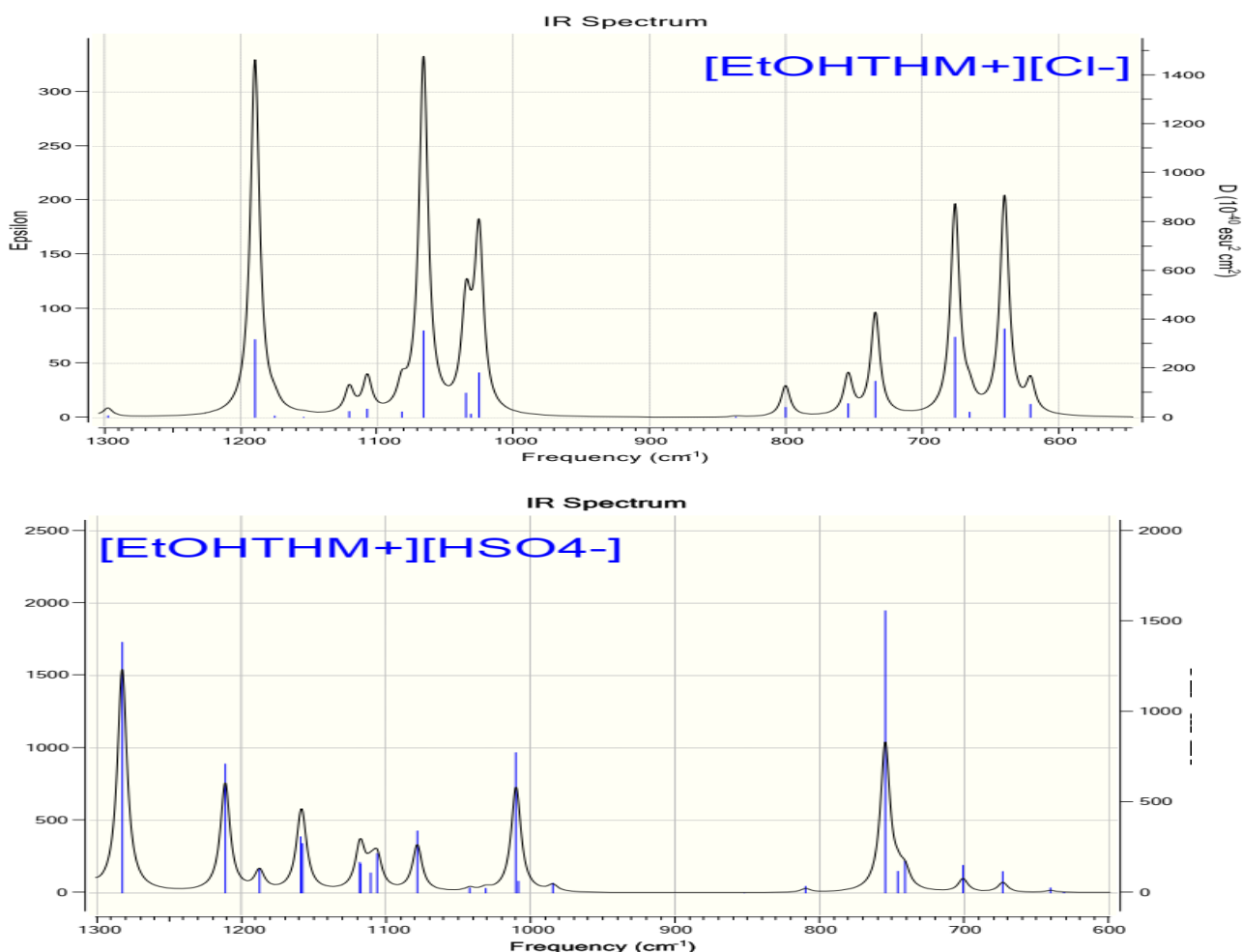
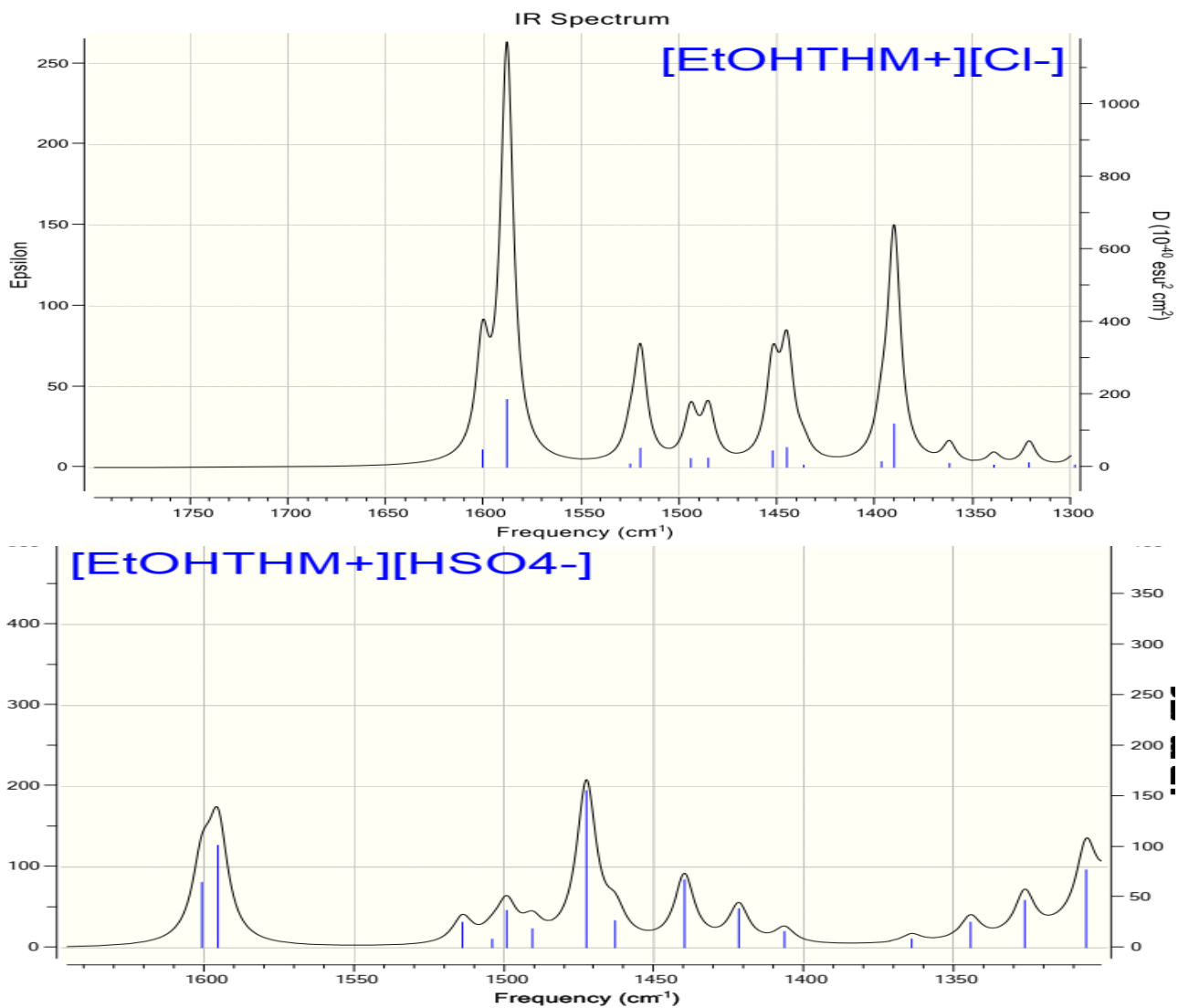


Fig IV.7. FTIR/ATR spectra of [EtOHMIM+][Cl-] and [EtOHMIM+][HSO4-] in the spectral range 1300-600  $\text{cm}^{-1}$

#### 4.2 Region 1800-1300 $\text{cm}^{-1}$

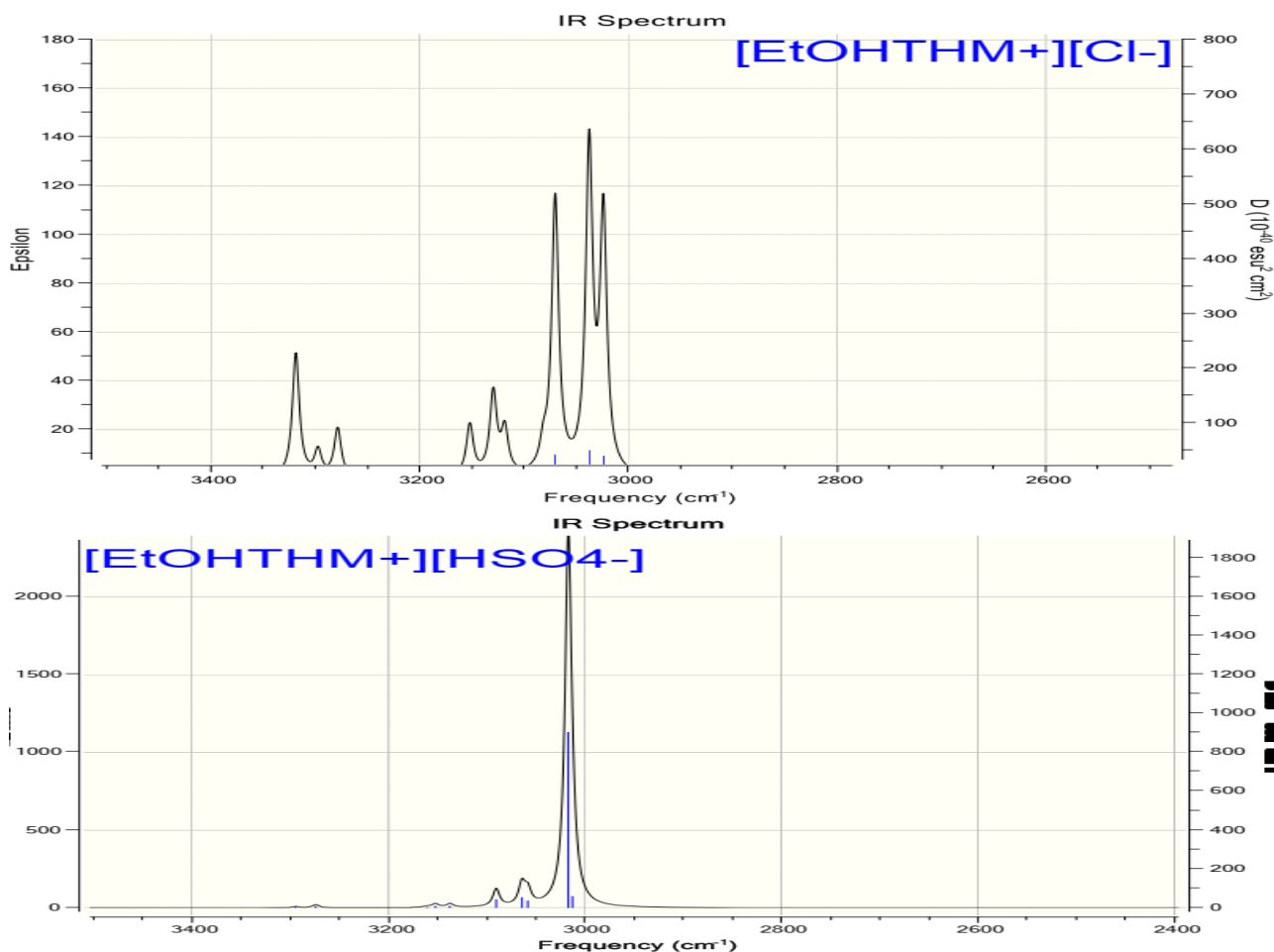
In this spectral zone (**Fig IV.8.**), we note that [EtOHTHM+][Cl-] spectral is more intense than [EtOHTHM+][HSO4-], For the  $\text{Cl}^-$  anion, we observed two modes 1388  $\text{cm}^{-1}$ , 1692  $\text{cm}^{-1}$ , assigned to (N-H) rocking and Ring C=C stretching, N=C-N stretching [9-10], Conversely for [EtOHTHM+][HSO4-] we note less intense with ascendancy of two modes: 1480  $\text{cm}^{-1}$  and 1578  $\text{cm}^{-1}$  assigned to deformation ( $\text{CH}_2$ )/CCH HCH asymmetric bending [9-10], Ring C=C stretching, N=C-N stretching [13].



**Fig IV.8.** FTIR/ATR spectra of [EtOHMIM+][Cl<sup>-</sup>] and [EtOHMIM+][HSO<sub>4</sub><sup>-</sup>] in the spectral range 1300-1800 cm<sup>-1</sup>

### 4.3 Region 3500-2400 cm<sup>-1</sup>

In this spectral zone (**Fig IV.9.**), for Cl<sup>-</sup> anion, we observe less intense with the ascendancy of only modes 3038 cm<sup>-1</sup>, assigned to = C-H Stretching [9-10], at the zone spectral 3200-3400 cm<sup>-1</sup> we observed a band assigned Ring NC(H)NCH Stretching [9-10] in the mode 3141 cm<sup>-1</sup>, whereas for the HSO<sub>4</sub><sup>-</sup> anion we observe only strong band in the spectral zone 3000-3250 cm<sup>-1</sup>, this mode assigned to stretching (O-H) [11-12], The presence of the HSO<sub>4</sub> anion seems the influence of the O-H group of (anion and cation) in the spectral zone .



**Fig IV.9.** FTIR/ATR spectra of [EtOHMIM+][Cl-] and [EtOHMIM+][HSO4-] in the spectral range 3500-2400  $\text{cm}^{-1}$

✓ **comparison between theoretical study and the experimental results**

In this study we compared the results obtained in the experimental and theoretical sections and based on infrared spectral analysis and discussions that were very similar.

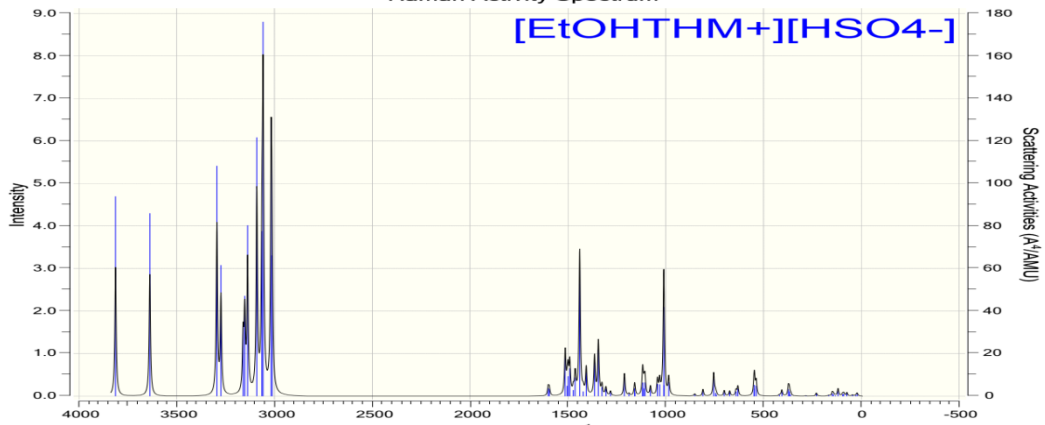
In the first region we registered a bands assigned to wagging (N-H)/CH<sub>3</sub>(N) CN Stretching and we observed intensity for CL- anion spectral in this zone.

all the modes assigned in this region is the same for the two spectra's with a little deferent's

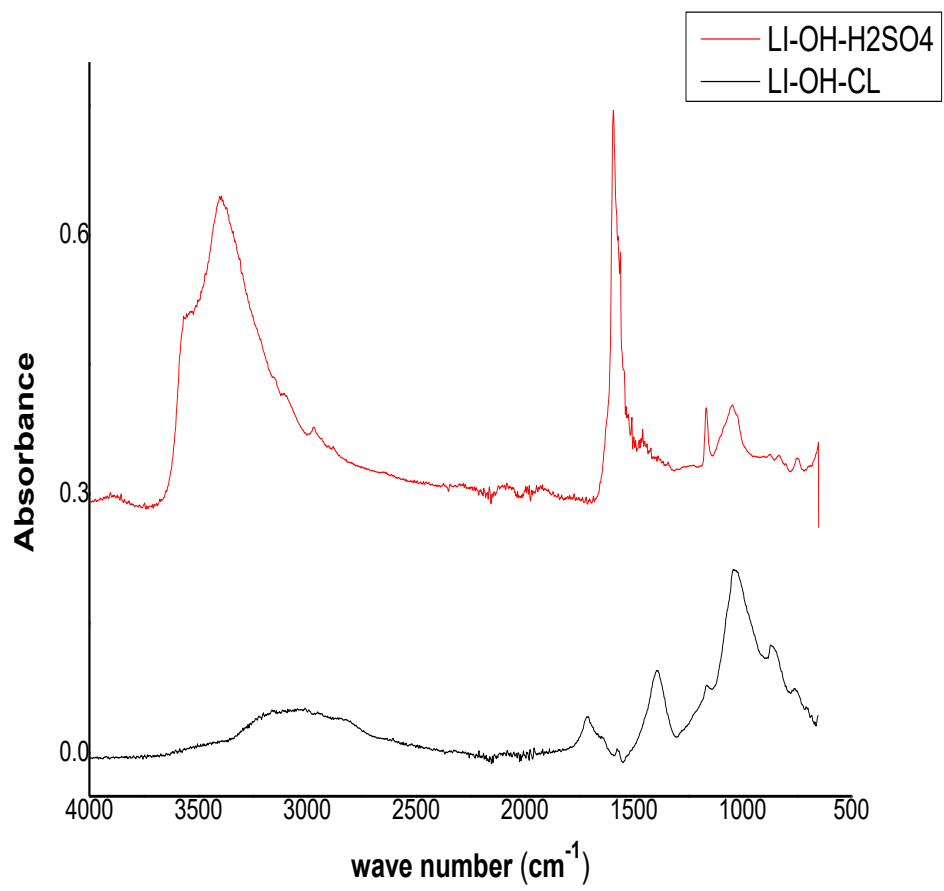
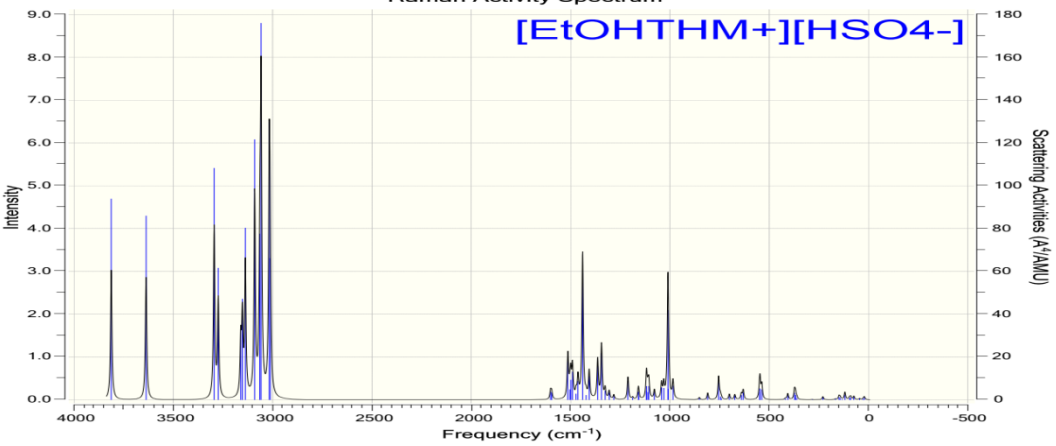
In the second region we registered a bands assigned to antisymmetric Stretching CH<sub>2</sub>(N)/CH<sub>3</sub>(N)CN and to (N-H) rocking and Ring C=C stretching for the two spectral

Finally, in last region we observed intense in the last part of the zone spectral seems the influence of the O-H group of (anion and cation), and this effect show up in two spectral zone.

Raman Activity Spectrum



Raman Activity Spectrum



## **Conclusion**

The main objective of the current work is to provide a direct approach and possible information on ion fluids, in particular “imidazolium-based” and through this theoretical study based software (GaussView and Gaussian), and based on the results obtained from IR spectrum and RAMAN spectrum, we have found that ions have a direct influence on vibrations of imidazolium structure, and This study is evidence of what we found in the previous chapter.

## *References*

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# General Conclusion

## General Conclusion:

In this work, we have investigated the synthesis of new ionic liquids corresponding to imidazolium. These compounds were characterized by spectroscopic analysis: NMR and FTIR/ATR.

Comparison between theoretical study and the experimental results, we theoretically investigated the IR spectrums of imidazolium-based ILs in the range of  $600\text{-}3500\text{ cm}^{-1}$ , demonstrating a better agreement with the reported experimental values. Through our discussions, we found that the ion change clearly affects the vibratory behavior of the Cations and the structure.

In addition, many ion liquids with special properties can be synthesized only by changing the ion to take advantage of its applications

We would like to understand in the future study the characteristics and other characterization methods of these ion liquids that have a wide range of potential applications, including the next generation of solar cells, hydrogen fuel cells and lithium batteries, which are a key energy technology, but can only charge and unload their electric power relatively slowly - Think about how a cell phone or computer battery takes hours to recharge, so that batteries play a big role in the afternoon and ion-based fuel cells that can soon appear with better performance will appear

This is about energy applications and there are many and many applications in which this ion liquid are involved and as we mentioned earlier, the goal of this research is

- ✓ Give more accurate results through simulation and show the ion-action position
- ✓ Know the properties through the spinning given in IR and NMR spectral and discover more application
- ✓ Give researchers more accurate information on synthesis to proceed with the lab



## Abstract

We prepared our liquids ionic by using imidazole as a starting, with a yield of 98% in the two-steps synthesis, For the first step, we change the previous synthetic way using 2-chloroethanol as starting material, and with 1 methylimidazole to prepare the 1-(hydroxyethyl)-3-methylimidazolium chloride [EtOHMIM<sup>+</sup>][Cl<sup>-</sup>] In the second step , we have exchanged the anion Cl<sup>-</sup> with HSO<sub>4</sub><sup>-</sup>, Our samples are characterized by FTIR/ATR, Our samples are characterized by FTIR/ATR at two ways, the first way we have used FTIR Spectrometer to Discuss the experimental resultat and the second way we have used (GaussView and Gaussian) softwar's .

This study showed the effect of anion on the cation and therefore the change of its chemical and physical properties, can be used in different applications

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## résumé

Nous avons préparé nos liquides ioniques en utilisant l'imidazole comme point de départ, avec un rendement de 98% dans la synthèse en deux étapes, Pour la première étape, nous changeons la manière synthétique précédente en utilisant 2-chloroéthanol comme matière de départ, et avec 1 méthylimidazole pour préparer le chlorure de 1-(hydroxyéthyl)-3-méthylimidazolium [EtOHMIM<sup>+</sup>][Cl<sup>-</sup>] Dans la deuxième étape, nous avons échangé l'anion Cl<sup>-</sup> avec HSO<sub>4</sub><sup>-</sup>, Nos échantillons sont caractérisés par FTIR/ATR, Nos échantillons sont caractérisés par FTIR/ATR de deux façons, la première façon dont nous avons utilisé le spectromètre FTIR pour discuter de la resultat expérimentale et la deuxième façon dont nous avons utilisé (GaussView et gaussien) softwar .

Cette étude a montré l'effet de l'anion sur le cation et donc le changement de ses propriétés chimiques et physiques, peut être utilisé dans différentes applications

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## ملخص

قمنا بإعداد سوائلنا الأيونية باستخدام الإيميدازول كبداية، مع محصول 98% في التخليق المكون من خطوتين، الخطوة الأولى، نغير الطريقة السابقة باستخدام 2-كلورو إيثانول كمادة بداية، ومع 1 ميثيل ميدازول لتحضير 1-(hydroxyethyl)-3-methylimidazolium chloride [EtOHMIM<sup>+</sup>][Cl<sup>-</sup>]، في الخطوة الثانية، قمنا بتغيير الأنيون Cl<sup>-</sup> مع HSO<sub>4</sub><sup>-</sup>، عيناتنا تم وصفها بـ FTIR/ATR، بطريقتين، الطريقة الأولى عبر جهاز المطياف الحراري FTIR/ATR، والطريقة الثانية عبر المحاكاة الحاسوبية باستخدام برامجي (GaussView and Gaussian)

أظهرت هذه الدراسة تأثير الأنيون على الكاتيون، وبالتالي يمكن استخدام تغيير خصائصه الكيميائية والفيزيائية في تطبيقات مختلفة.