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**Faculty: Chemistry**

**Specialty: molecular chemistry**

**Presented by: LAIDOUI Asmaa**

**ALLOUACHE Khadidja**

***Theme***

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**The influence of chloride and hydrogen sulfate anions in  
ionic liquid based on the thiazolium cation.**

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**Supported on: 19.06.2022**

**Before the Jury:**

Mr. BELHOUCIN Mohamed	President	M.C.A	Univ-Tissemsilt
Mr. CHAKER Yassine	Supervisor	M.C.A	Univ-Tissemsilt
Mr. KAAS Sid Ahmed	Co-supervisor	M.A.A	Univ-Tissemsilt
Mr. BOUCHETA Abess	Examiner	M.C.B	Univ-Tissemsilt

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## *Dedication*

I dedicate this work to the dearest people in the world.

To my very dear parents **Abderrahmane** and **Zohra** who made many sacrifices and continue to do so to see me succeed, who have watched over my education, and who have supported me during all these years. This work is the fruit of rigor, of their education, that they find here the expression of my deep love and my gratitude.

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## **Dedication**

Praise belongs to Allah who commands benevolence and mutual aid in piety, may his salvation and blessing be upon the last of the prophets.

I dedicate this modest work:

To my very dear **father**, this brave man who fought and always sacrifices himself so that I lack nothing, while filling me with love and blessing, I will never thank you enough, my respect and my gratitude for you!

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To my dear **sisters** for their constant and continued encouragement

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## ABSTRACT

The objective of this work is to see the influence of the change of anions on the behavior vibrational modes of a new ionic liquid, We have used the thiazole as a starting compound for the preparation of a new ionic liquid 1- (hydroxyethyl)-3 methylthiazolium sulfate, with a yield of 94% in the two-steps synthesis. For the first step, we change the previous synthetic route using 2-chloroethanol as starting material, and with 1-methylthiazolium to prepare the 1-(hydroxyethyl)-3-methylthiazolium chloride [EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>]. In the second stage, we have exchanged the anion Cl<sup>-</sup> with HSO<sub>4</sub><sup>-</sup>. Our product was characterized by ATR/FTIR and <sup>1</sup>H-NMR spectroscopic analysis. The result proved the change of the anion effect in the vibrational of IL.

**Keywords:** Ionic liquid, anion, Cl<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, thiazolium, behavior vibrational, ATR/FTIR.NMR

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## Résumé

L'objectif de ce travail est de voir l'influence du changement d'anions sur le comportement des modes vibrationnels d'un nouveau liquide ionique, Nous avons utilisé le thiazole comme composé de départ pour la préparation d'un nouveau liquide ionique 1-(hydroxyéthyl)-3 sulfate de méthylthiazolium, avec un rendement de 94% dans la synthèse en deux étapes. Pour la première étape, nous changeons la voie de synthèse précédente en utilisant le 2-chloroéthanol comme produit de départ, et avec le 1-méthylthiazolium pour préparer le chlorure de 1-(hydroxyéthyl)-3-méthylthiazolium [EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>]. Dans la deuxième étape, nous avons échangé l'anion Cl<sup>-</sup> avec HSO<sub>4</sub><sup>-</sup>. Notre produit a été caractérisé par analyse spectroscopique ATR/FTIR et RMN. Le résultat a prouvé le changement de l'effet anionique dans la vibration de LI.

**Mots clés :** Liquide ionique, anion, Cl<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, thiazolium, comportement vibrationnel, ATR/FTIR. NMR

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## المخلص

الهدف من هذا العمل هو معرفة تأثير تغيير الأنيونات على أنماط السلوك الاهتزازي لسائل أيوني جديد، وقد استخدمنا الثيازول كمركب أولي لتحضير سائل أيوني جديد 1- (هيدروكسي إيثيل) -3- كيرينات ميثيل ثيازوليوم ، مع عائد 94% في التركيب المكون من خطوتين. بالنسبة للخطوة الأولى، قمنا بتغيير المسار الاصطناعي السابق باستخدام 2-كلورو إيثانول كمادة أولية، مع 1-ميثيل ثيازوليوم لتحضير 1- (هيدروكسي إيثيل) -3-ميثيل ثيازوليوم كلوريد [EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>]. في المرحلة الثانية، قمنا بتغيير الأنيون Cl<sup>-</sup> مع HSO<sub>4</sub><sup>-</sup>. تميز منتجنا بالتحليل الطيفي ATR / FTIR و NMR. أثبتت النتيجة أن تغيير الأنيون يؤثر في اهتزاز السائل الأيوني.

**الكلمات المفتاحية:** سائل أيوني، أنيون، Cl<sup>-</sup>، HSO<sub>4</sub><sup>-</sup>، ثيازوليوم، سلوك اهتزازي، ATR / FTIR. NMR.

## List of Figures

<b>Figure I.2.1:</b> Class of ionic liquids cations.....	03
<b>Figure I.2.2:</b> some examples of anions.....	04
<b>Fig I.3.1:</b> Chronology of the appearance and development of Ionic Liquids.....	05
<b>Fig I.4.1.1:</b> Synthesis of ionic liquids of N, N'-dialkyl imidazolium salts.....	06
<b>Fig I.4.1.2:</b> Synthesis of ionic liquids of N-alkyl pyridinium salts.....	06
<b>Fig I.4.1.3:</b> Synthesis of ionic liquids of N-alkyl pyrrolidinium salts.....	06
<b>Fig I.4.1.4:</b> Synthesis of 1-[2-(2-hydroxy-ethoxy) ethyl]-3-methylimidazolium hydrogen sulfate [hmim <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ] et [heemim <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ].....	07
<b>Fig I.4.1.5:</b> synthesis of 1-(2-hydroxyethyl)-3-hexafluorophosphate methylimidazolium ([hydemim <sup>+</sup> ][PF <sub>6</sub> <sup>-</sup> ]).....	07
<b>Fig I.4.1.6:</b> synthesis of an ionic liquid with a sulphonic acid function at the end of the side chain using a 1,4-butasulfone.....	07
<b>Fig I.4.1.7:</b> Synthesis of ionic liquid monomers with an acrylic function.....	08
<b>Fig I.4.1.8:</b> Synthesis of PLI-X and PLI-OH.....	08
<b>Fig I.4.1.9:</b> Synthesis of poly (1-butyl-3-methyl-4-vinylimidazolium).....	08
<b>Fig I.4.1.10:</b> Preparation of cationic vinyl monomers.....	08
<b>Fig I.4.1.11:</b> Preparation of anionic vinyl monomers from different acids polymerizable.....	09
<b>Fig I.6:</b> The main fields of application of ionic liquids.....	12
<b>Fig I.7.1:</b> basic core structure of thiazole and isothiazole.....	13
<b>Fig I.7.2:</b> Equation synthesis of Hantzsch.....	13
<b>Fig I.7.3.1:</b> synthesis of 4-amino-1, 3-thiazole.....	14
<b>Fig I.7.3.2.:</b> Synthesis of 4-chloro-1, 3-thiazole.....	14



<b>Fig I.7.3.3:</b> Synthesis of 4-bromo-1,3-thiazoles.....	14
<b>Fig I.7.3.4:</b> synthesis of 2, 4-diaminothiazole.....	14
<b>Fig I.7.4:</b> application of thiazole in the pharmaceutical.....	15
<b>Fig II.2.2.2:</b> Visible and invisible light.....	22
<b>Fig II.2.2.3:</b> infrared spectroscopy.....	23
<b>Fig II.2.2.4.1:</b> Principle of attenuated total reflection (ATR).....	24
<b>Fig III.1:</b> Heating and stirring step.....	30
<b>Fig III.2:</b> the step of filtration and drying.....	30
<b>Fig III.3:</b> Elimination of traces of solvent by Rota-vap.....	31
<b>Fig III.4:</b> Reaction of Quaternization.....	31
<b>Fig III.5:</b> anion exchange reaction.....	32
<b>Fig. IV.1:</b> Agilent Cary 630 FTIR Spectrometer.....	33
<b>Fig. IV. 2.</b> FTIR/ATR spectra of [EtOHMTHM <sup>+</sup> ][Cl <sup>-</sup> ] and [EtOHMTHM <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ] in the spectral range 3500–600 cm <sup>-1</sup> .....	35
<b>Fig. IV.3.</b> FTIR/ATR spectra of [EtOHMTHM <sup>+</sup> ][Cl <sup>-</sup> ] in the spectral range 3500–600 cm <sup>-1</sup> .....	35
<b>Fig. IV. 4.</b> FTIR/ATR spectra of [EtOHMTHM <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ] in the spectral range 3500–600 cm <sup>-1</sup> .....	36
<b>Fig. IV.5.</b> FTIR/ATR spectra of [EtOHMTHM <sup>+</sup> ][Cl <sup>-</sup> ] and [EtOHMTHM <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ] in the spectral range 1300–600 cm <sup>-1</sup> .....	39
<b>Fig. IV.6.</b> FTIR/ATR spectra of [EtOHMTHM <sup>+</sup> ][Cl <sup>-</sup> ] and [EtOHMTHM <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ] in the spectral range 1800–1300 cm <sup>-1</sup> .....	40
<b>Fig. IV.7.</b> FTIR/ATR spectra of [EtOHMTHM <sup>+</sup> ][Cl <sup>-</sup> ] and [EtOHMTHM <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ] in the spectral range 3500–2400 cm <sup>-1</sup> .....	42
<b>Fig IV.8:</b> Structure of 1-(hydroxyethyl)-3 methylthiazolium chloride [EtOHMTHM <sup>+</sup> ][Cl <sup>-</sup> ].....	44

**Fig IV.9:**  $^1\text{H}$ -NMR spectra of 1-(hydroxyethyl)-3 methylthiazolium chloride

$[\text{EtOHMTHM}^+][\text{Cl}^-]$ .....45

**Fig IV.10:** Structure of 1-(hydroxyethyl)-3 methylthiazolium hydrogen sulfate

$[\text{EtOHMTHM}^+][\text{HSO}_4^-]$ .....46

**Fig IV.11:**  $^1\text{H}$ -NMR spectra of 1-(hydroxyethyl)-3 methylthiazolium hydrogen sulfate

$[\text{EtOHMTHM}^+][\text{HSO}_4^-]$ .....46



## List of Tables

<b>Table III.1:</b> the reagents used during the various syntheses.....	28
<b>Table. IV. 1:</b> The observed FTIR/ATR bands and their assignment for the 1-(hydroxyethyl)-3-methylthiazolium chloride and 1-(hydroxyethyl)-3-methylthiazolium hydrogen sulfate samples.....	36

## Abbreviations list

**VOCs:** volatile organic solvents

**ILs:** ionic liquids

**RTIL:** Room temperature ionic liquid

**[hmim<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>] and [heemim<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>]:** 1-[2-(2-hydroxy-ethoxy) ethyl]-3-methylimidazolium hydrogen sulfate

**[hydemim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]:** 1-(2-hydroxyethyl)-3-hexafluorophosphate methylimidazolium

**PLI:** polyionic liquid

**OH:** ion hydroxide

**NTf:** bis(trifluoromethanesulfonyl)imide *anion*

**Cl:** chlore

**PF<sub>6</sub><sup>-</sup>:** Hexafluorophosphate

**BF<sub>4</sub><sup>-</sup>:** Tétrfluoroborate.

**NO<sub>3</sub><sup>-</sup>:** Nitrate

**[Br<sup>-</sup>]:** bromure

**CF<sub>3</sub>:** Trifluoromethyl

**SO<sub>2</sub>:** Sulphur dioxide

**UV:** ultraviolet

**NMR:** Nuclear Magnetic Resonance

**IR:** Infrared radiation

**DSC:** Differential Scanning Calorimetry

**C<sub>3</sub>H<sub>3</sub>NS:** thiazole

**[EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>]:** 1-(hydroxyethyl)-3- methylthiazolium chloride

**[EtOHMTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>]:** 1-(hydroxyethyl)-3- methylthiazolium sulfate

**ATR/FTIR:** Attenuated Total Reflection – Fourier Transform Infrared

# SUMMARY

**Thanks**

**Dedication**

**Abstract**

**List of Figures**

**List of tables**

**Abbreviations list**

**Summary**

**General Introduction .....01**

## **Bibliographic part**

### **Chapter I: Generality of ionic liquids.**

I.1. Introduction .....	03
I.2. what is an ionic liquid? .....	03
I.3. History .....	04
I.4. Synthesis and preparation of ionic liquid .....	05
I.4.1. some examples of ionic liquid synthesis .....	06
I.5. Properties of ionic liquids .....	09
I.5.1. Melting temperature .....	09
I.5.2. Density .....	09
I.5.3. Vapor pressure .....	10
I.5.4. Viscosity .....	10
I.5.5. Conductivity .....	10
I.5.6. Stability and acidity .....	11

I.6. Application of ionic liquids .....	11
I.7. Thiazole .....	12
I.7.1. Definition and structure .....	12
I.7.2. Synthesis .....	13
I.7.3. some examples of synthesis of thiazole .....	14
I.7.4. Application of thiazole .....	15
I.8. Conclusion.....	15
References.....	16

## **Chapter II: Analysis methods and experimental techniques.**

II.1. Introduction .....	21
II.2. Spectroscopic analysis .....	21
II.2.1. Definition .....	21
II.2.2. Infrared Spectroscopy .....	21
II.2.2.2. Infrared radiation (IR) .....	21
II.2.2.3. Principle .....	22
II.2.2.4. Case of the ATR/FTIR .....	22
II.2.2.5. Benefits of this technique .....	25
II.3. Conclusion .....	25
References .....	26

## **Experimental part**

### **Chapter III: experimental part**

III.1. Introduction .....	28
III.2. Materials and methods .....	28
III.2.1. Reagents .....	28
III.2.2. Materials .....	29

III.3. Synthesis and characterization .....	29
III.3.1. calculates Part .....	29
III.3.2. Synthesis and characterization of 1-(hydroxyethyl)-3- methylthiazolium chloride [EtOHMTHM <sup>+</sup> ] [Cl <sup>-</sup> ] .....	30
III.3.3. Synthesis and characterization of 1-(hydroxyethyl)-3- methylthiazolium sulfate [EtOHMTHM <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ] .....	30
III.4. Conclusion .....	32
References.....	33

**CHAPTER IV: Results and discussion “Vibrational behaviors of new ionic liquids”.**

IV.1. Introduction .....	36
IV.2. Infrared spectroscopy .....	36
IV.2.1. FTIR/ATR measurements .....	36
IV.2.1.1. Experimental device .....	36
IV.2.1.2. Experimental conditions .....	36
IV.2.2. Vibrational study of 1-(hydroxyethyl)-3-methylthiazolium chloride and hydrogen sulfate: Influence of the choice of anion on the vibrational behavior of ionic liquids.....	35
IV.2.2.1. Study in FTIR/ATR spectroscopy of ionic liquids 1-(hydroxyethyl)-3 methylthiazolium chloride [EtOHMTHM <sup>+</sup> ][Cl <sup>-</sup> ] and 1-(hydroxyethyl)-3 methylthiazolium hydrogen sulfate [EtOHMTHM <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ] .....	35
IV.2.2.1.1. Study in the spectral region 1300-600 cm <sup>-1</sup> .....	39
IV. 2.2.1.2. Study in the spectral region 1800-1300cm <sup>-1</sup> .....	41
IV. 2.2.1.3. Study in the region 3500-2600cm <sup>-1</sup> .....	42
IV.3. Study in <sup>1</sup> H-NMR spectroscopy of ionic liquids 1-(hydroxyethyl)-3 methylthiazolium chloride [EtOHMTHM <sup>+</sup> ][Cl <sup>-</sup> ] and 1-(hydroxyethyl)-3	

methylthiazolium	hydrogen	sulfate	[EtOHMTHM <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ]	
.....				43
IV.3.1.Characterization	of	[EtOHMTHM <sup>+</sup> ][Cl <sup>-</sup> ]	by	<sup>1</sup> H-NMR
spectroscopic.....				44
IV.3.2.	Characterization	of	[EtOHMTHM <sup>+</sup> ][HSO <sub>4</sub> <sup>-</sup> ]	by
spectroscopic .....				45
IV.3.Conclusion.....				47
References.....				48
<b>General conclusion</b> .....				<b>50</b>

# GENERAL INTRODUCTION

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## General introduction:

Today, the scientific approach for a large number of chemists is part of the research and development of new processes that are ever more respectful of the environment. The concept of "green chemistry" has led organic chemists to rethink their synthetic methods.

Within the framework of eco-compatible chemistry, the use of ionic liquids as new reaction media seems to be a good alternative to pre-existing methods. [1]

However, ionic liquids are new solvents that do not have these drawbacks. On the one hand, they could replace the organic phase, thus eliminating the risks of inflammation and toxicity. On the other hand, facilitating reprocessing would eventually make it possible to separate other elements.

Thus, they have a low vapor pressure, which facilitates their recycling. Their particularly interesting and unique physicochemical properties make them attractive candidates for various applications, particularly in organic synthesis and catalysis. [2]

The work described in this thesis will be mainly based on the study of the influence of chloride and hydrogen sulfate anions on an ionic liquid based on thiazolium.

This manuscript is divided into 4 chapters:

We firstly (chapter I) presented a bibliographical synthesis of ionic liquids and the nature of their constituents (anions, cations). We cite also a detailed study of their physicochemical properties. Mention some syntheses elaborated on previously and see their various applications. Thus, we cite a generality of thiazole, its structure, synthesis and applications.

The presentation of the different physico-chemical analysis methods and their principles is the subject of the second chapter.

Chapter III is devoted to the description of the experiment carried out of 1-(hydroxyethyl)-3-methylthiazolium chloride and hydrogen sulfate.

Chapter IV is reserved for analytical methods used in the vibrational study and the results obtained at the end.

A general conclusion will close this work and summarize the main results. Obtained new ionic liquid, synthesized, and studied.



## GENERAL INTRODUCTION

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### References:

[1] Lucie Bouchardy. Elaboration de liquides ioniques (chiraux) réversibles et applications en catalyse organique et en glycochimie. Carbènes N-hétérocycliques chiraux : synthèse et application dans la réaction d'addition conjuguée. Chimie organique. Université Paris Saclay (COmUE), 2016. Français.

[2] Haddad Boumediene; « Nouveaux liquides ioniques Bis-Pipéridinium : Synthèse, Etude des propriétés thermiques et relaxation diélectrique » juin 2012

# **BIBLIOGRAPHIC PART**

**CHAPTER I:**  
**GENERALITY OF IONIC LIQUIDS**

## I.1. Introduction:

Research into safer environmental solvents to replace hazardous volatile organic solvents (VOCs) is one of the "Twelve Principles of Green Chemistry". In this line, ionic liquids (**LI**) have been proposed as "greener" alternatives to traditional VOCs. IL is classified as molten salts and consists of a large organic cation and an organic or inorganic anion. [1]

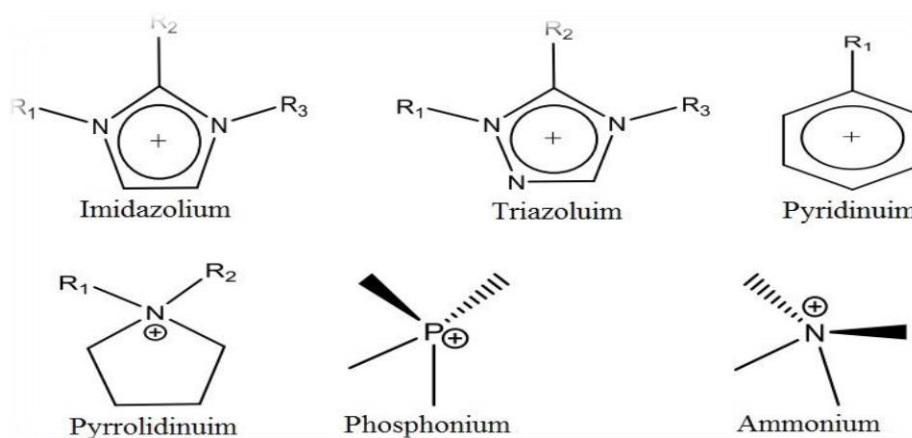
Ionic liquids are a category of materials with various possible applications. Their potential arises because their properties differ significantly from traditional molecular solvents, and they can be modified by changing the ion combinations that produce the substance. [2]

## I.2. what is an ionic liquid?

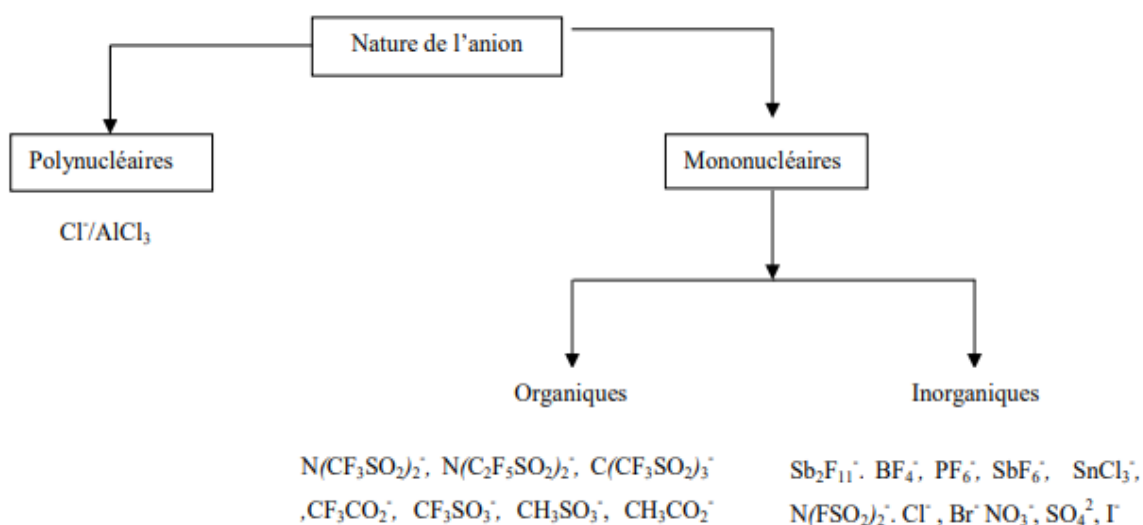
The term 'ionic liquid' was only recently developed to describe ambient-temperature liquid salts, and its definition has subsequently been the subject of significant discussion and development. 'A liquid made entirely of ions,' is the most practical definition of an IL. [3]

IL is salt having a melting point below 100 °C. With such a broad description, there is a lot of space for interpretation, which is why IL is referred to be designer solvents. [4]

It is composed of an organic cation and associated with an organic or inorganic anion.



**Figure I.2.1:** Class of ionic liquids cations. [5]



**Figure I.2.2:** some examples of anions. [6]

### I.3. History:

The first ionic liquid discovered was ethyl ammonium nitrate. Walden et al. synthesized it in 1914 during the First World War while searching for new explosives. [7]

The discovery of chloroaluminates, which were generated by mixing quaternary heterocyclic cations with aluminum chloride, sparked the next wave of interest. These materials had a lot of promise for use. Although it is used in a variety of settings, it was extremely sensitive to humidity.

Wilkes took a significant step forward in the early 1990s with his report; Moisture-stable ionic liquids are made by substituting different metals for aluminum chloride. Tetrafluoroborate and hexafluorophosphate are examples of anions. Since the publication of that landmark report According to Wilkes and colleagues, the RTIL family has grown at a breakneck pace. To begin with, the cationic component of imidazolium cations has been changed to incorporate pyridinium. Species of ammonium, phosphonium, thiazolium, and triazolium. [4]

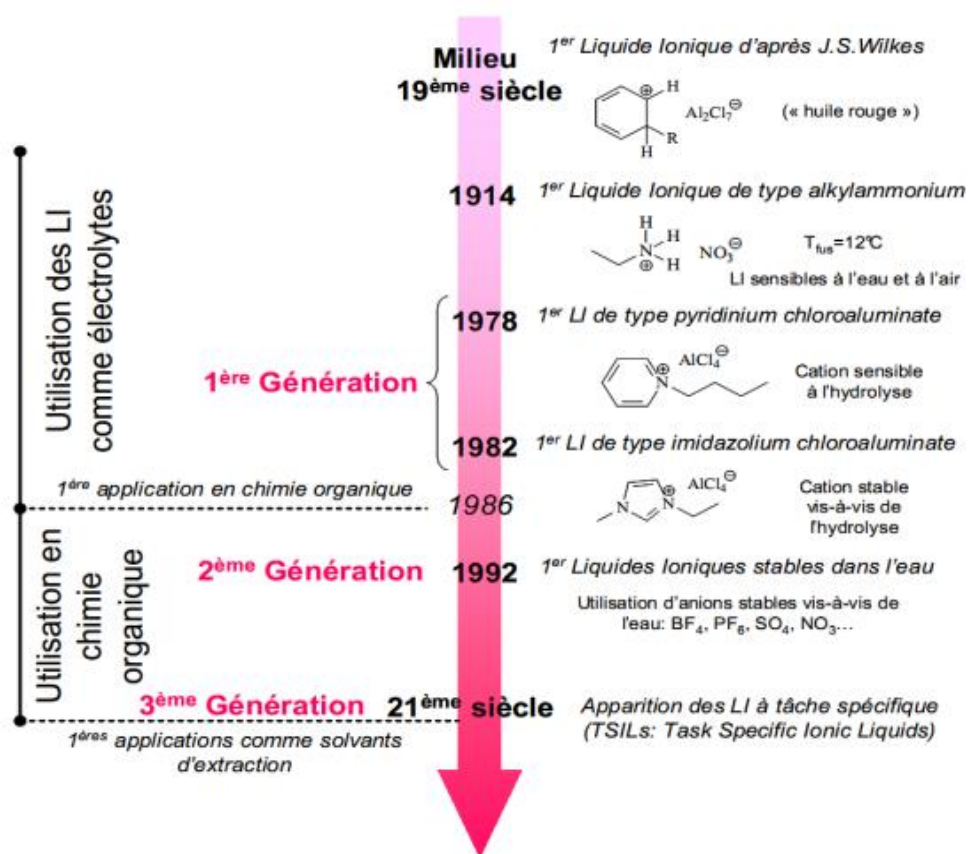


Fig I.3.1: Chronology of the appearance and development of Ionic Liquids. [8]

#### I.4. Synthesis and preparation of ionic liquid:

The synthesis of LI is well established, and many articles discuss the manufacture and purification of these materials. As in this memoir, we are exclusively interested in the imidazolium family of ILS. Therefore, we will limit ourselves to attaching to the description of the methods specific to their synthesis. The synthesis of IL based on thiazolium cations takes place in two stages: protonation in an acid medium and quaternization of the thiazole nucleus, followed by anion exchange. [09]

The purification of IL is the most important step after any synthesis and probably before any use. Small traces of impurities can sometimes affect seriously the physicochemical properties of IL [10]. IL is not volatile; therefore, purification by simple methods such as distillation is not possible except in exceptional cases [11]. Finally, the presence of small quantities of water can be removed by heating around  $100^{\circ}\text{C}$  under a vacuum [12].

## I.4.1. some examples of ionic liquids synthesis:

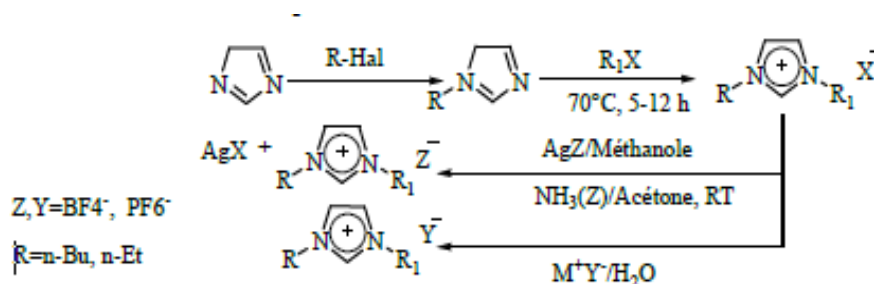


Fig I.4.1.1: Synthesis of ionic liquids of N, N'-dialkyl imidazolium salts. [13]

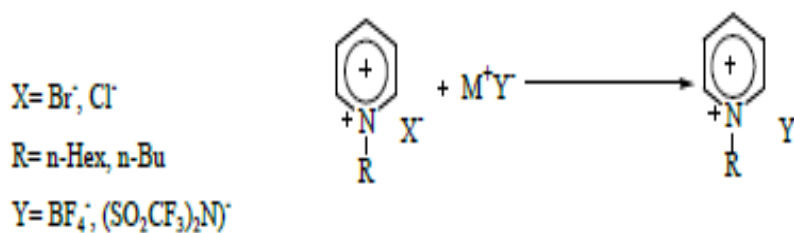


Fig I.4.1.2: Synthesis of ionic liquids of N-alkyl pyridinium salts. [14]

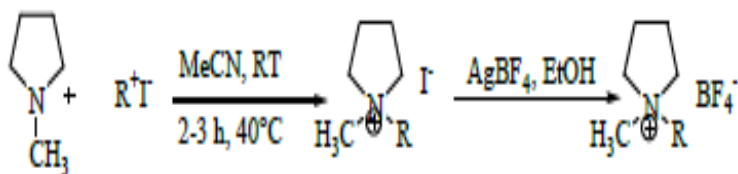
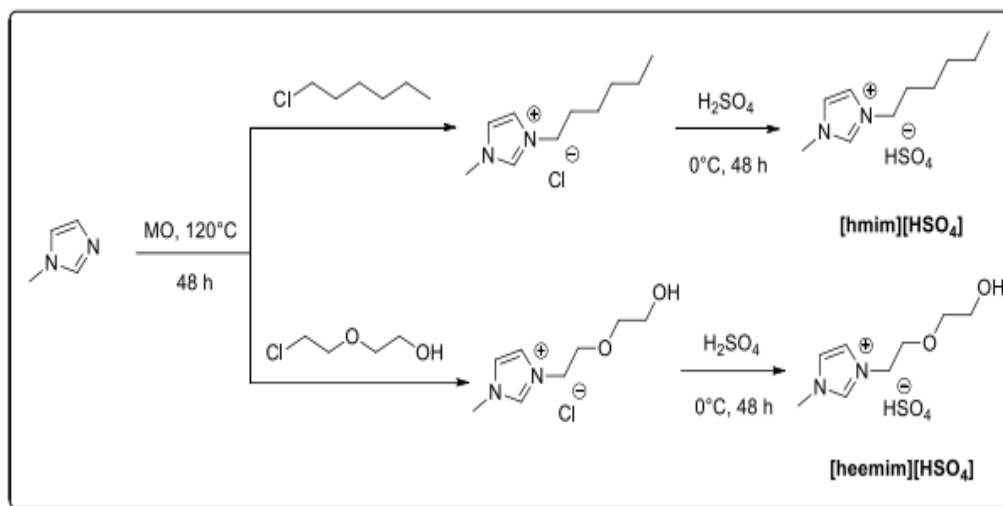
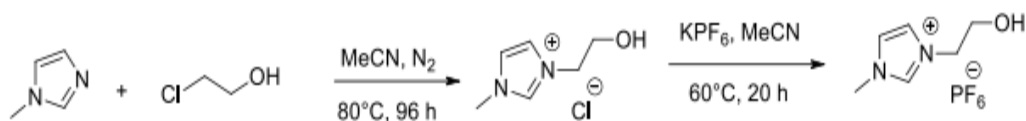


Fig I.4.1.3: Synthesis of ionic liquids of N-alkyl pyrrolidinium salts. [15]

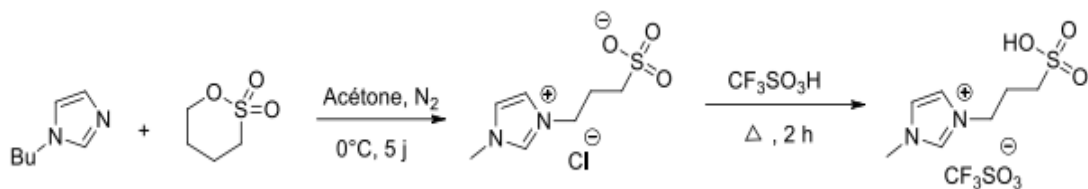




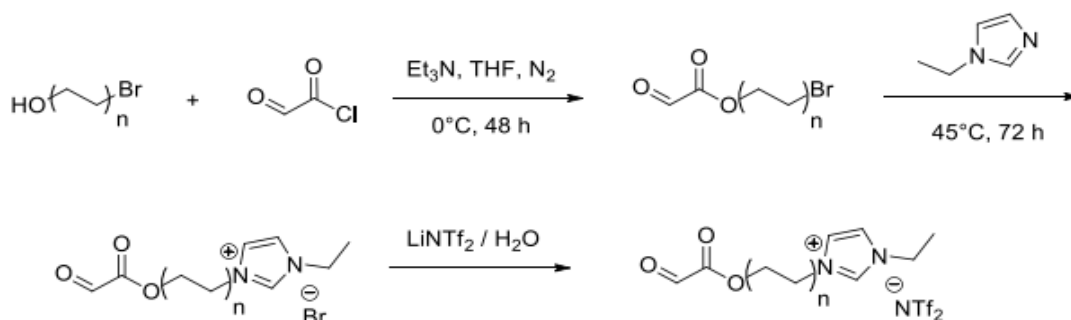
**Fig I.4.1.4:** Synthesis of 1-[2-(2-hydroxy-ethoxy) ethyl]-3-methylimidazolium hydrogen sulfate [hmim<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>] and [heemim<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>]. [16]



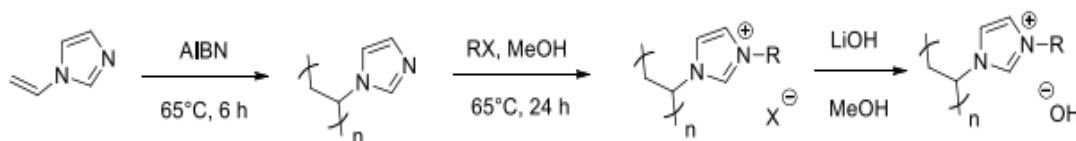
**Fig I.4.1.5:** synthesis of 1-(2-hydroxyethyl)-3-hexafluorophosphate methylimidazolium ([hydemim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]). [17]



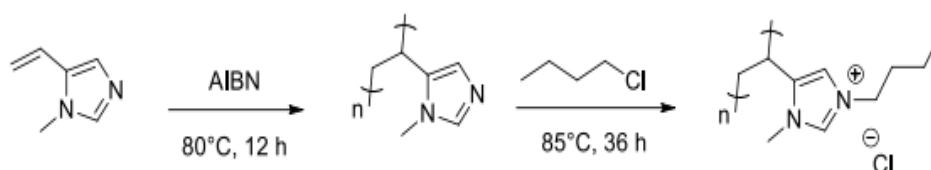
**Fig I.4.1.6:** synthesis of an ionic liquid with a sulphonic acid function at the end of the side chain using a 1,4-butasulfone. [18]



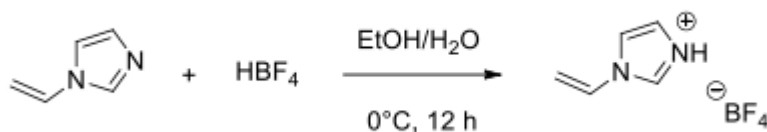
**Fig I.4.1.7:** Synthesis of ionic liquid monomers with an acrylic function. [19, 20]



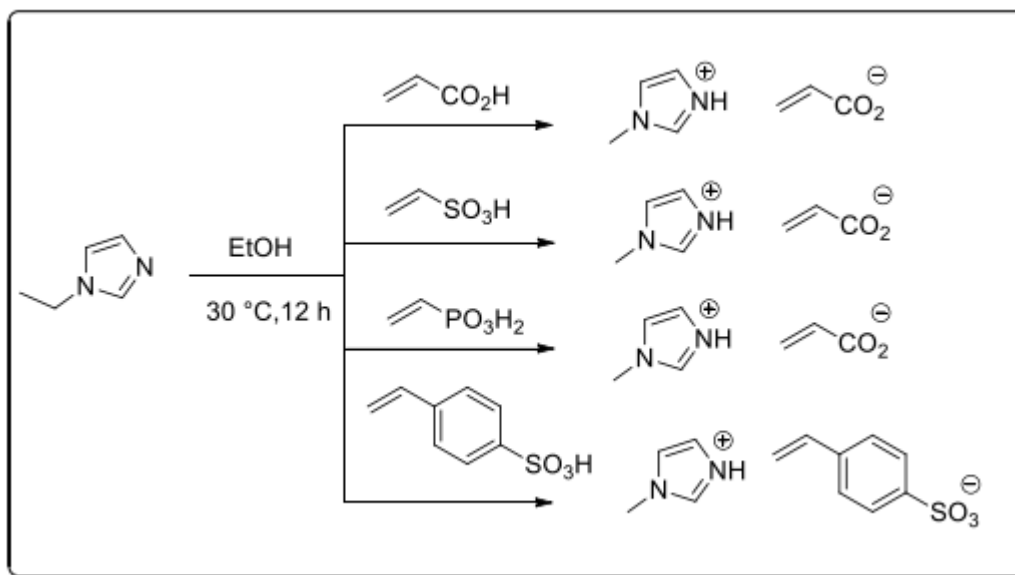
**Fig I.4.1.8:** Synthesis of PLI-X and PLI-OH. [21]



**Fig I.4.1.9:** Synthesis of poly(1-butyl-3-methyl-4-vinylimidazolium). [22]



**Fig I.4.1.10:** Preparation of cationic vinyl monomers. [23]



**Fig I.4.1.11:** Preparation of anionic vinyl monomers from different acids polymerizable. [23]

## I.5. Properties of ionic liquids:

The physical and chemical properties of ionic liquids can vary depending on the structure and the nature of their corresponding cations and anions.

### I.5.1. Melting temperature:

One of the most important properties for the evaluation of an ionic liquid is its point of merger. Molten salt is defined as an ionic liquid when its melting point is less than 100°C. [07]

The melting temperature can be influenced by different parameters that are: [24]

- ✓ The charge distribution on the ions.
- ✓ The nature of cations.
- ✓ The nature of anions.
- ✓ The length of the alkyl chains

### I.5.2. Density:

In general, the density of class 1,3 dialkyl imidazolium LI is greater than that of water (0.9 to 1.6 g.cm<sup>-3</sup>). For hydrophilic and hydrophobic IL, the density decreases almost linearly with the length of the alkyl chain of the cation [25]. Note that the increase in water content causes a decrease in density. [26]

**I.5.3. Vapor pressure:**

Ionic liquids do not have a measurable vapor pressure, this will allow separation efficiency of the products by simple distillation of the reaction mixture, and the problem of the formation of azeotrope between the solvent and the products is eliminated.

Thus, we easily recover and purify the reaction products by distillation without the solvent evaporating or degrading over distillations. [27]

**I.5.4. Viscosity:**

The viscosity of LI is determined essentially by their tendency to form hydrogen bonds and by the strength of Van Der Waals interactions. [09]

The delocalization of the charge on the anion favors a low viscosity by the weakening of the hydrogen bond with the cation, as is the case of the anion NTF. [28]

Moreover, the length of the alkyl chain carried by the cation is a parameter that influences viscosity. When this chain increases, the viscosity, due to stronger Van Der Waals interactions, thus increases. [28] For the same cation, the viscosity decreases according to the anion. For example: Cl- PF6- BF4- NO3-NTf2-.

**I.5.5. Conductivity:**

Ionic liquids have high ionic conductivity, generally of the order of  $10^{-1} \text{ S.m}^{-1}$ . Bonhote et al. report the relation between conductivity and different properties. [29]

$$\sigma = \frac{y F^2 d}{(6\pi N_A M W \eta)((\zeta_a r_a)^{-1} + (\zeta_c r_c)^{-1})}$$

Where: ( $\eta$ ) viscosity, ( $MW$ ) molar mass, ( $N_A$ ) Avogadro's number, ( $F$ ) Faraday's number, ( $d$ ) Density, ( $0 < y < 1$ ) degree of dissociation, ( $r_a, r_c$  respectively) radius of anion and cation, ( $\zeta_a, \zeta_c$  respectively) corrected microviscosity factor of anion and cation.

It appears that viscosity is not the only parameter influencing the value of the conductivity: the size and molecular mass of the ions must also be taken into consideration, which also has a significant effect.

This is in contradiction with the Walden model which expresses that the product of conductivity and viscosity, known as the Walden product, is a constant at a given temperature. Such products vary by LI in a ratio from 1 to 2. [27]

In general, an increase in the size of the cation induces a decrease in the conductivity, probably due to lower mobility for larger cations [30]: imidazolium > sulfonium > ammonium > pyridinium.

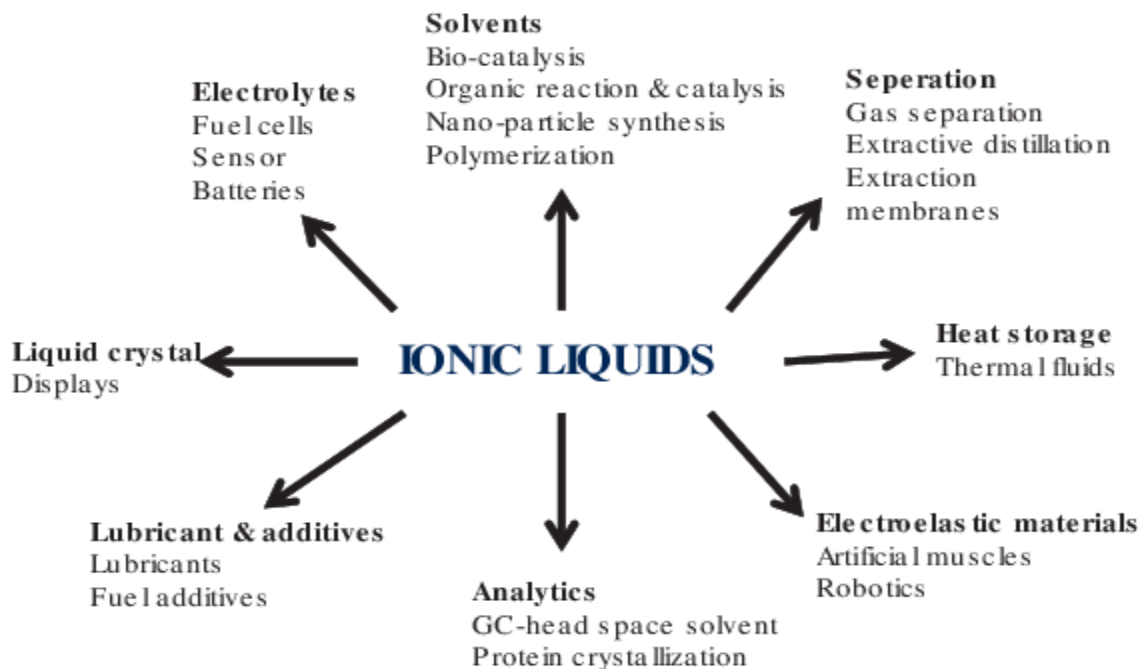
#### **I.5.6. Stability and acidity:**

Several ionic liquids are immiscible with water depending on the nature of the anion, salts hydrophilic [BMIM+][Br-], [BMIM+][CF<sub>3</sub>COO-], [BMIM+][CF<sub>3</sub>SO<sub>3</sub>-] and [BMIM+][BF<sub>4</sub>-] are very soluble in water, on the other hand, the ionic salts with the same cation but the anions hydrophobic such as [PF<sub>6</sub>-] and [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>-] at 20 °C forms a biphasic mixture.[31]

The reactivity of the imidazolium cation is mainly linked to the strong acidity of the proton in position 2 (pK<sub>a</sub>=21-24) [32] which is known to deprotonate in basic conditions or presence of electron-rich transition metals and generate carbenes.[33] Some LI can even behave like superacids. However, the dealkylation of the cation by Hoffman elimination is also possible in the presence of water and palladium, in sonochemistry<sup>81</sup> or at high temperatures <sup>82</sup>. The imidazolium cation is chemically more stable when substituted in position 2. [34]

#### **I.6. Application of ionic liquids:**

For the past ten years, ionic liquids or molten salts have represented a growing field. Booming for their applications in organic synthesis, In catalysis, as stationary phase or electrolytes depending on the fields of application. ...etc. [24]



**Fig I.6:** The main fields of application of ionic liquids. [24]

In addition, as our thesis will study an ionic liquid based on thiazolium, we take into account to quote the importance of this heterocyclic molecule.

## 1.7. Thiazole:

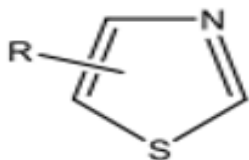
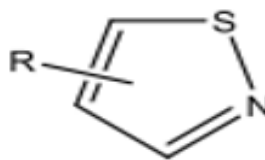
### 1.7.1. Definition and structure:

Hantzsch and Weber first defined thiazole in 1887 [35]

Thiazole is a clear, pale yellow, flammable liquid; its molecular formula is  $C_3H_3NS$ . It was a family of organic compounds comprising five-membered heterocycle atoms, one of which is a nitrogen atom, and another is a sulfur atom. Those are sulfur derivatives of azoles.

There are two subgroups of thiazole: [36]

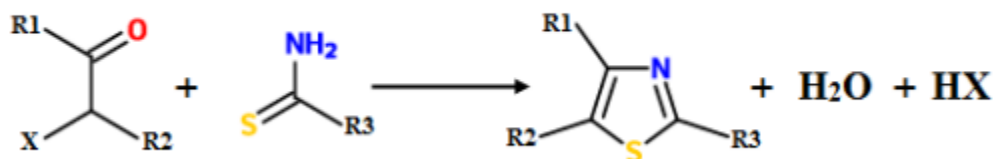
- ✓ Thiazole, where sulfur and nitrogen are separated by a carbon atom
- ✓ Isothiazole, where sulfur and nitrogen are directly linked

**Thiazole****Isothiazole****Fig I.7.1:** basic core structure of thiazole and isothiazole. [36]

### I.7.2. Synthesis:

Given the importance of thiazoles and their derivatives, several methods for the synthesis of thiazole derivatives have been developed by Hantzsch in 1887 [37], Gabriel in 1910 [38], Cook-Heilborn in 1949 [39], G. Sarodnick et al. in 2003 [40] and by several other research teams. [41]

Among these many methods of synthesis of thiazole derivatives, the Hantzsch synthesis remains in general the most commonly used method, although it is a century old. This method consists of a condensation of a compound bearing the two heteroatoms on the same carbon with a compound bearing a halogen and a carbonyl function on two neighboring carbons. A wide variety of compounds can serve as the nucleophilic reagent in this reaction, such as thioamide, thiourea, thiocarbamate or ammonium dithiocarbamate and their derivatives.[42]

**Fig I.7.2:** Equation synthesis of Hantzsch.[42]



## I.7.3. Some examples of synthesis of thiazole:

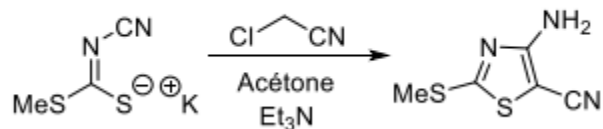


Fig I.7.3.1: synthesis of 4-amino-1, 3-thiazole [43]

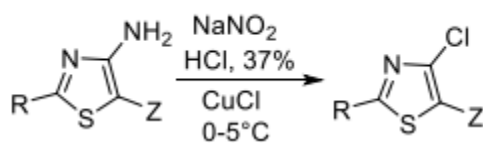


Fig I.7.3.2.: Synthesis of 4-chloro-1, 3-thiazole. [44]

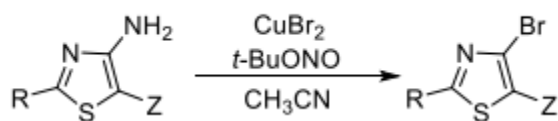


Fig I.7.3.3: Synthesis of 4-bromo-1,3-thiazoles.[44]

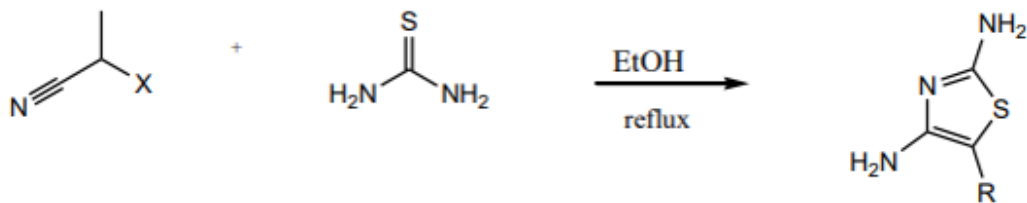


Fig I.7.3.4: synthesis of 2, 4-diaminothiazole. [45]

### I.7.4. Application of thiazole:

In recent years, the thiazole nucleus and its derivatives have also been used in the preparation of superconducting materials. They have been the subject of several studies to their potential applications in the field of optoelectronics and the field of photovoltaics. [46]

It is present in many natural products such as vitamin B1-thiamine. Alkaloids, steroids, as well as in various pharmaceuticals. [47]

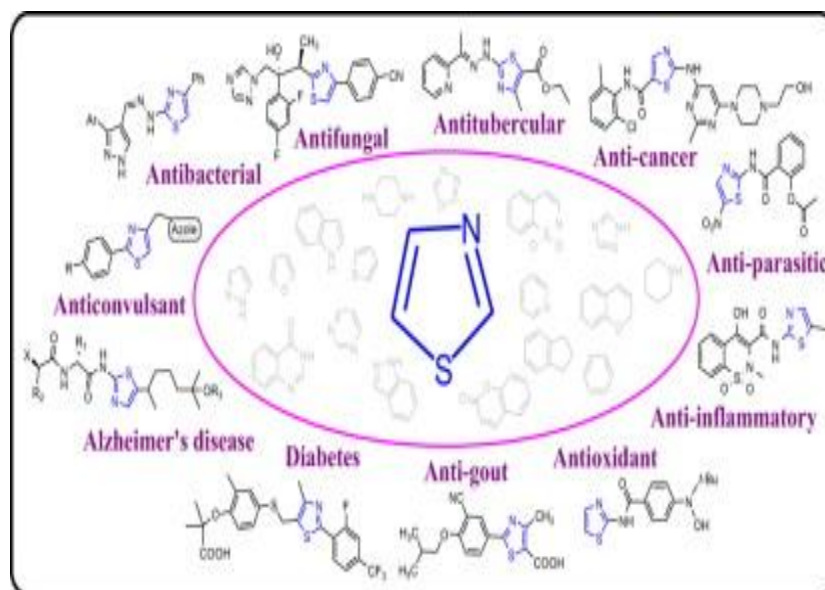


Fig I.7.4: application of thiazole in the pharmaceutical field.[48]

### I.8. Conclusion

IL are liquids generally formed by an organic cation and an organic or inorganic anion and having a melting temperature below  $\mu\text{a } 100\text{ }^{\circ}\text{C}$ . Their remarkable properties have aroused great interest in their applications. Potential in many industrial fields. In particular, it is possible to create tailor-made IL for particular applications by combining cation and specific anion. However, this objective requires a thorough knowledge of the origin at the molecular level of their macroscopic properties, and in particular their molecular structures and dynamics.

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**CHAPTER II:**  
ANALYSIS METHODS  
AND EXPERIMENTAL TECHNIQUES

## II.1. Introduction:

To analyze a synthesized product, various physical techniques are available. Such as infrared, UV-visible, NMR spectroscopy, and differential scanning calorimetry ‘DSC’. These methods of physical study of organic compounds involve the interaction of a wave electromagnetic with the matter. Depending on the energy domain involved, different transitions can be excited. The principle consists of recording the energy absorbed, or the energy emitted depending on the frequency of the incident wave or its wavelength.

## II.2. Spectroscopic analysis:

### II.2.1. Definition:

Spectroscopic analysis methods make it possible to probe the matter by different methods to obtain information on *the* structure of the molecules that make up this matter. Absorption spectroscopy results from the interaction between electromagnetic radiation and a molecule. The energy of a molecule results from four contributions: the energy of the electrons ( $E_e$ ), the energy of translation ( $E_t$ ), the energy of vibration ( $E_v$ ), and the energy of rotation ( $E_r$ ). These energies are quantized. Each energy corresponds to a type of spectroscopy. Each type of spectroscopy will give different information on the nature of the chemical compound studied, namely, the establishment, the functions, the environment of the atoms, and the number of atoms by spectroscopy UV-visible, infrared, and nuclear.[1]

### II.2.2. Infrared Spectroscopy:

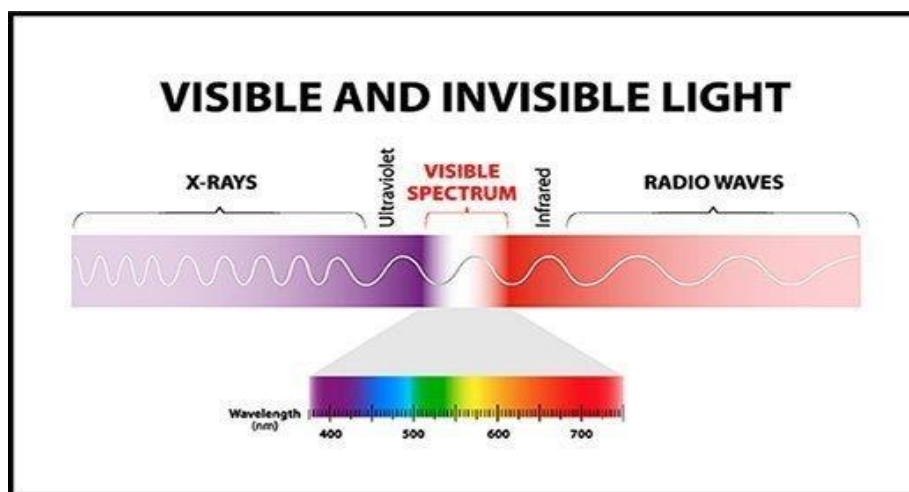
#### II.2.2.1. Definition:

Infrared absorption spectroscopy studies the vibrations and rotations of molecules when they are irradiated by an electromagnetic wave of frequency included in the infrared domain. [2]

#### II.2.2.2. Infrared radiation (IR):

Infrared radiation (IR), sometimes referred to simply as infrared, is a region of the electromagnetic radiation spectrum where wavelengths range from about 700 nanometers (nm) to 1 millimeter (mm). Infrared waves are longer than those of visible light, but shorter than those of radio waves. Correspondingly, the frequencies of IR are higher than those of microwaves but lower

than those of visible light, ranging from about 300 GHz to 400 THz. The near-IR band contains the range of wavelengths closest to the red end of the visible light spectrum. It is generally considered to consist of wavelengths measuring from 750 nm to 1,300 nm -or 0.75 to 1.3 microns. Its frequency ranges from about 215 THz to 400 THz. This group consists of the longest wavelengths and shortest frequencies, and it produces the least heat. [3]



**Fig II.2.2.2:** Visible and invisible light. [3]

### II.2.2.3. Principle:

IR spectroscopy works on the principle that molecules absorb specific frequencies that are characteristic of their structure. At temperatures above absolute zero, all the atoms in molecules are in continuous vibration concerning each other. [4]

The IR spectroscopy theory utilizes the concept that molecules tend to absorb specific frequencies of light that are characteristic of the corresponding structure of the molecules. [5]

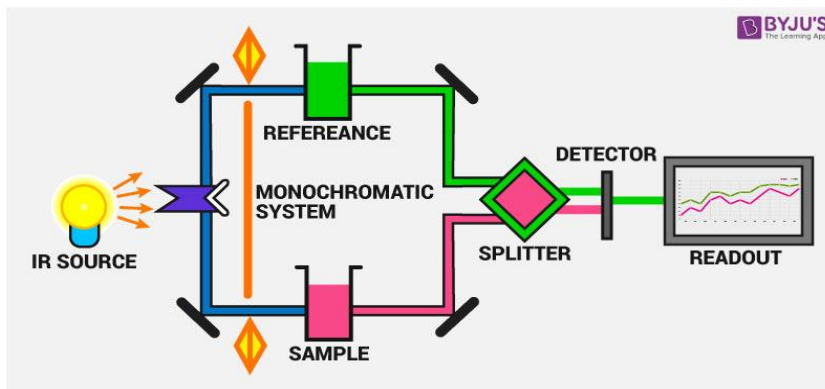


Fig II.2.2.3: infrared spectrophotometry. [5]

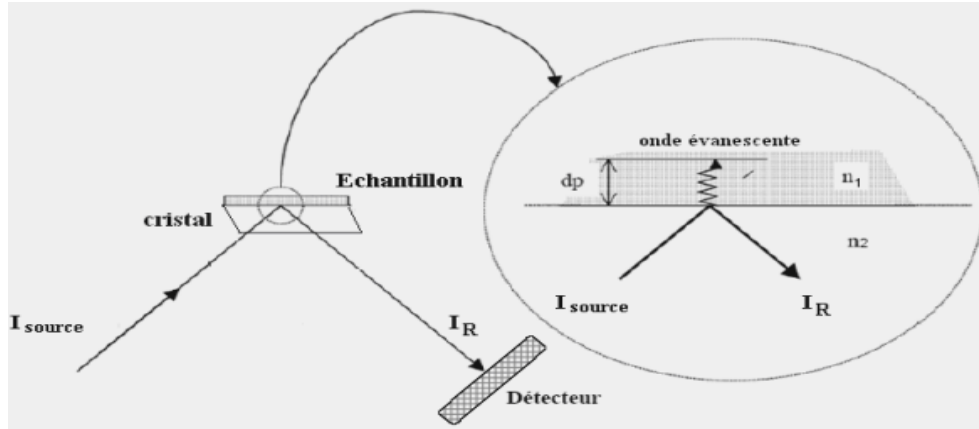
The instrumentation of infrared spectrophotometry is illustrated above. First, a beam of IR light from the source is split into two and passed through the reference and the sample respectively. [6]

The infrared range is between  $10\text{ cm}^{-1}$  and  $12500\text{ cm}^{-1}$  ( $0.8\text{ }\mu\text{m}$  to  $1000\text{ }\mu\text{m}$ ) and is divided into three areas. [7]

- ✓ Near infrared (NIR):  $0.8$  to  $2.5\text{ }\mu\text{m}$ ;  $12500 - 4000\text{ cm}^{-1}$ . [8.9]
- ✓ Medium infrared (MIR):  $2.5$  to  $25\text{ }\mu\text{m}$ ;  $4000 - 400\text{ cm}^{-1}$ . [8.9]
- ✓ Far infrared (FIR):  $25$  to  $1000\text{ }\mu\text{m}$ ;  $400 - 10\text{ cm}^{-1}$ . [8.9]

#### II.2.2.4. Case of the ATR/FTIR:

FT-IR spectrophotometers have been developed to provide an answer to limitations of dispersive spectrometers. The main difficulty to be resolved was that of slow acquisition. It was essential to imagine a device determined every frequency simultaneously. This device is the interferometer. The attenuated total reflection is called ATR (Attenuated Total Reflection). The principle of ATR is detailed on the figure below: [10]

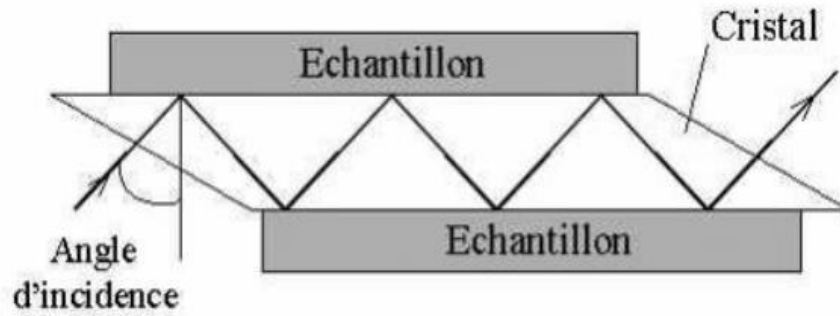


**Fig II.2.2.4.1:** Principle of attenuated total reflection (ATR). [10]

The principle of ATR devices is to subject the optical beam to several reflections at the interface between the sample and a parallelepipedic crystal (25x10x2 mm), transparent in IR but with a high refractive index  $n_2$  (ZnSe, TlBr, AgCl, diamond...) and in most cases, higher than that of the sample ( $n_1$ ). As a first approximation, according to Descartes' law, the initial IR beam of intensity  $I$  (source) passes through the crystal and undergoes total reflection at the crystal-sample interface then is directed towards the detector. In reality, the phenomenon is disturbed by the existence of a progressive wave called evanescent. This penetrates a few micrometers into the sample in direct contact with the crystal and can be absorbed.

Part of the energy is then retained, and the total reflection is attenuated. The intensity of reflected IR light is measured by a reflection detector. We call  $I_0$  the intensity reflected by a non-absorbing material taken as a reference. The reluctance  $R$  is  $R=I_R/I_0$  ( $R$  %: Percentage of reflection).

In practice, multiple internal reflections are used to amplify the absorption intensity. [11]



**Fig II.2.2.4.2:** Multi-Reflection Crystal. [11]

#### **II.2.2.5. Benefits of this technique:**

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

#### **II.3. Conclusion:**

Infrared makes it possible to find the functional groups associated with their various vibrations, sometimes unequivocally, at specific frequencies in the IR domain (middle infrared).

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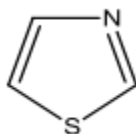
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CHAPTER III  
EXPERIMENTAL PART

### III.1. Introduction:

Heterocycle chemistry is a very important branch of organic chemistry. Among them, thiazole are a class of organic compounds related to azoles through the thiazole functional group, which has a five-chain  $C_3H_3NS$  cyclic molecular structure. [1]



In this chapter we used 1-methylthiazole as starting compounds for the preparation of a new ionic liquid 1-(hydroxyethyl)-3-methylthiazolium chloride and hydrogen sulfate thus to determine by the method of ATR / FTIR the nature of the chemical bonds present in this molecule and  $^1H$  NMR spectroscopic to determine their structure.

### III.2. Materials and methods:

#### III.2.1. Reagents:

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

Trade name	Chemical Formula	Molar mass
Thiazole	$C_4H_7NS$	101,17 g/mol
Chloroethanol	$C_2H_5ClO$	80,52 g/mol
Sulfiric acid	$H_2SO_4$	98,079 g/mol
Diethyl ether	$(C_2H_5)_2O$	74,12 g/mol
Acetonitrile	$C_2H_3N$	41,05 g/mol
Distilled water	$H_2O$	98.07 g.mol <sup>-1</sup>

**Table III.1:** the reagents used during the various syntheses.

**III.2.2. Materials:**

- ✓ Bi-glove
- ✓ Refrigerant
- ✓ Crystallizer (for prepared oil bath)
- ✓ Micropipette
- ✓ Agitator
- ✓ beakers
- ✓ Magnetic bar
- ✓ Filter paper
- ✓ funnel

**III.3. Synthesis and characterization:****III.3.1. calculates Part:**

We calculate the volume (V) of thiazole for  $n_1=0.1\text{mol}$

We calculate the mass of thiazole (m):

$$n=m/M \rightarrow m=n*M$$

$$m=0.1*101$$

$$m = 10.1 \text{ g}$$

So the mass of thiazole equal 10.1 g

We calculate the volume (V) of thiazole:

$$d= m/v \rightarrow V= m/d$$

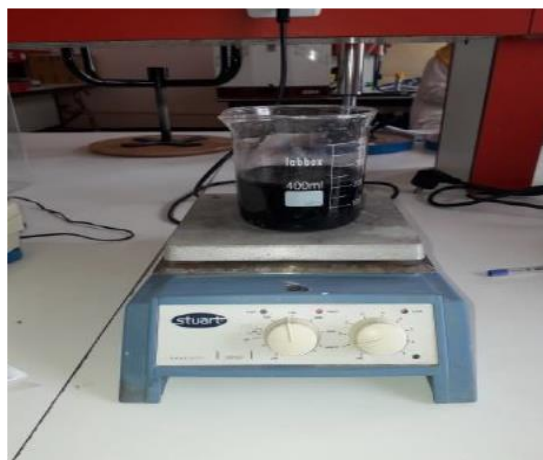
$$V= 10.1/1.067$$

$$V \approx 10 \text{ mL}$$

The volume of thiazole equal 10 mL

### III.3.2. Synthesis and characterization of 1-(hydroxyethyl)-3- methylthiazolium chloride [EtOHMTHM<sup>+</sup>] [Cl<sup>-</sup>]:

A mixture of 2-chloroethanole (0.67 mL, 10 mmol) and 1- methylthiazolium (1.1 g, 10 mmol) was heated for 24 h under vigorous magnetic stirring at 120° C.



**Fig III.1:** Heating and stirring step.

#### **Purification:**

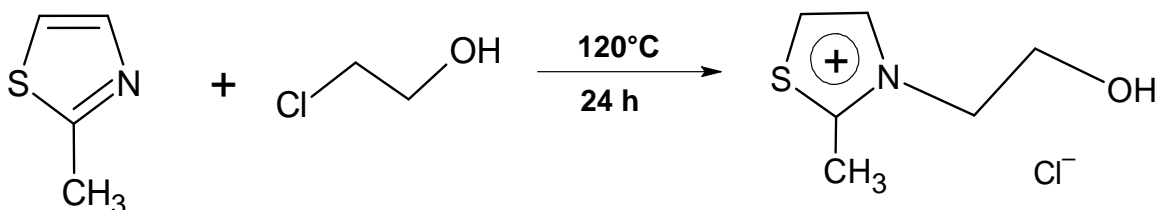
After cooling to room temperature, the product obtained (crystalline at room temperature) is finely ground, washed with diethyl ether (5 x 80 ml) then filtered with filter paper. The product is finally dried under reduced pressure for 10 hours to eliminate traces of solvent (**Fig III.4**).



**Fig III.2:** the step of filtration and drying.



**Fig III.3:** Elimination of traces of solvent by Rota-vap.



**FigIII.4:** Reaction of Quaternization. [2]

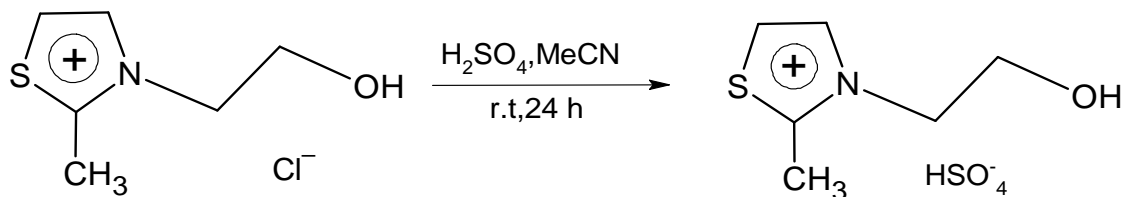
Yield: 94%

$$R_s = \frac{\text{Total mass of pure}}{\text{Theoretical mass}} \times 100$$

Appearance: Brown liquid.

### III.3.3. Synthesis and characterization of 1-(hydroxyethyl)-3- methylthiazolium sulfate [EtOHMTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>]:

An equimolar mixture of 1-(2- hydroxyethyl)-3- methylthiazolium chloride (0.01mol/ 1.5256 g) and sulfuric acid H<sub>2</sub>SO<sub>4</sub> (0.01 mol/0.5355 ml) dissolved in 30 ml acetonitrile was stirred vigorously at room temperature (initial liquid homogeneous medium) for 24 h (**Fig III.5**). Then, the product obtained was ground, washed with diethyl ether (5 X80 ml), and filtered on a sintered glass of porosity N0,4. The product was finally dried under reduced pressure for 10 h to remove traces of solvent.



**Fig III.5:** anion exchange reaction. [2]

#### III.4.Conclusion:

In this chapter we have prepared two new ionic liquids 1-(hydroxyethyl)-3-methylthiazolium chloride and 1-(hydroxyethyl)-3-methylthiazolium hydrogen sulfate.

These compounds were characterized by spectroscopic measurements of ATR/FTR to determine the nature of the chemical bonds present in this molecule and <sup>1</sup>H NMR to determine their structure.

**References:**

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## CHAPTER IV

### Results and discussion

#### Vibrational behaviors of new ionic liquids



### IV.1. Introduction:

Vibrational spectroscopies include several different techniques; the most important is the mid-infrared (IR) and NMR. These techniques provides the fundamental vibrational characteristics which are employed for the elucidation of the molecular structure.

Much recent research on vibrational modes of ionic liquids explains the effect of cation and anion at the vibrational modes. [1]

In this chapter, we study the effect of anions on the vibrational behavior of our samples by comparison between [EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>] and [EtOHMTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>]. The studied spectra are obtained by vibrational spectroscopy measurements (FTIR/ATR) and <sup>1</sup>H NMR.

### IV.2. Infrared spectroscopy:

Infrared spectroscopy is a diagnostic tool for determining the nature of the chemical bonds present in a molecule [2-3]. Indeed, the experience shows that certain frequencies of vibration, called "group frequencies", are characterized by the presence of a chemical group in the molecule studied. The mechanical theory of vibrations makes it possible to predict the existence of group frequencies from disorders of the magnitude of the different types of force constant [4-5]. Thus, infrared spectroscopy is a very powerful means of characterization for identifying molecular groups and obtaining numerous microscopic information on their conformations and their possible interactions [6-7].

#### IV.2.1. FTIR/ATR measurements:

##### IV.2.1.1. Experimental device

The measurements were carried out at the University of Tissemsilt Algeria.

##### IV.2.1.2. Experimental conditions

- Incident laser: Nd YAG (yttrium-aluminum-garnet doped with neodymium)
- Excitation wavelength: 1064 nm with an intensity of 300 mW
- Detector: Germanium diode
- Spectral resolution: 1 cm<sup>-1</sup>
- Number of scans: 8.



**Fig. IV.1:** Agilent Cary 630 FTIR Spectrometer.

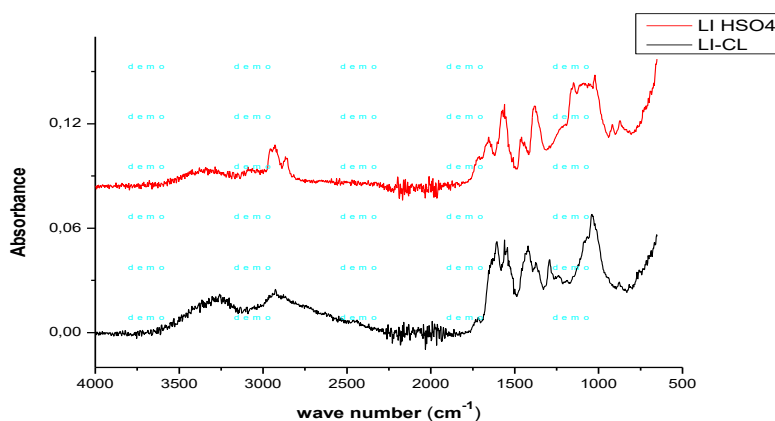
### **IV.2.2. Vibrational study of 1-(hydroxyethyl)-3-methylthiazolium chloride and hydrogen sulfate: Influence of the choice of anion on the vibrational behavior of ionic liquids.**

In this part, we will present a comparison between the two new monocationic ionic liquids 1-(hydroxyethyl)-3-methylthiazolium chloride  $[\text{EtOHMTHM}^+][\text{Cl}^-]$  and 1-(hydroxyethyl)-3-methylthiazolium hydrogen sulfate  $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$  following one spectroscopic study: FTIR/ATR.

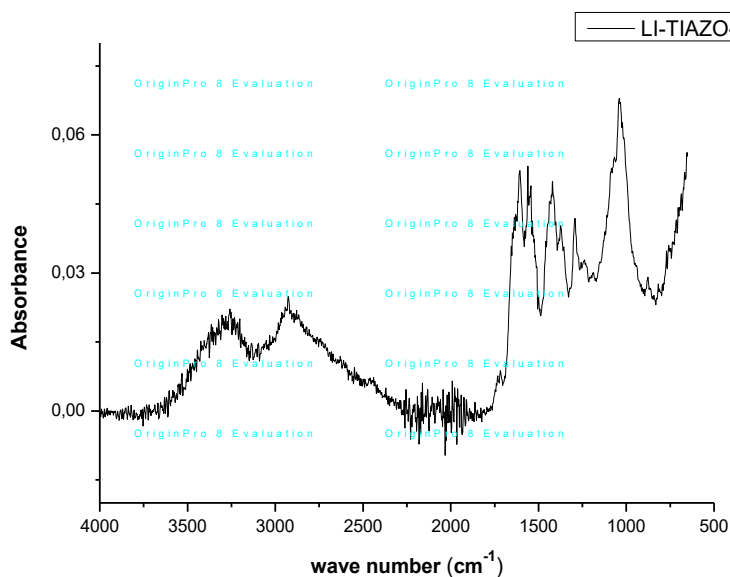
#### **IV.2.2.1. Study in FTIR/ATR spectroscopy of ionic liquids 1-(hydroxyethyl)-3-methylthiazolium chloride $[\text{EtOHMTHM}^+][\text{Cl}^-]$ and 1-(hydroxyethyl)-3-methylthiazolium hydrogen sulfate $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$ :**

The FTIR/ATR spectra  $[4000\text{-}600\text{ cm}^{-1}]$  of the two ionic liquids are illustrated in (Fig. IV.2). Both spectra were normalized with the  $620\text{ cm}^{-1}$  modes. The assignments of the modes observed in this region of the spectrum are shown in (Table. IV. 1) .all reported values of the peaks were based on the maximum peak height of the unadjusted spectra. The adjustment of the curves and the values of the frequencies were carried out according to the method of adjustment by the Lorentzian function as indicated by Bresson et al. [8]. On the IR spectra (Fig. IV.2), three well-defined spectral regions can be distinguished:  $3500\text{-}2600$ ,  $1800\text{-}1300$  and  $1300\text{-}600\text{ cm}^{-1}$ . For  $[\text{EtOHMTHM}^+][\text{Cl}^-]$ , the modes in the three spectral regions seem to have a homogeneous

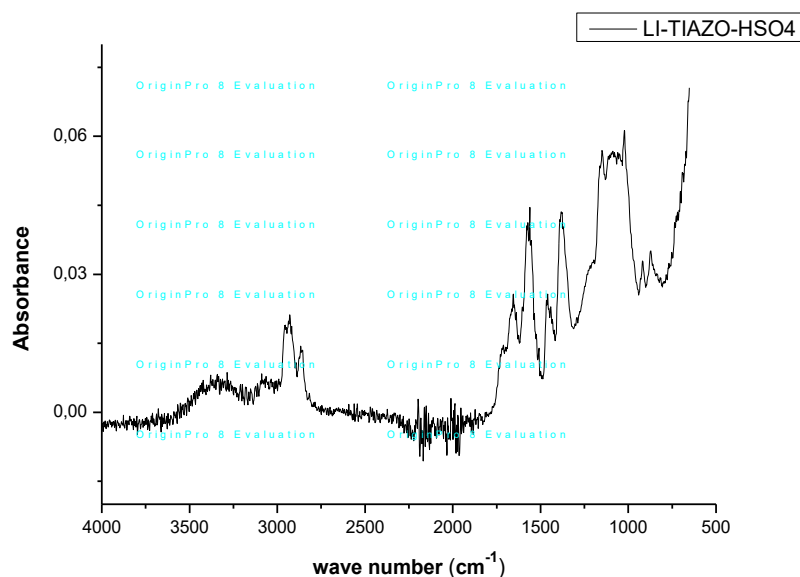
intensity, whereas for  $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$  the modes seem more intense in the spectral range  $1300\text{--}600\text{ cm}^{-1}$ .



**Fig. IV. 2.** FTIR/ATR spectra of  $[\text{EtOHMTHM}^+][\text{Cl}^-]$  and  $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$  in the spectral range  $3500\text{--}600\text{ cm}^{-1}$ .



**Fig. IV.3.** FTIR/ATR spectra of  $[\text{EtOHMTHM}^+][\text{Cl}^-]$  in the spectral range  $3500\text{--}600\text{ cm}^{-1}$ .



**Fig. IV. 4.** FTIR/ATR spectra of  $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$  in the spectral range  $3500\text{--}600\text{ cm}^{-1}$ .

**Table. IV. 1:**

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

$[\text{EtOHTHM}^+][\text{Cl}^-]$	$[\text{EtOHTHM}^+][\text{HSO}_4^-]$	ASSIGNEMENT	Refs
652 (s)		$\omega$ (N-H)/ $\text{CH}_3(\text{N})$ CN Str	[9,10]
654 (s)		$\omega$ (N-H)/ $\text{CH}_3(\text{N})$ CN Str	[9,10]
	660 (s)	$\omega$ (N-H)/ $\text{CH}_3(\text{N})$ CN Str	[9,10]
	661 (w)	$\omega$ (N-H)/ $\text{CH}_3(\text{N})$ CN Str	[9,10]
687 (s)		$\omega$ (C-H) + $\omega$ (N-H)	[9,10]
705 (m)	705(m)	$\text{CH}_2(\text{N})/\text{CH}_3(\text{N})\text{CN}$ bend	[9,10]
	735* (sh)	$\omega$ (C-H)	[9,10]
	753 (m)	$\omega$ (C-H)	[9,10]
	771 (s)	$\nu$ (N-C)	[9,10]
797 (s)		Ring HCCH as bend	[9,10]
	850* (sh)	$\rho_{\text{as}}(\text{CH}_2)$	[9,10]

873 (s)	873 (s)	$\rho_{as}(\text{CH}_2)$	[9,10]
	903 (s)	$\nu (\text{N-S})$	[11]
942 (vw)		$\rho_{as}(\text{CH}_2)$	[9,10]
	968 (vw)	$\nu (\text{N-S})$	[11]
	1017 (s)	S-OH	[11]
1027* (sh)		$\text{CH}_3\text{N Str/CH}_2\text{N Str}$	[9,10]
1038 (m)		$\text{CH}_3\text{N Str/CH}_2\text{N Str}$	[9,10]
1062 (m)	1068 (s)	$\nu (\text{C-O})$	[12]
1074 (s)		CC Str	[11]
1090 (vw)	1090* (sh)	CC Str	[11]
1119 (vw)	1119 (w)	CC Str	[9,10]
1175 (m)	1175 (m)	Ring as Str $\text{CH}_2(\text{N})$ and $\text{CH}_3(\text{N})\text{CN}$ Str/CC	[9,10]
1198 (m)	1198 (m)	Ring s $\text{CH}_2(\text{N})$ and $\text{CH}_3(\text{N})\text{CN}$ Str	[9,10]
	1224 (m)	$\nu (\text{S-O})$	[11]
1256 (w)	1256 (m)	Ring ip as strstr	[9,10]
	1336 (m)	$\nu (\text{C-C})$	[9,10]
1353 (m)	1353 (m)	$\nu (\text{C-C})$	[9,10]
1372 (w)	1372* (sh)	$\delta (\text{CH}) - \delta_s (\text{CH}_3)$	[12]
1388* (sh)	1388(m)	$\rho(\text{N-H})$	[9,10]
	1412* (sh)	$\rho(\text{N-H})$	[9,10]
1431 (m)	1431* (sh)	$\rho(\text{N-H})$	[9,10]
1438 (m)	1438 (m)	$\delta (\text{CH}_2)/\text{CCH HCH}$ as bend	[9,10]
	1462* (sh)	$\delta (\text{CH}_2)/\text{CCH HCH}$ as bend	[9,10]
1481 (w)	1481 (m)	$\delta (\text{CH}_2)/\text{CCH HCH}$ as bend	[9,10]
1570 (s)	1570* (sh)	as Str $\text{CH}_2(\text{N})/\text{CH}_3(\text{N})\text{CN}$ 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]
1742 (w)	1742 (w)	Overtone =C-H str	[13]
2481(w)	2481 (vw)	$\nu (\text{C=C})$	[9,10]
2600 (vw)		$\nu_s(\text{CH}_2)$	[9,10]
2672 (w)		$\nu_s(\text{CH}_2)$	[9,10]

2714 (vw)		$v_s(\text{CH}_2)$	[9,10]
			[9,10]
	2842 (vw)	$v_s(\text{CH}_2)$	[9,10]
2865 (m)	2865 (w)	$v_s(\text{CH}_2)$	[9,10]
2877 (m)		$v_{as}(\text{CH}_2)$	[9,10]
	2907(m)	$v_{as}(\text{CH}_2)$	[9,10]
2928 (w)		$v_s(\text{CH}_3)$	
2954 (m)		$\text{CH}_3(\text{N})\text{HCH}$ as Str	[9,10]
2966 (m)		$v_{as}(\text{CH}_3)$	[9,10]
	2972 (w)	$v_{as}(\text{CH}_3)$	[9,10]
2992* (sh)	2992 (w)	$v_{as}(\text{CH}_3)$	[9,10]
3038 (s)		= C-H Str	[9,10]
3040 (sh)	3040* (sh)	= C-H Str	[9,10]
	3086 (s)	= C-H Str	[9,10]
3116 (s)	3116 (s)	Ring NC(H)NCH Str	[9,10]
3154 (s)	3154 (m)	Ring NC(H)NCHStr	[9,10]
3165 (sh)		Ring NC(H)NCH Str	[9,10]
	3250* (sh)	$v(\text{O-H})$	[11,12]
3254 (w)		$v(\text{O-H})$	[11,12]

#### IV.2.2.1.1. Study in the spectral region 1300-600 $\text{cm}^{-1}$ :

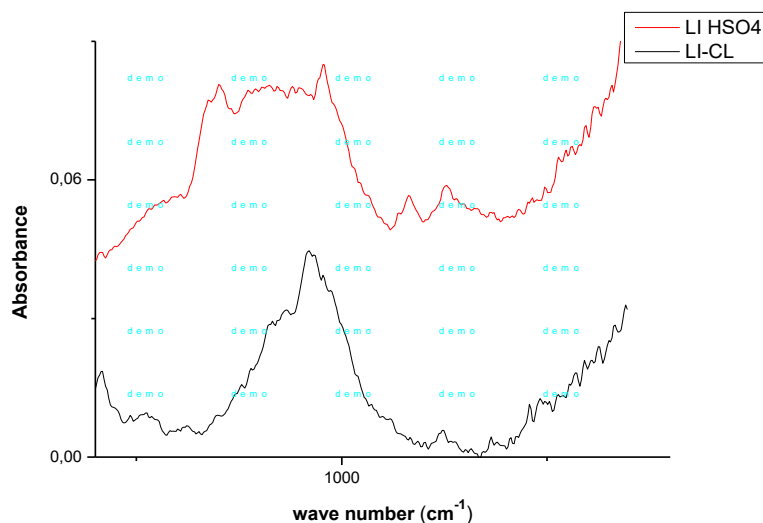
In this spectral region (**Fig. IV. 5**) where the two spectra have been normalized with the mode at  $1175 \text{ cm}^{-1}$ , numerous differences in vibrational behavior are observed depending on the choice of anion. For the anion  $\text{Cl}^-$ , the spectral region  $700\text{-}600 \text{ cm}^{-1}$  is more intense than for  $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$  with the predominance of 3 modes at  $661$ ,  $686$ , and  $706 \text{ cm}^{-1}$  while the single-mode at  $661 \text{ cm}^{-1}$  corresponding to the anion  $\text{HSO}_4^-$  seems to be intense. The modes at  $661$ , and  $687 \text{ cm}^{-1}$  are assigned to the out-of-plane wagging mode (N-H) and the stretching mode  $\text{CH}_3(\text{N}) \text{CN}$ , and the peak at  $706 \text{ cm}^{-1}$  corresponds to the deformation mode  $\text{CH}_2(\text{N})/\text{CH}_3(\text{N})\text{CN}$  (bending) [9,10].

Conversely, in the spectral region of  $950$  to  $700 \text{ cm}^{-1}$ , the vibrational behavior for  $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$  seems to present several modes with two doublets and a shoulder ( $735$ ,

754, 771  $\text{cm}^{-1}$  and 850, 873, 903  $\text{cm}^{-1}$ ). While for  $[\text{EtOHMTHM}^+][\text{Cl}^-]$  we observe only two modes in 796 and 868  $\text{cm}^{-1}$  assigned to the deformation of the HCCH cycle and the asymmetric rocking modes (rocking) of  $\text{CH}_2$  respectively.

The intense peak at 903  $\text{cm}^{-1}$  observed for  $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$  is assigned to the stretching mode of (N-S) [14,9]. All the assignments of the modes observed in the (Fig. IV.5) are presented in the (table. IV. 1) we notice the presence of new intense modes by comparing the two samples: at 1017 and 1224  $\text{cm}^{-1}$  assigned to the mode stretching (S-O) of the  $\text{HSO}_4^-$  anion and the splitting of other vibrational modes [11].

Thus, the presence of the  $\text{HSO}_4^-$  anion seems to split the single peak at 1175  $\text{cm}^{-1}$  observed for the  $\text{Cl}^-$  anion: we note the doublet 1156, 1175  $\text{cm}^{-1}$  for the  $\text{HSO}_4^-$  anion, attributed to the mode of CN stretch of  $\text{CH}_2$  (N)/ $\text{CH}_3$  (N) [9, 10]. Conversely, the doublet observed for the  $\text{Cl}^-$  anion at 1062 and 1074  $\text{cm}^{-1}$  appears as a single peak for the  $\text{HSO}_4^-$  anion centered at 1068  $\text{cm}^{-1}$  assigned to the stretch mode (C-O) [12]. It is therefore noted that this spectral zone seems to be very sensitive to interactions with anions and can serve as a witness to the influence of one or the other anion in the vibrational behavior of thiazolium.



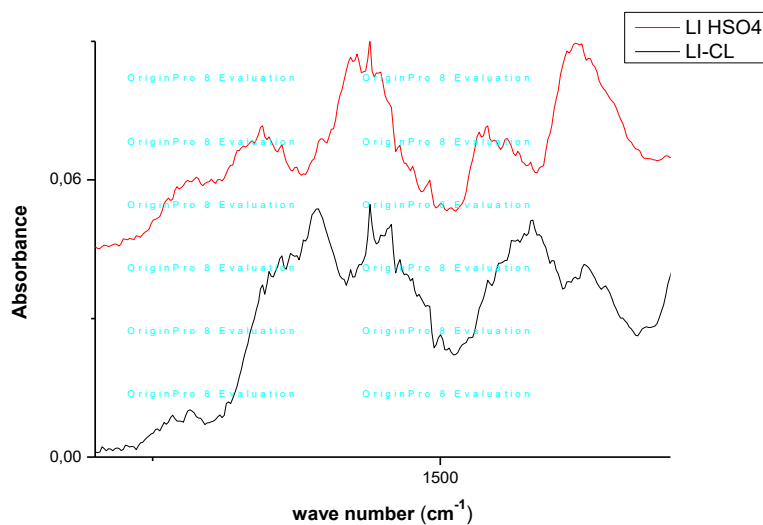
**Fig. IV.5.** FTIR/ATR spectra of  $[\text{EtOHMTHM}^+][\text{Cl}^-]$  and  $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$  in the spectral range 1300–600  $\text{cm}^{-1}$ .

#### IV. 2.2.1.2. Study in the spectral region 1800-1300cm<sup>-1</sup>:

In this spectral zone (**Fig. IV.6**) in which the spectra have been normalized to the mode at 1571 cm<sup>-1</sup> for [EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>] and 1578 cm<sup>-1</sup> for [EtOHMTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>], spectra with several modes are observed for the HSO<sub>4</sub><sup>-</sup> anion than for the Cl<sup>-</sup> anion. We note that the stretch mode C-C at 1347 cm<sup>-1</sup> is transformed for the HSO<sub>4</sub><sup>-</sup> anion at 1353 and 1336 cm<sup>-1</sup> [9,10]. The spectral range of the CH<sub>2</sub> deformation modes (1500-1400 cm<sup>-1</sup>) also seems to be influenced by the choice of anion less importantly.

In the 1800-1500 cm<sup>-1</sup> spectral region, there is a change in the frequency of the stretching vibrational mode attributed to the C=C ring and H-C-H bonds. A frequency shift is observed for the vibrational mode at 1571 cm<sup>-1</sup> observed for the Cl<sup>-</sup> anion at 1578 cm<sup>-1</sup> with a shoulder at 1570 cm<sup>-1</sup> for the HSO<sub>4</sub><sup>-</sup> anion.

Conversely, the vibrational mode at 1645 cm<sup>-1</sup> for the ionic liquid with the HSO<sub>4</sub><sup>-</sup> anion transforms into an unresolved doublet at 1677 and 1692 cm<sup>-1</sup> for the Cl<sup>-</sup> anion [13]. We also observe the presence of C-H harmonic stretching modes with a frequency shift between the two anions: 1743 cm<sup>-1</sup> for HSO<sub>4</sub><sup>-</sup> against 1750 cm<sup>-1</sup> for Cl<sup>-</sup>.



**Fig. IV.6.** FTIR/ATR spectra of [EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>] and [EtOHMTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>] in the spectral range 1800–1300 cm<sup>-1</sup>.



### IV. 2.2.1.3. Study in the region 3500-2600cm<sup>-1</sup>:

In this spectral region (**Fig. IV.7**) where the spectra have been normalized to the mode at 3096 cm<sup>-1</sup> for [EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>] and 3086 cm<sup>-1</sup> for [EtOHMTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>], we observe the vibrational modes assigned to the valence vibrations of C-H, N-H and OH. We observe different vibrational behaviors depending on the anion: for the anion Cl<sup>-</sup>, there are more vibrational modes than for the anion HSO<sub>4</sub><sup>-</sup>. [9, 10].

To quantify these differences, one can decompose the infrared spectra according to 4 spectral zones. Covering the following 4 groups of vibrational modes:

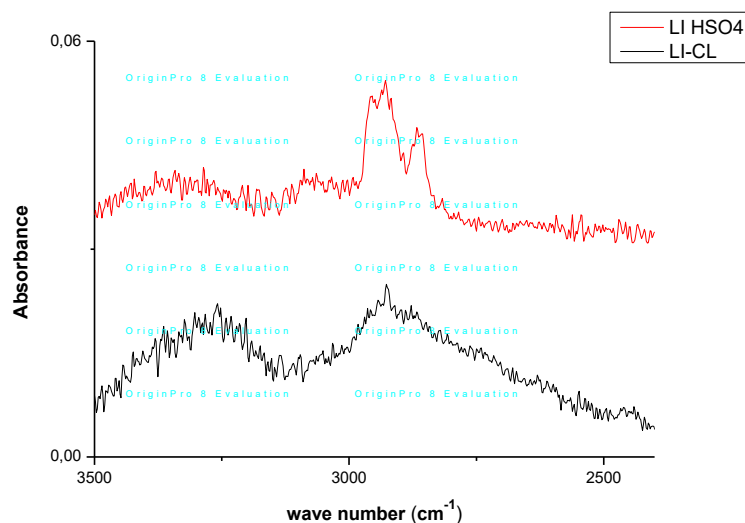
- ✓ 2995–2650 cm<sup>-1</sup> assigned to the C-H valence vibrational modes.
- ✓ 3090–3035 cm<sup>-1</sup> assigned to the vibrational mode of the valence of =C-H.
- ✓ 3200–3100 cm<sup>-1</sup> assigned to vibrational modes of the valence of N-H.
- ✓ 3500–3200 cm<sup>-1</sup> assigned to vibrational modes of the valence of O-H (**Fig. IV.7**).

In the 2995–2650 cm<sup>-1</sup> spectral region. Many more peaks are observed in the 2950 cm<sup>-1</sup> region assigned to the vibrational modes  $\nu$  as (CH<sub>3</sub>) in the case of the anion Cl<sup>-</sup>, certainly due to a degree of greater freedom of vibration linked to the fact that the Cl<sup>-</sup> anion has a smaller size than the HSO<sub>4</sub><sup>-</sup> anion in the structure of the ionic liquid. In 3090–3035 cm<sup>-1</sup>, we notice that the mode assigned to the vibration =C-H stretching admits a well-resolved doublet with the frequencies 3055 and 3038 cm<sup>-1</sup> for the anion Cl<sup>-</sup> whereas in the case of the ionic liquid with the anion HSO<sub>4</sub><sup>-</sup> we observe a peak at 3086 cm<sup>-1</sup> and a shoulder at 3042 cm<sup>-1</sup>.

This change in vibrational behavior is also accompanied by a significant shift in frequency of about 30 cm<sup>-1</sup> for the first component. In the area of vibrational modes of the valence of N-H, we note the same two peaks at different frequencies and amplitudes: for the anion Cl<sup>-</sup>, we observe the peaks at 3141 and 3096 cm<sup>-1</sup> whereas for the anion HSO<sub>4</sub><sup>-</sup> they are found with a frequency shift greater than 15 cm<sup>-1</sup>:

3154 and 3116 cm<sup>-1</sup>. In terms of amplitudes, the intensity ratio I<sub>3141</sub>/I<sub>3096</sub> can be compared with the ratio I<sub>3154</sub>/I<sub>3116</sub>: I<sub>3141</sub>/I<sub>3096</sub> = 1.09 and I<sub>3154</sub>/I<sub>3116</sub> = 0.69. We notice an inversion of intensity between the two peaks depending on the anion chosen. For the last spectral zone, we also observe a significant shift in frequency for the vibrational mode of the valence of O-H since for the anion Cl<sup>-</sup> we observe a broad low intensity peak centered on 3254 cm<sup>-1</sup> while for the anion HSO<sub>4</sub><sup>-</sup> there is a wide shoulder at 3250 cm<sup>-1</sup>. All these vibrational changes confirm that the spectral region

3500-2600  $\text{cm}^{-1}$  is very sensitive to the choice of the anion in the constitution of the ionic liquid and its physical properties.



**Fig. IV.7.** FTIR/ATR spectra of  $[\text{EtOHMTHM}^+][\text{Cl}^-]$  and  $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$  in the spectral range 3500–2400  $\text{cm}^{-1}$ .

### IV.3. Study in $^1\text{H}$ -NMR spectroscopy of ionic liquids 1-(hydroxyethyl)-3-methylthiazolium chloride $[\text{EtOHMTHM}^+][\text{Cl}^-]$ and 1-(hydroxyethyl)-3-methylthiazolium hydrogen sulfate $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$ :

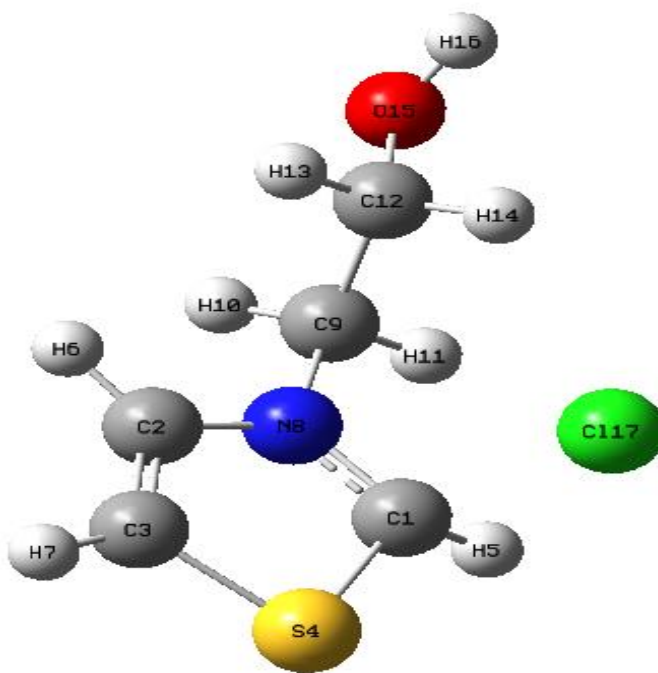
We did an optimization before doing the NMR

Nuclear magnetic resonance (NMR) is considered a basic technique for characterizing organic materials. The  $^1\text{H}$ -NMR isotropic chemical shifts for  $[\text{EtOHMTHM}^+][\text{Cl}^-]$  and  $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$  are calculated by using the GIAO (gauge-independent atomic orbital) method at DFT/B3LYP/6-31G (d, p) level of theory with respect to the TMS values. So before using the NMR.

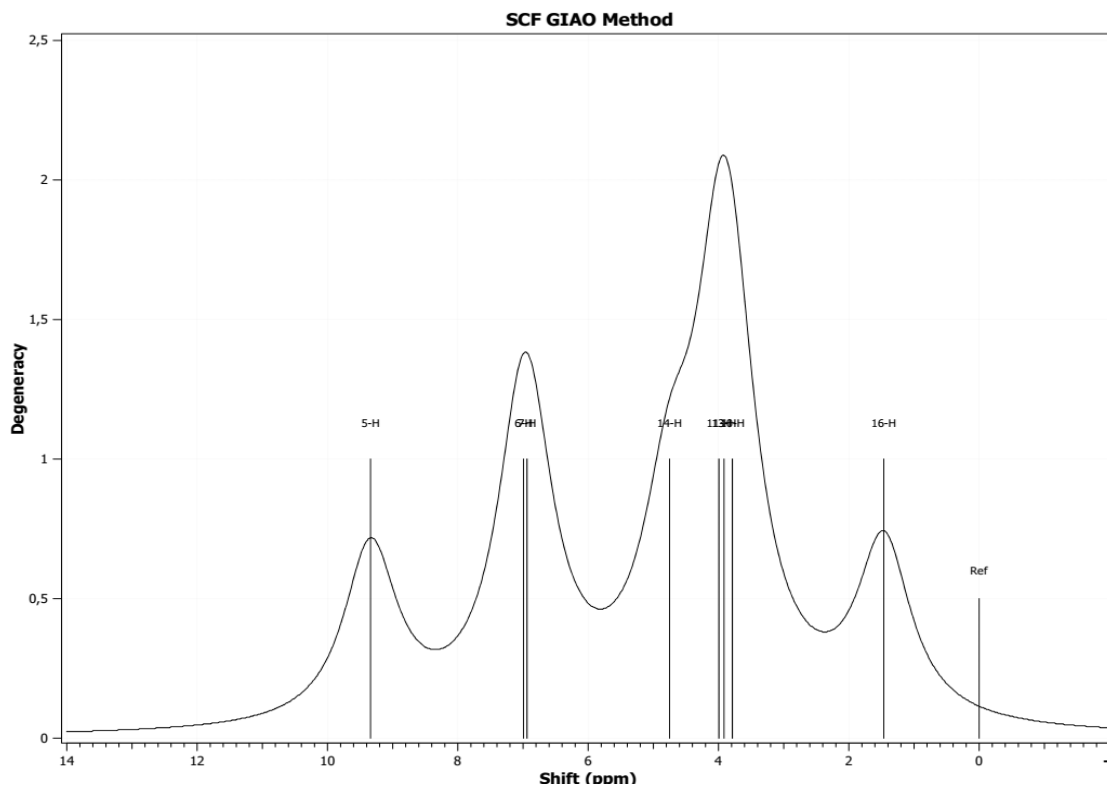
**IV.3.1. Characterization of [EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>] by <sup>1</sup>H-NMR spectroscopic:**

[EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>] EMTh2 contains 8 hydrogen atoms, Three are linked to the thiazole ring, four are connected to the ethyl fragment, and one to the hydroxyl fragment.

As detailed in **Fig IV.9** The <sup>1</sup>H isotropic chemical shifts are calculated in the range 0.93 - 10 ppm, and observed in the range 1.5- 9.3 ppm. For [EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>], the computed isotropic chemical shifts of thiazole ring protons (H5, H6, H7,) appear in the range 6.9 -9.3 ppm. The range 3.8- 4.7ppm corresponds to the ethyl's protons (H10, H11, H13, H14) for the protons of the Hydroxyl group, the chemical was calculated at the value 1.5 ppm.



**Fig IV.8:** Structure of 1-(hydroxyethyl)-3 methylthiazolium chloride  
[EtOHMTHM<sup>+</sup>][Cl<sup>-</sup>]



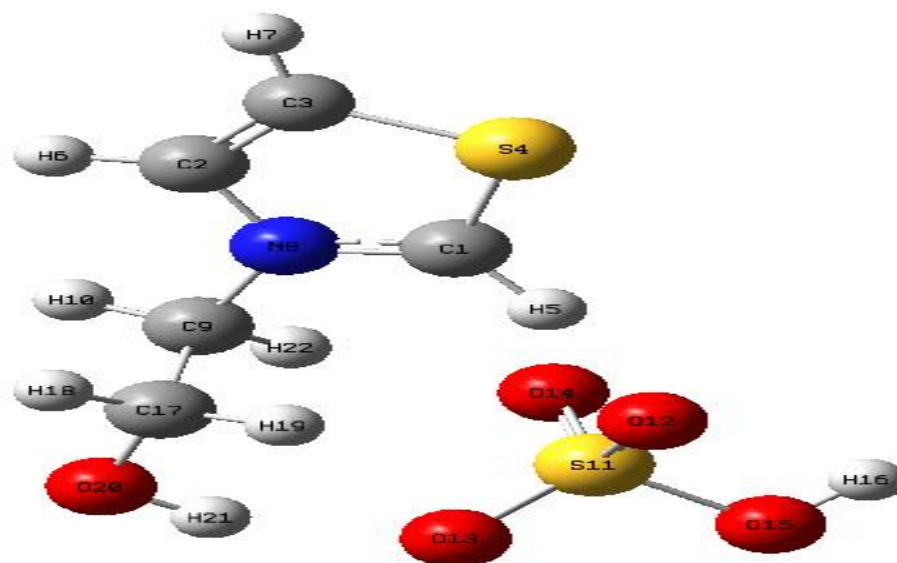
**Fig IV.9:**  $^1\text{H}$ -NMR spectra of 1-(hydroxyethyl)-3 methylthiazolium chloride  $[\text{EtOHMTHM}^+][\text{Cl}^-]$ .

### IV.3.2. Characterization of $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$ by $^1\text{H}$ -NMR spectroscopic:

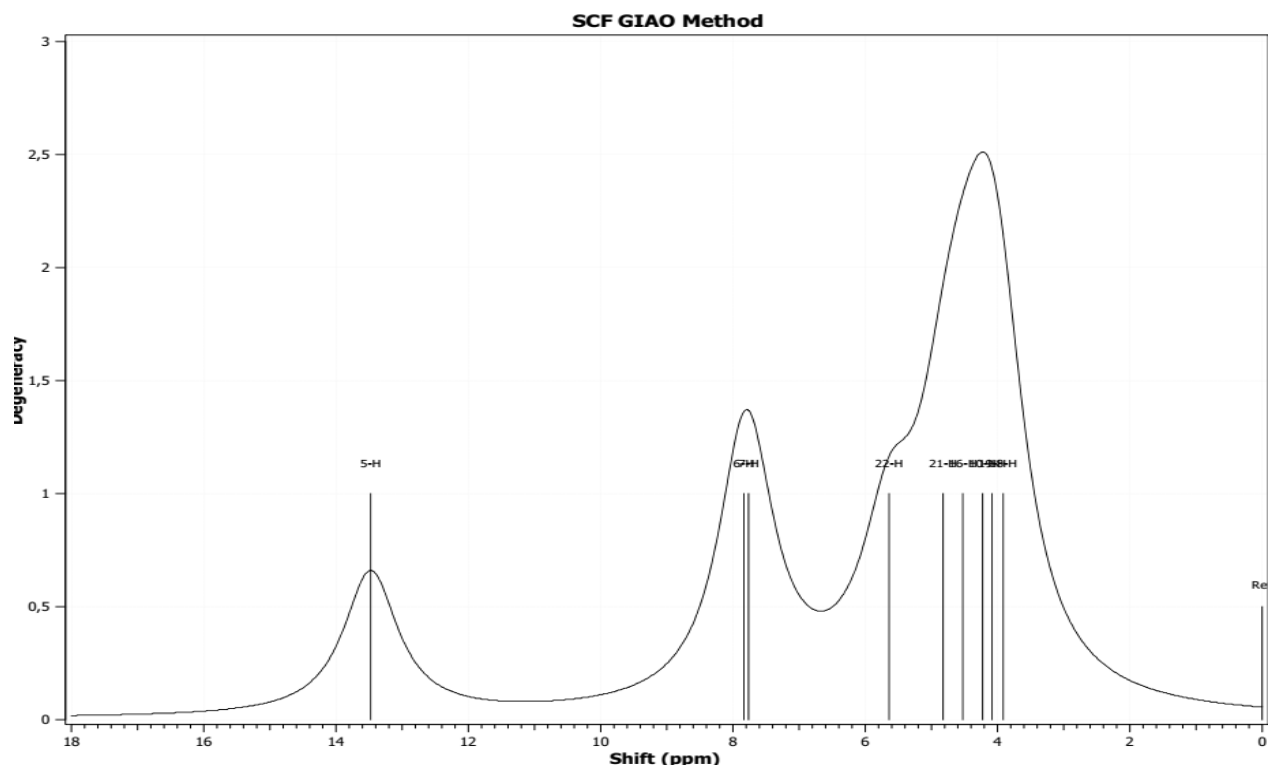
$[\text{EtOHMTHM}^+][\text{HSO}_4^-]$  Contains 9 hydrogen atoms. 8 was connected in the same way similar to  $[\text{EtOHMTHM}^+][\text{Cl}^-]$  and 1 hydrogen was linked in sulfate atom.

As detailed in **Fig IV.11**. The  $^1\text{H}$  isotropic chemical shifts are calculated in the range 0,93 -14 ppm, and observed in the range 3,9- 13,5 ppm. For  $[\text{EtOHMTHM}^+][\text{HSO}_4^-]$ , the computed isotropic chemical shifts of thiazole ring protons (H5, H6, H7) appear in the range 7.9 -13.5 ppm. The range 3.9- 5.6ppm corresponds to the ethyl's protons (H10, H18, H19, and H22). For the protons of the Hydroxyl group, the chemical was calculated at the value 4.8 ppm (H21). The range 4.5ppm corresponds to the sulfate protons (H16).

**Remark:** It was observed that there is a shift of the peaks and also the appearance of a new peak corresponds to the sulfate proton.



**Fig IV.10:** Structure of 1-(hydroxyethyl)-3 methylthiazolium hydrogen sulfate  
[EtOHMTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>].



**Fig IV.11:** <sup>1</sup>H-NMR spectra of 1-(hydroxyethyl)-3 methylthiazolium hydrogen sulfate  
[EtOHMTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>].

**IV.3.Conclusion:**

In this study, we synthesized a new Ionic liquid [EtOHMTHM<sup>+</sup>][HSO<sub>4</sub><sup>-</sup>] which was characterized by FTIR/ATR and <sup>1</sup>H-NMR. The results of vibrational spectroscopies were compared with those obtained on the same intermediate compound [EtOHMTHM<sup>+</sup>] [Cl<sup>-</sup>] that differs only by the type of anion. The anion seems to play an important influence in vibrational behavior.

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### **General Conclusion :**

We conclude this thesis by confirming that this new class of solvents with real properties is not encountered with conventional solvents. Their non-volatility allows easy recycling since, in the distillation of the reaction mixture, they are the only liquids not to evaporate, even during distillation under reduced pressure. As solvents, they have certain properties that approximate a polar solvent like ethanol and others that would correspond to a solvent apolar, such as insolubility in water. The domains remaining to be explored are vast. Many Cation-anion associations are capable of producing new ionic liquids. There are probably still many possible applications of these molten salts at ambient temperature, both in organic chemistry and analytical chemistry.

We recall that the objective of this work is the synthesis of new ionic liquids corresponding to thiazolium.

These compounds were characterized by spectroscopic analysis: FTIR/ATR and  $^1\text{H-NMR}$

In this part, we made a comparison between the vibrational modes obtained by FTIR/ATR and  $^1\text{H-NMR}$  of 1-(hydroxyethyl)-3-methylthiazolium chloride and 1-(hydroxyethyl)-3-methylthiazolium hydrogen sulfate in order to determine the vibration modes of the anion  $\text{HSO}_4^-$ . So the choice of the anion can affect vibrational behavior.