ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

SYNTHESIS AND CHARACTERIZATION OF TRIFLOUROACETYLATED IMIDAZOLE BASED IONIC LIQUIDS

Graduate Project (Chem. 774)

BY: Tarekegn Heliso

June, 2010

SYNTHESIS AND CHARACTERIZATION OF TRIFLOUROACETYLATED IMIDAZOLE BASED IONIC LIQUIDS

A Project Work Submitted to the School of Graduate Studies of
Addis Ababa University in Partial Fulfilment of the Requirements for the
Degree of Master of Science in Chemistry

By: Tarekegn Heliso

June, 2010

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTEMENT OF CHEMISTRY

SYNTHESIS AND CHARACTERIZATION OF TRIFLOUROACETYLATED IMIDAZOLE BASED IONIC LIQUIDS

Approved by the examining board:

Signature

Dr. Ignacio. V. Garcia
(Advisor) ----------------------------

Prof. V. J. T. Raju
(Examiner) -----------------------------

Dr. Yonas Chebude
(Examiner) ------------------------------

Declaration

I, the undersigned declare that this is my original work and has not been submitted for a degree in any other university and all sources of material used for the project have been duly acknowledged.

Name: Tarekegn Heliso

Signature____________________________

This project has been submitted for examination with my approval as a university advisor:

Name: Dr. Ignacio. V. Garcia

Signature____________________

Prof. V. J. T. Raju
(Examiner)

Signature____________________

Dr. Yonas Chebude
(Examiner)

Signature____________________

TABLE OF CONTENTS

Page

Acknowledgements

Looking at all the things I have had a chance to do thus far, I realize that many of those things (or may be all of them) might never have happened if for not the people who have been involved in my life. I feel privileged to acknowledge these individuals for what I have right now.

First and above all I want to acknowledge the almighty God. Then I sincerely thank Dr. Ignacio V. Garcia, my advisor, who introduced me to the field of ionic liquids and made it a very challenging and enjoyable experience. Heartfelt thanks goes to Ato Atakilit who patiently helped me technically and in every aspect of my project.

Finally, I want to acknowledge the head of the chemistry department of Addis Ababa Unversity, Dr. Yonas Chebude for his cooperation and some of the department members; Prof. V.J.T. Raju and Prof. Wondimagegn Mamo for their providence of suggestions and chemicals.

List of Tables

List of Figures

List of Schemes

List of Abbreviations

cP	Centi poise
ESI	Eletrospray ionization
GC	Gas chromatography
ILs	Ionic liquids
MS	Mass spectroscopy
NMR	Nuclear magnetic resonance
RTIL	Room temperature ionic liquids
TFAA	Triflouroacetic anhydride
TSILs	Task-specific ionic liquids
[BMIM][PF$_6$]	1-butyl-3-methylimidazolium hexflourophosphate
[BMIM][BF$_4$]	1-butyl-3-methylimidazolium tetraflouroborate

Abstract

The ionic liquid field has been extensively dominated by imidazolium salts with anions most frequently being fluorine-containing. By modifying the anion or the fluorine containing cation, a wide range of properties can be tuned. Ionic liquids with fluorine-containing groups in the cation are promising solvents for electrochemical, photovoltaic, surfactant and synthetic applications. Previously, 1-methyl-3-triflouroacetyl imidazolium trifluoroacetate ionic liquid was synthesised but with high melting point. Following this synthesis, in the present study, a triflouroacetylated imidazole based ionic liquid with longer alkyl chain; 1-pentyl-3-triflouroacetyl imidazolium based ionic liquid was synthesized by alkylation of imidazole followed by triflouroacetylation and resulted in a viscous solid. The ionic liquid was characterized by NMR. In the second trial, the same procedure was repeated increasing the reaction time and the crude product was distilled under vacuum and yielded a new crystalline hydroxide anion based 1-pentyl-3-triflouroacetyl imidazolium ionic liquid. This result was evident from NMR characterization and elemental analysis. This ionic liquid was soluble in water and in most of organic solvents and was found to be highly hygroscopic and an electrolyte.

Key words: *alkylation; triflouroacetylation; ionic liquids*

1. Introduction

1.1 Ionic Liquids (ILs)

Ionic liquids (ILs) are defined as salts with melting points below 100 ^{0}C that consists entirely of ions, typically an organic cation and an inorganic anion. They are of interest to green chemists as alternative solvents because of their inherent low volatility. Ionic liquids have many properties that have led to their use as reaction media and in materials processing. They are thermally stable and can be used over a wide temperature range compared with conventional solvents and their properties can be readily adjusted by varying the anion and cation. This new chemical group can reduce the use of hazardous and polluting organic solvents due to their unique characteristics as well as taking part in various new syntheses. The terms room temperature ionic liquid (RTIL), non-aqueous ionic liquid, molten salt, liquid organic salt and fused salt have all been used to describe these salts in the liquid phase [1].

Ionic liquids have also been described as designer solvents as their properties can be adjusted to suit the requirements of a particular process. Properties such as melting point, viscosity, density, and hydrophobicity can be varied by simple changes to the structure of the ions [2]. Therefore, the covalent tethering of a functional group to one or both of the ions of an ordinary ionic liquid can imbue the resulting salt with a capacity to interact with dissolved substrates in specific ways. These low-melting salts are called task-specific ionic liquids (TSIL). Until recently, this area of TSIL research has been the most active, and TSILs are finding an increasing number of applications in synthesis, separations, catalysis, and electrochemistry [3].

Until recently, the ionic liquid field has been extensively dominated by imidazolium salts with anions most frequently being fluorine-containing. Following the synthesis of the first fluorine containing ionic liquids, 3-methyl-1-(2,2,2-trifluoroethyl) imidazolium salts, which were characterized as hydrophobic, highly conductive ambient-temperature molten materials, the interest in ionic liquids with fluoroalkyl-substituted cations has grown markedly [4]. By modifying the anion or the fluorine- containing substituent on the cation, a wide range of properties of fluorine-containing ionic liquids can be tuned, including, for example, viscosity, melting point, density, conductivity, solubility, liquid range, thermal and hydrolytic stability, and heat of formation. The influence of inter-ion hydrogen bonding can be diminished by introducing fluorine-containing groups into the cation and especially when employing anions such as bis(trifluorosulfonyl) amide and perfluoroalkyldiketonate [5]. They are promising solvents for electrochemical, photovoltaic, surfactant and synthetic applications.

The "work horses" in the field of ionic liquids research used to be [BMIM][PF_6] and [BMIM][BF_4] which are still widely used because of their relatively easy preparation and purification. However, these two ionic liquids suffer from the instability of their anions to hydrolysis, which will restrict their use to applications under anhydrous conditions since their reaction with water releases toxic and highly corrosive HF. Other ionic liquids that are stable to hydrolysis, such as those carrying the bis(trifluoromethylsulfonyl)imide ion have subsequently been developed but these systems suffer from the intrinsically high price of the anion. Taking these considerations into account, ionic liquids with halogen-free anions have become an important area of research. Several of these systems have been described such as alkyl sulfonates, alkyl sulfates and dialkyl phosphates [10a].

1.2 History of Ionic Liquids

Ionic liquids have been known for a long time, but their extensive use has recently become significant. The earliest discovery of an ionic liquid can be dated to the middle of the nineteenth century, when some "red oil" was observed in a Friedel-Crafts reaction. A few decades later, in 1914, the first room-temperature ionic liquid (RTIL) ethylammonium nitrate, [$EtNH_3$][NO_3], was synthesized. In the 1970s Osteryoung and Wilkes succeeded in preparing room-temperature liquid chloroaluminate melts. In the 1980s Hussey and Seddon started to use these alkylpyridinium tetrahalidoaluminate, [Rpy][$AlCl_3X$], ionic liquids as solvents in transition metal complex studies. The first organic reaction that was carried out in an acidic tetrachloroaluminate ionic liquid was Friedel-Crafts alkylation, and since then ionic liquids have been used as reaction solvents in various organic reactions. Following this discovery, Hussey and Wilkes began studying the effect of changing the cation, which led to the dialkylimidazolium-based ionic liquids. The first was 1-ethyl-3-methylimidazolium chloride, shown in Figure 1. However, these liquids were extremely sensitive to moisture, and were not suitable for open-air applications. This led Wilkes and Zaworotko to study the synthesis of water- and air-stable dialkylimidazolium ionic liquids [6].

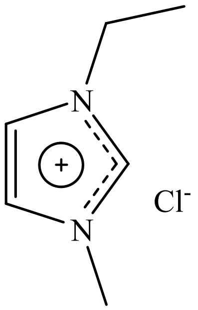


Figure 1. The first dialkylimidazolium-based ionic liquid synthesized by Wilkes .et al.

The first generation of ionic liquids that contain aluminium were very hygroscopic and air-sensitive, and therefore they are not easy to handle. A few years later this problem was solved when new air- and water-stable anions, such as halides, $[PF_6]^-$, $[BF_4]^-$ and $[CF_3CO_2]^-$, were discovered. Since then, a wide selection of different ionic liquids has been synthesized. These ionic liquids are the second generation of ILs [7].

Only recently, ionic liquids are being considered and studied as potential “clean” solvents for synthesis. In 1998, a report on the formation of relatively large, structurally complex cations derived from the antifungal drug miconazole was published by Davis et al. (Figure 2). This initiated the idea that ionic liquids could incorporate functional groups in their structure. Such ionic liquids are called task-specific ionic liquids or functionalized ionic liquids. These can be defined as ionic liquids containing a functional group that is covalently tethered to the anion or cation or even both. These kinds of ionic liquids are often especially designed to perform a specific task [8].

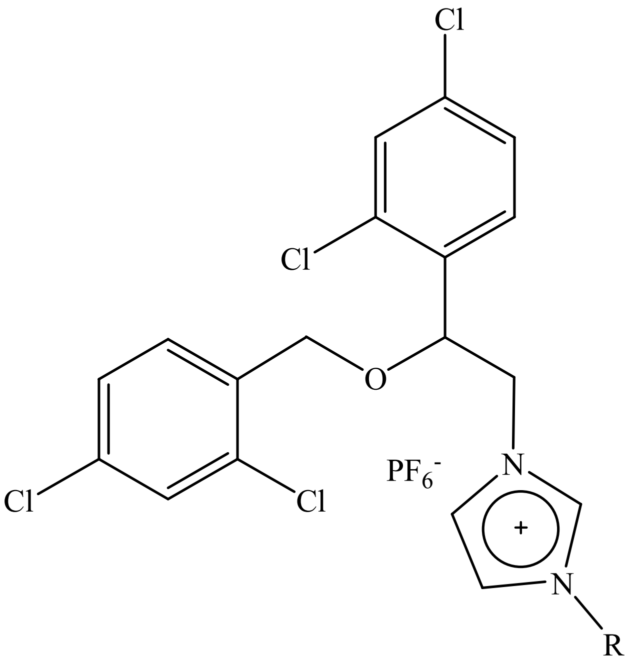


Figure 2. The first "task-specific ionic liquid" based on the miconazole cation.

1.3 Basic properties of Ionic Liquids

The chemical and physical properties of ionic liquids can be tuned by selecting a certain anion and cation combination. Also, different ionic liquids can be mixed together to make binary or ternary ILs.

1.3.1 Melting point

ILs are made of positively and negatively charged ions, whereas water and organic solvents, such as toluene and dichloromethane, are made of molecules. The structure of ILs is similar to the table salt such as sodium chloride which contains crystals made of positive sodium ions and negative chlorine ions, not molecules. While, salts do not melt below 800 ^{o}C, most of ILs remain liquid at room temperature. The melting points of sodium chloride and lithium chloride are known as 801 and 614 °C, respectively. Since these conventional molten salts exhibit high melting points, their use as solvents in applications is severely limited. However, RTILs are liquid generally up to 200 °C. ILs have a wide liquidus ranges. The adopted upper melting temperature limit for the classification as 'IL' is known as 100 °C and higher melting ion systems are generally referred as molten salts [10a].

The melting point of large, unsymmetric ions, whose charge can be distributed over a large volume, is low and hence the melting point of the IL can be far below 0 ºC. Furthermore, ILs do not evaporate like volatile organic compounds do, but they will decompose at high temperatures. The decomposition temperature depends on the IL, and particularly on the anion. The low melting point and negligible vapour pressure lead to a wide liquid range, often more than 300-400 ºC. Conventional molten salts exhibit high melting points; their use as solvents in applications is severely limited. The ILs remain liquid at room temperature due to the reason that their ions do not pack well. Combination of bulky and asymmetrical cations and evenly shaped anions form a regular structure namely a liquid phase. The low melting points of ILs are a result of the chemical composition. The combination of larger asymmetric organic cation and smaller inorganic counterparts lower the lattice energy and hence the melting point of the resulting ionic medium. In some cases, even the anions are relatively large and play a role in lowering the melting point [9, 10b].

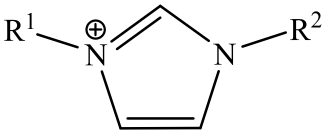


Figure 3. The imidazolium cation (R^1 = H or -alkyl-chain, R^2 = H or alkyl-chain).

Increasing side chain length has a dual effect on the melting point of imidazolium salts (Figure 4). If R^1 remains constant and R^2 is changed (Figure 3), the melting point starts to decrease until a certain chain length is achieved and then starts to increase again. Short side chain increases the unsymmetry of the cation and thus melting point is decreased. With long side chains molecular weight starts to dominate and melting point starts to increase with increasing chain lengths. Branching, functional groups on the side chain or other substituents on the imidazolium ring increase the melting point [11].

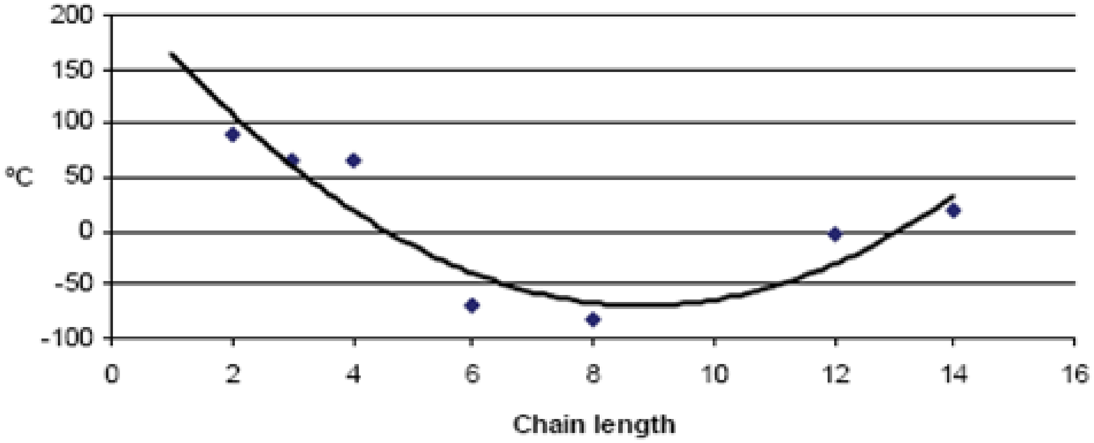


Figure 4.The effect of increasing chain length on melting point on 1-alkyl-3-methylimidazolium chlorides.

1.3.2 Solvent properties

ILs are good solvents for a wide range of substances; organic, inorganic, organometallic compounds, bio-molecules and metal ions. They are usually composed of poorly coordinating ions which makes them highly polar but non-coordinating solvents. ILs are immiscible with most of the organic solvents, thus they provide a nonaqueous, polar alternative for two-phase systems. Furthermore, ILs which are not miscible with water can be used as immiscible polar phases with water. Water solubility is an important property, and it also varies according to the anion. Halides, tetrafluoroborate and triflate containing ILs commonly are miscible with water, and hexafluorophosphate and bis(trifluoromethylsulfonyl)imide-containing ILs are immiscible. Although all other conventional solvents evaporate to the atmosphere, ILs do not evaporate and their nonvolatility gives an opportunity to utilize them in high-vacuum systems. The negligible volatility is the basic property which characterizes them as green solvents. Considering potential as solvents, ILs can easily replace other conventional organic solvents which are used in large quantities in chemicals processing industries to eliminate major environmental problems [9].

1.3.3 Ionic Conductivity

The ionic conductivity of a solvent is of critical importance in its selection for an electrochemical application. The conductivity of an electrolyte is a measure of the available charge carriers and their mobility. On the surface one would expect ionic liquids to possess very high conductivities because they are composed entirely of ions. Unfortunately, this is not the case. As a class, ionic liquids possess reasonably good ionic conductivities, comparable to the best non-aqueous solvent/electrolyte systems (∼10 mS cm^{-1}). However, they are, in general, significantly less conductive than concentrated aqueous electrolytes. The smaller than expected conductivity of ionic liquids can be attributed to the reduction of available charge carriers due to ion pairing and/or ion aggregation, and to the reduced ion mobility resulting from the large ion size found in many ionic liquids [10c].

1.3.4 Viscosity

As a group, ionic liquids are more viscous than most common molecular solvents. Ionic liquid viscosities at room temperature range from a low of around 10 cP to values in excess of 500 cP. The viscosity of many ionic liquids is strongly dependent on temperature, cation and anion [10c].

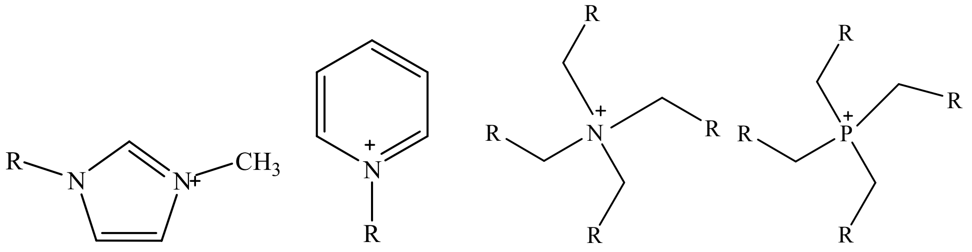
1.3.5 Air and moisture stability

Many of ILs are both air and moisture stable, some are even hydrophobic. On the other hand, most imidazolium and ammonium salts are hydrophilic and if they are used in open vessels, hydration will certainly occur. The hydrophobicity of an IL increases with increasing length of the alkyl chain [12]. Despite their wide spread usage, ILs containing PF_6^- and BF_4^- have been reported to decompose in the presence of water, giving off HF. Wasserscheid et al. [13] pointed out that ILs containing halogen anions generally show poor stability in water, and also give off toxic and corrosive species such as HF or HCl.

1.4 Synthesis of ILs

There are a great number of different cation and anion combinations to synthesize IL. Different types of ILs give an opportunity to modify the physical and chemical properties of the IL. The most widely used cations are imidazolium, pyridinium, phosphonium and ammonium (Fig. 5) [14].

There are two basic methods to synthesize ILs: metathesis reaction and acid–base neutralization reaction. Many alkylammonium halides are commercially available; they can also be prepared simply by the metathesis reaction of the appropriate halogenoalkane and amine. Pyridinium and imidazolium halides are also synthesized by metathesis reaction. On the other hand, monoalkylammonium nitrate salts are best prepared by the neutralization of aqueous solutions of the amine with nitric acid [10a].



1-alkyl-3-methyl-imidazolium	N-alkyl-pyridinium	Tetraalkyl-ammonium	Tetraalkyl-phosphonium

Some possible anions: Water-insoluble ⟶ Water-soluble

[PF_6^-]	[$CF_3SO_3^-$]	[$CH_3CO_2^-$]
[$(CF_3SO_2)_2N^-$]	[BF_4^-]	[$CH_3SO_2^-$]
[$BR_1R_2R_3R_4^-$]		[NO_3^-],
		[$CF_3CO_2^-$]
		Cl^-, Br^-, I^-

Most commonly used alkyl chains:

ethyl	octyl
butyl	decyl
hexyl	

Figure 5. The building blocks of ionic liquids.

The vast majority of ionic liquid chemistry based on the nitrogen-containing heterocycles focuses on the use of 1-alkyl-3-methylimidazolium and N-alkylpyridinium cations. The general synthesis involves a consecutive quaternization-metathetic/acid–base procedure. The first step affords an alkylated halide precursor, which upon metathesis with a metal salt or acid–base neutralization reaction gives an ionic liquid with a different anion. Using conventional heating methods, the first step in ionic liquid synthesis is time-consuming and usually requires a large molar excess of haloalkane (10–400%) to achieve good yields [15].

The synthesis of ionic liquids can generally be split into two steps: the formation of the desired cation and anion exchange where necessary to form the desired product. In some cases only the first step is required, as with the formation of ethylammonium nitrate. In many cases the desired cation is commercially available at reasonable cost, most commonly as a halide salt, thus requiring only the anion exchange reaction. The formation of the cations may be carried out either via protonation with a free acid or by quaternization of an amine, phosphine or sulfide, most commonly using a haloalkane or dialkylsulfates. Alkylation leads to quaternization of the heteroatom. The halide salts formed can be easily converted to salts with other anions. In general, the reaction may be carried out using chloroalkanes, bromoalkanes and iodoalkanes, with the reaction conditions required becoming steadily gentler in the order Cl → Br → I, as is expected for nucleophilic substitution reactions. The reactivity of the haloalkanes also generally decreases with increasing alkyl chain length [9]. Most alkylations involve two steps: deprotonation and nucleophilic displacement (Scheme 1.). The reactions are usually run in one pot, that is, the same solvent is used in both solvents. The process is optimized by selection of base, solvent and electrophile. But in some cases, the reaction may be performed in two steps by using one solvent for the deprotonation and a second one for the nucleophilic displacement [16].

$$\mathrm{AH} \xrightarrow[\text{Solvent 1}]{\text{Base}} \mathrm{A}^{-} \xrightarrow[\text{Solvent 2}]{\text{R-X}} \mathrm{AR}$$

Scheme 1. Alkylations reactions in the presence of a base.

After synthesis of ionic liquids, the lack of significant vapour pressure prevents the purification of ionic liquids by distillation. The counterpoint to this is that any volatile impurity can, in principle, be separated from an ionic liquid by distillation. In general, however, it is better to remove as many impurities as possible from the starting materials by distillation, more importantly vacuum distillation, prior to use, and, where possible, to use synthetic methods that either generate as few side products as possible, or allow their easy separation from the final ionic liquid product. All solvents used in quaternization or anion-exchange reactions should also be dried and distilled before use. If these precautions are not taken, it is often difficult to prepare colorless ionic liquids. Most ionic liquids based on the common cations and anions should be colorless. In practice the salts often take on a yellow color, particularly during the quaternization step. Where it is important that the liquids are colorless, however, the color may be minimized by carrying out the quaternization reaction either in a system that has been degassed and sealed under nitrogen, or else under a flow of inert gas such as nitrogen. Furthermore the reaction temperature should be kept as low as possible (no more than ca. 80 ^{o}C for Cl− salts, and lower for Br− and I− salts) [10a].

The imidazole ring is a predominant building block for ionic liquids, dialkylimidazolium-based compounds in particular. The ring is easily ionized upon quaternization of the tertiary nitrogen atom, resulting in a permanent positive charge. They are recognized for their potential as green organic solvents due to their lack of volatility. Furthermore, a unique combination of various alkyl substituents and counteranions enables tuning of the properties of the liquid to meet the demands of the application [17]. Imidazole has gained this attention for a variety of reasons, particularly its tunable structure, thermal stability, relatively high ionic conductivity, wide electrochemical window, and its amphoteric behaviour in solution. The structure is uniquely tunable because of the inherent amphoteric behaviour, i.e. the imidazole ring both accepts and donates protons. This allows for substitution using facile SN_2 reactions at the 3-ring position. The 1-position on the ring is a secondary amine, which undergoes a variety of reactions [18]. However, there are a couple of drawbacks associated with imidazolium cations. The first and probably the most fatal is sensitivity toward basic reaction conditions. The carbon between nitrogen on imidazolium has an acidic proton attached and in basic conditions imidazolium deprotonates and the cation is changed or decomposed [19].

Most preparations of ionic liquids have been carried out by the formation of an organic halide salt. The halide anion is then exchanged to give the desired ionic liquid by a metathesis reaction. As a consequence the ionic liquid usually contains some halide contamination. Subsequent separation of the halide can be difficult, and impurities can change the properties of the ionic liquid. Therefore, halide-free ionic liquids have recently received much some attention [14].

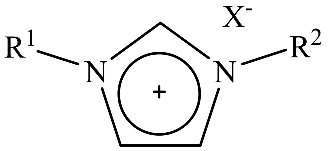
1.5 Task-Specific Ionic Liquids (TSILs)

Currently, ionic liquids (ILs) are receiving great attention for application as innovative solvents or additives in a variety of different areas reaching from material synthesis to separation science as well as alternative reaction media. However, despite promising results evidenced by the many studies in which they have been used as solvents, evidencing unique properties, their widespread application in process chemistry is still hampered by doubts generally related to some practical drawbacks [20a]. To overcome these drawbacks more recently functionalized ILs, the so-called Task-Specific ILs (TSILs), have been synthesized. They are a unique subclass of ionic liquids which possess a potential spectrum of utility extending far beyond that likely for more conventional IL. Some of these ILs have been used as solvents in selected metal catalyzed reactions, evidencing that TSILs can favour the activation of the catalyst, generate new catalytic species, improve the stability of the catalyst. Moreover, properly designed TSILs are able to optimize immobilization and recyclability, facilitate product isolation, and influence the selectivity of the reaction [20b].

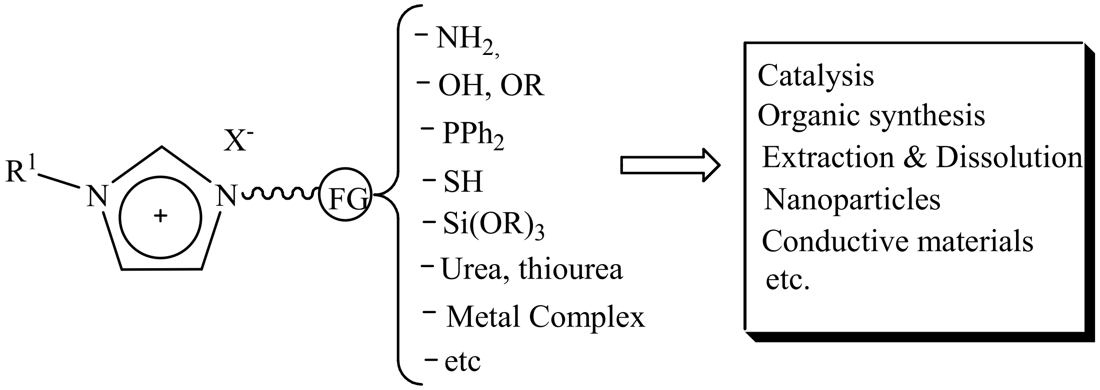
A range of different functional groups providing properties similar or identical to those of the major classes of organic solvents has been incorporated into IL cations, including vinyl and allyl, amine, amide, ether and alcohol, acid, urea and thiourea, fluorous chains, alkyne, phosphoryl, nitrile, thiols, and ferrocenyl groups [21]. Many of them were focused on the incorporation of functionality into a branch appended to the cation, especially imidazolium cation (Figure 6).

Basic ionic liquids (BILs), a new class of TSILs, used in some base-catalyzed processes offer a new possibility for developing environmentally friendly basic catalysts due to the combination of the advantages of inorganic bases, stability in water and air, easy separation, high catalytic efficiency and reusability. These strong BILs exhibited great potential for the replacement of conventional basic catalysts because they are flexible, nonvolatile, noncorrosive, and immiscible with many organic solvents. They are used to replace traditional bases such as KOH, NaOH, K_2CO_3, $NaHCO_3$, NaOAc, triethylamine, or tetrabutylammonium acetate. They have been used in base-catalyzed processes such as Michael addition, Markovnikov addition, Knoevenagel condensation, Henry reaction, Mannich reaction, oximation, Feist-Benary reaction and *etc*. The first basic ionic liquid that became popular and applied in based catalyzed reactions is 1-butyl-3-methyl imidazolium hydroxide, [Bmim]OH [29].

Recent developments in task specifically functionalized imidazolium salts, which can be used for specific tasks ranging from catalysts recycling, supports for organic synthesis, catalysis, separation of specific metal ions from aqueous solution, and construction of nanostructures and ion conductive materials, have also been reviewed [22].



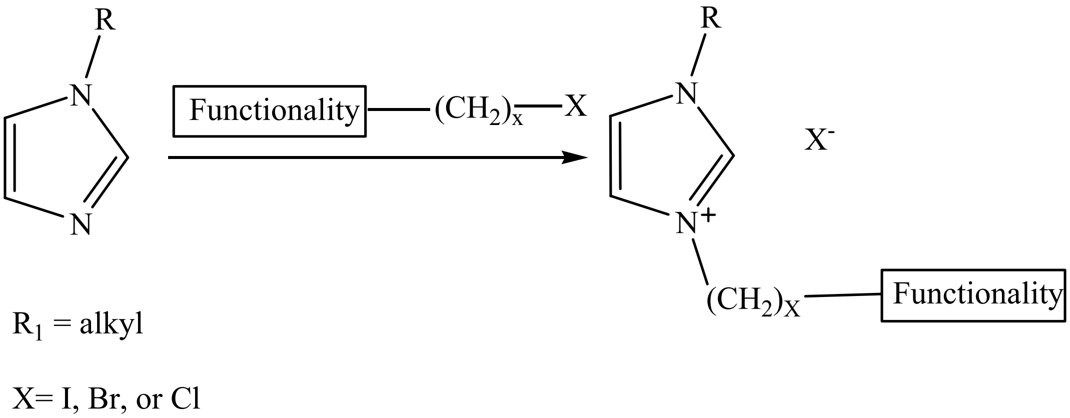
(R^1, R^2 =alkyl, X= halogen, BF_4, PF_6, NTf_2 etc.)



Functionalized imidazolium salts for task-specific ionic-liquids

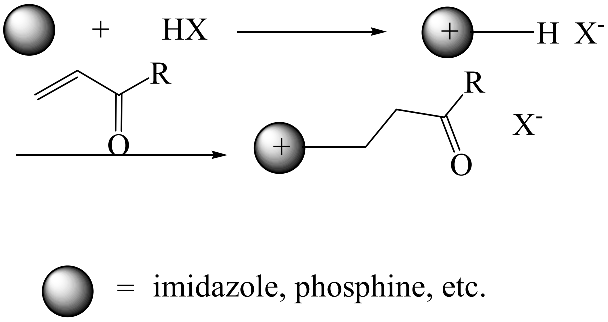
Figure 6. Imidazolium salts for conventional ionic liquids and functionalized imidazolium salts for task-specific ionic liquids.

The preparation of “task-specific” or functionalized ILs is normally realized through the incorporation of functional groups on the cations, to date, mostly the imidazolium cation, although a few examples involving functionalized anions are known. Starting from 1-alkylimidazoles and using functionalized alkyl halides, the quaternization method usually gives the desired functionalized ILs as imidazolium halides in good yield (Scheme 2). The reaction is usually facile and in many cases solvent is not required unless the reaction is highly exothermic. However, in most cases, solvent is required to purify the imidazolium halide from unreacted starting materials. If a long chain alkyl halide is used, longer reaction times are needed and heating is also necessary. Electron-withdrawing groups attached to the alkyl halide enhance electrophilicity, and consequently shorten the reaction time [23].



Scheme 2. Synthetic route used to prepare functionalized ILs precursors.

Recently, Wasserscheid and co-workers introduced a complimentary method for TSIL synthesis, making use of the Michael reaction (Scheme 3) [24]. In this approach, the imidazole or other nucleophile of interest is protonated using the acid form of the anion which will eventually be incorporated into the IL. To this salt is added the desired Michael acceptor, which inserts into the N–H (or element–H) bond. The approach is broadly effective, giving TSIL in good yields. Moreover, the procedure dispenses with the need for an anion metathesis step, and provides IL free of halide.



Scheme 3. Michael reaction used for TSIL synthesis.

1.6 Characterization of ionic liquids

1.6.1 Quality of ionic liquids

The preparations of the ionic liquids are monitored with ^{1}H NMR, GC and MS (ESI). ^{1}H NMR proved to be generally the most efficient method for monitoring a quaternization reaction. Both the reagents and the resulting ionic liquid could be detected from the ^{1}H NMR spectrum. Monitoring with GC or GCMS can also be applied in some cases. Ionic liquids do not evaporate, and hence the only compounds expected to be detect were the starting components, *N*-alkylimidazole and the alkylating reagent. MS proved to be a very useful technique for following the metathesis reactions, because ions are easily detected with it. ^{1}H NMR was not as reliable as MS for monitoring metathesis reactions, because the cation remained the same and only the anion was changed. Purified ionic liquids can also be studied with ^{13}C NMR, and an elemental analysis can be carried out. The observed and calculated elemental contents of the studied compounds can be compared for consistency [5]. The presence of halide impurities usually causes drastic changes in the physical properties of ionic liquids. The Vollhard method or an ion-selective electrode can be used to measure halide contents [14].

1.6.2 Melting points

Generally, symmetric ions with a localized charge and strong interactions between ions result in good packing efficiency and hence a high melting point. Ionic liquids based on large, unsymmetric cations with a delocalized charge often have low melting points. Packing efficiency depends on interactions between ions. Hydrogen bonding (or similar non-bonded interactions) increases the order of the system and thus raises the melting point [25]. The melting points of the solid ILs prepared with the quaternization reaction are determined with differential scanning calorimetry and a melting point apparatus.

1.6.3 Thermal stability

The thermal stability of an ionic liquid is determined by the strength of the formed heteroatom-carbon or heteroatom-hydrogen bonds and the stability of the formed ion species. A N-C bond is stronger than a N-H bond and accordingly, the stability of ammonium cations decreases in the following order: quaternary > tertiary > secondary > primary [26]. The degradation temperature is measured by using thermogravimetric analysis (TGA) or differential thermal analysis.

The general trend between different cations seems to be that a phosphonium cation is more stable than an imidazolium cation, and an ammonium cation is least stable in terms of thermal degradation. The stability of an imidazolium cation increases when nitrogen atoms and the carbon atom between nitrogens in the ring have alkyl substituents. Stability increases with straight alkyl chains compared with branched ones, not to mention the hydrogen atom as a substituent. TGA measurements show that quaternary ammonium chlorides decompose at around 150 ºC and imidazolium-based ionic liquids at above 200 ºC [10c].

1.6.4 Crystal structures

Crystal structure determination indicates the number of contacts and the strength of contacts between the ions with respect to the ions of the ionic liquid. The stronger the interaction between the ions, the higher the melting point of the IL. Recent crystal structure studies have revealed that disorder is common in ionic liquids, especially when the imidazolium cation has long alkyl side chains. It has been interpreted that disorder in the cation is a direct reflection of poor packing efficiency in the imidazolium ions. Hence, factors such as the size of the ions, delocalization of charge, interactions between ions and disorder in the cation will affect the packing of the ionic liquid and also the observed melting point [27].

1.7 Applications of ionic liquids

The research areas on ILs are growing very rapidly and the potential application areas of ILs are numerous. The unique chemical and physical properties of ILs bring about several application areas including reaction and synthesis media. The application areas of ILs can be expressed as solvents for organic, organometallic synthesis and catalysis; electrolytes in electrochemistry, in fuel and solar cells; lubricants; stationary phases for chromatography; matrices for mass spectrometry; supports for the immobilization of enzymes; in separation technologies; as liquid crystals; templates for synthesis nano-materials and materials for tissue preservation; in preparation of polymer–gel catalytic membranes; in generation of high conductivity materials [28].

We became interested in developing new halide free ILs. Here, we report on the synthesis and characterization of new triflouroacetylated imidazole based salts.

2. Objective of the study

The main objective of this study is to prepare a new triflouroacetylted imidazole based ionic liquids with longer alkyl chain than the existing triflouroacetylated imidazole based ionic liquid with a lower melting point.

3. Experimental

3.1 General

All chemicals were purchased from commercial sources and used without further purification. ^{1}H- and ^{13}C-NMR were recorded on a Bruker 400 MHz NMR spectrometer operating at 400 and 100.9 MHz, respectively. Chemical shifts are reported relative to TMS as reference for proton and carbon. Elemental analyses were carried out on Flash EA 1112 elemental analyzer.

3.2 General procedure for the alkylation of imidazole with alkyl bromides

After many trials of deprotonation and alkylation to find optimum conditions by varying solvents, temperature, bases and excess of alkylating agents, we lastly came up with a better procedure.

Synthesis of 1-pentylimidazole

To the solution of $NaOC_2H_5$ (12.6 g, 0.22 mol) in ethanol (60 mL) at 25°C, a solution of imidazole (7.4 g, 0.11 mol) was added and the reaction mixture was stirred with a magnetic stirrer at room temperature in a flask fitted with air condenser for about 72 hours. Then equivalent amount of 1-pentylbromide (10.02 mL, 0.11 mol) was added to the mixture drop wise using a syringe. The stirring continued for another 72 hours. The solution was filtered to remove any precipitated NaBr and the resulting solution was then evaporated to dryness to afford deep orange oily liquid with a 92% yield. Water was added to the oily liquid and the solution was extracted with CH_2Cl_2. The organic layer was dried over $CaCl_2$ and the solvent was rotavaped under vacuum at 80^0C. Half of this is distilled in a vacuum and a very pure colourless product is obtained. The compound was analyzed by ^{1}H NMR and ^{13}C NMR, and the spectral data tally with the structure: ^{1}H-NMR (400 MHz, DMS0-d_6): δ 7.67 (s, 1H, CH), 7.15 (s, 1H, CH), 7.04 (s, 1H, CH), 3.96 (t, 2H, CH_2, J=7.1 Hz), 1.73 (pent, 2H, CH_2, J=7.3 Hz), 1.32 (m, 4H, CH_2), 0.90 (t, 3H, CH_3, J=7.2 Hz). ^{13}C NMR (101 MHz, DMSO-d_6): δ 137.34, 128.82, 119.15, 46.47, 30.99, 28.66, 22.24, 13.90.

3.3 Synthesis of 1-pentyl-3-triflouroacetylimidazolium trifluoroacetate [C_5–TFAIm]CF_3CO_2

Part I

TFAA (7 ml) was added to a stirred solution of undistilled 1-pentylimidazole (26 mmol) in CH_2Cl_2 (50 ml) at 0 °C for 10 min under nitrogen atmosphere. The mixture was stirred at 25 °C for 3 h. Then a deep orange viscous oily solid was obtained and then rotavaped at 100 ^{0}C to afford a crude [C_5–TFAIm]CF_3CO_2. But the ^{1}H-NMR obtained was not good and ^{13}C-NMR indicates that the product is not pure rather a mixture of unreacted pentylimidazole and impurities from the pentylimidazole itself.

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.72 (q, $^2J_{C\text{-}F}$ =35.9Hz), 161.69 (q, $^2J_{C\text{-}F}$= 37—38 Hz), 134.82, 120.88, 120.63, 116.31 (q, $^1J_{C\text{-}F}$ =290.0Hz), 115.96 (q, $^1J_{C\text{-}F}$ =290.8Hz), 49.34, 29.86, 28.08, 21.84, 13.56.

Part II

The same procedure was repeated with distilled 1-pentylimidazole under the same condition stirred for overnight. A colourless solution was obtained and rotavaped at 100 ^{0}C. Finally the product was distilled under reduced pressure (vacuum) to give a glassy solid crystal. Conductivity was done and it was found to be a conductor. The compound was analyzed by ^{1}H- and ^{13}C-NMR, and the spectral data is given as:

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8 (t, 3H, J=7.0 Hz), 1.2 (m, 4H), 1.8 (pent, 2H), 4.13 (t, 2H, J=7.3 Hz), 7.2 (s, 1H), 7.35 (s, 1H), 8.85 (s, 1H), 15.35 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.86 (q, C, $^2J_{C\text{-}F}$ = 34.9 Hz), 134.82, 120.88, 120.63, 116.73 (q, CF_3, $^1J_{C\text{-}F}$ =293.1Hz), 49.34, 29.86, 28.08, 21.84, 13.56. Elemental analysis calcd. for $C_{10}H_{15}O_2N_2F_3$ (252): C 47.62, H 5.95, O 12.69, N 11.11, F 22.62; Found: C 46.74, H 6.11, N 10.79.

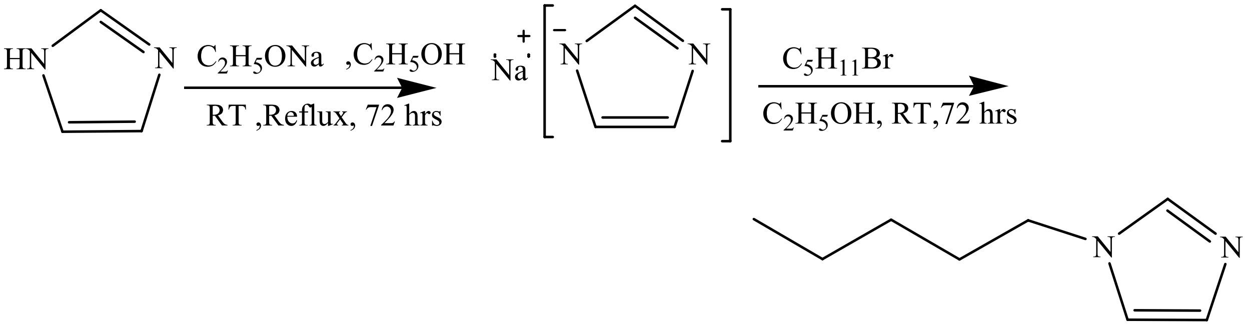
3.4 Solubility test for the 1-pentyl-3-triflouroacetyl imidazolium ionic liquid synthesized in part II

The solubility of the ionic liquid synthesized in part II was checked in dichloromethane, chloroform, water, dimethylsulfoxide, and acetone. Small amount of the ionic liquid sample was taken in vials and each of the organic solvents was added to each vials and shaken well. It was observed that the ionic liquid sample is soluble in all of the solvents.

4. Results and Discussion

Synthesis of alkylimidazole

The alkylimidazole precursor that was required for the triflouroacetylation has been prepared by the reaction of imidazole with pentylbromide in ethanol with sodium ethoxide as a base according to scheme 3. It took several times to get optimum conditions for the deprotonation and alkylation of imidazole.



Scheme 4. Synthesis of 1-pentylimidazole.

The deprotonation and alkylation was first tried in different solvents like methanol, acetonitrile, 1,1,1-trichloroethane and at different temperatures. But finally a better yield obtained in ethanol with sodium ethanoate as a base and both alkylation and deprotonation took place in the same solvent refluxing at room temperature. The pentylimidazole obtained contained some mixture of 1,3-dialkyl imidazolium and 1,2-

dialkylimidazolium salt as a side product and small amount of the starting materials as well as it was evident from the distillation and NMR spectroscopy (Figure 7 and 9).

There are a couple of drawbacks associated with imidazolium cations. The first and probably the most fatal is sensitivity toward basic reaction conditions. The carbon between nitrogen on imidazolium has an acidic proton attached and in basic conditions imidazolium deprotonates and the cation is changed in being alkylated at C-2 postion.

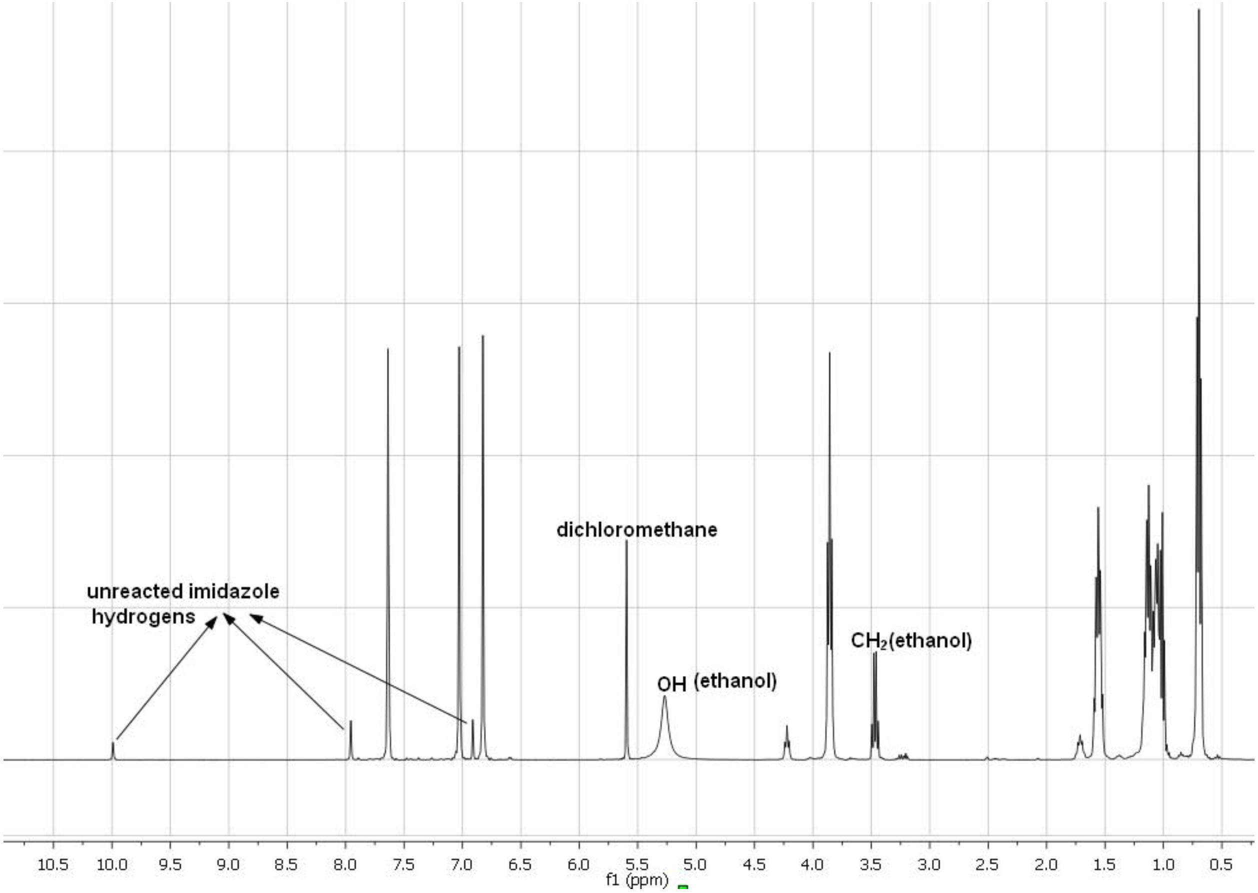


Figure 7. ^{1}H NMR of 1-pentylimidazole (undistilled) in DMSO.

Thus, the vacuum distillation of the 1-pentylimidazole was necessary and done to get rid of the side products and get pure 1-alkylimidazole precursor for the preparation of the ionic liquid as it is evident from the spectra in figures 8 and 10.

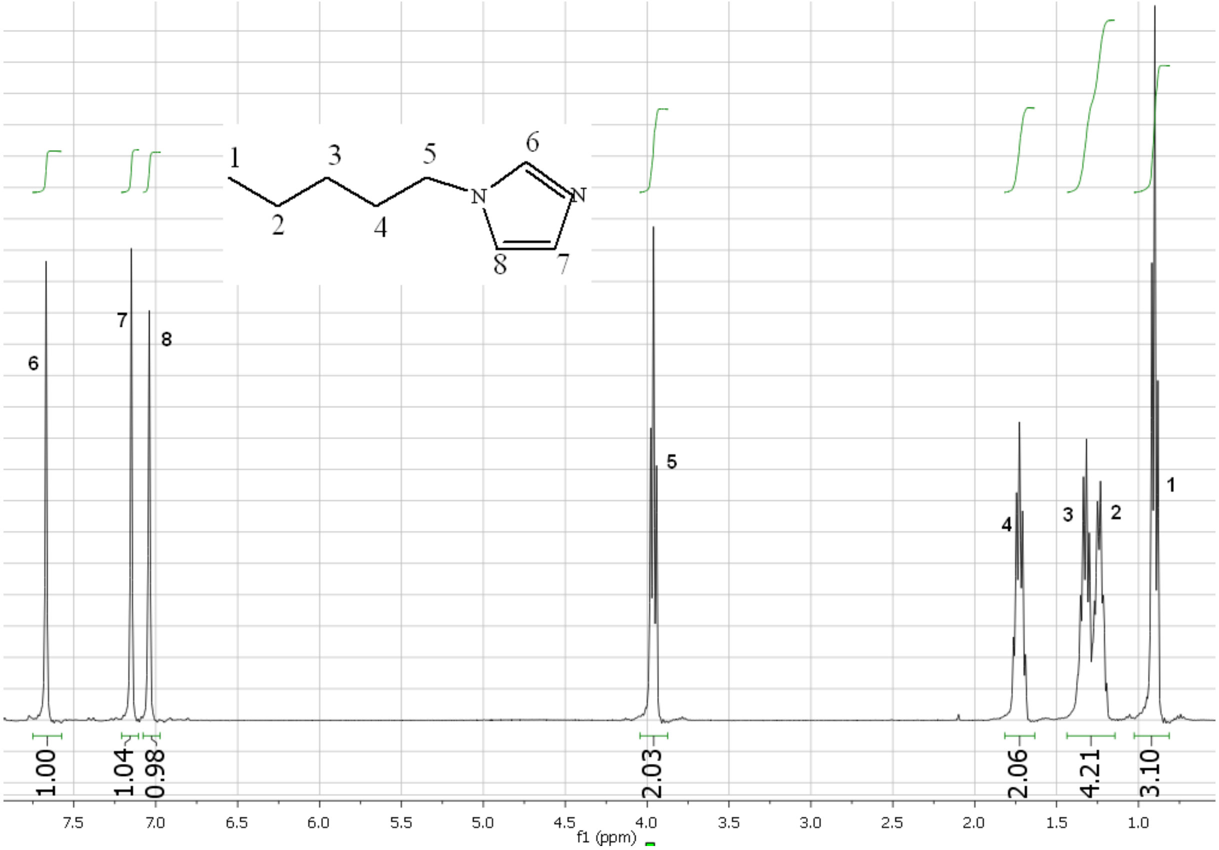


Figure 8. ^{1}H NMR of 1-pentylimidazole (distilled) in DMSO.

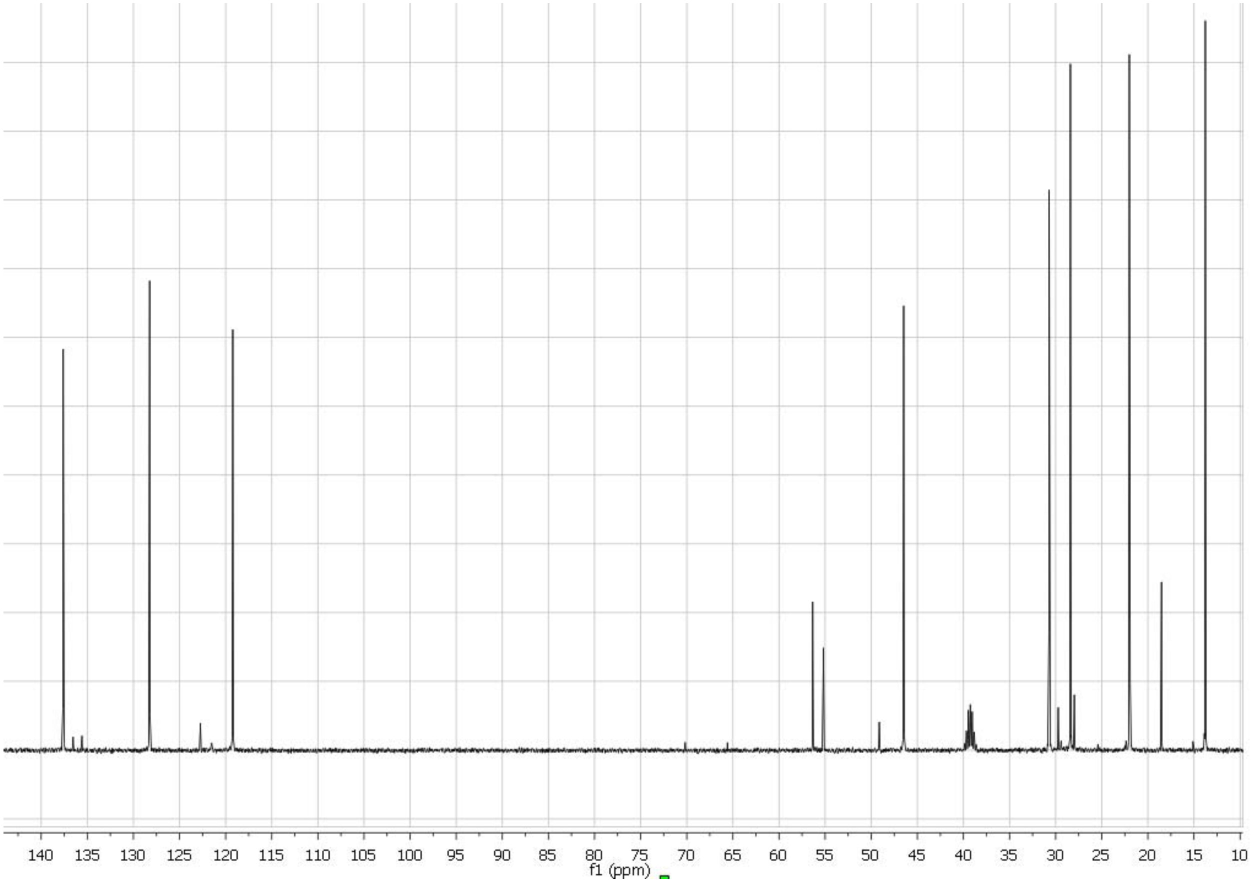


Figure 9. ^{13}C NMR of 1-pentylimidazole (undistilled) in DMSO.

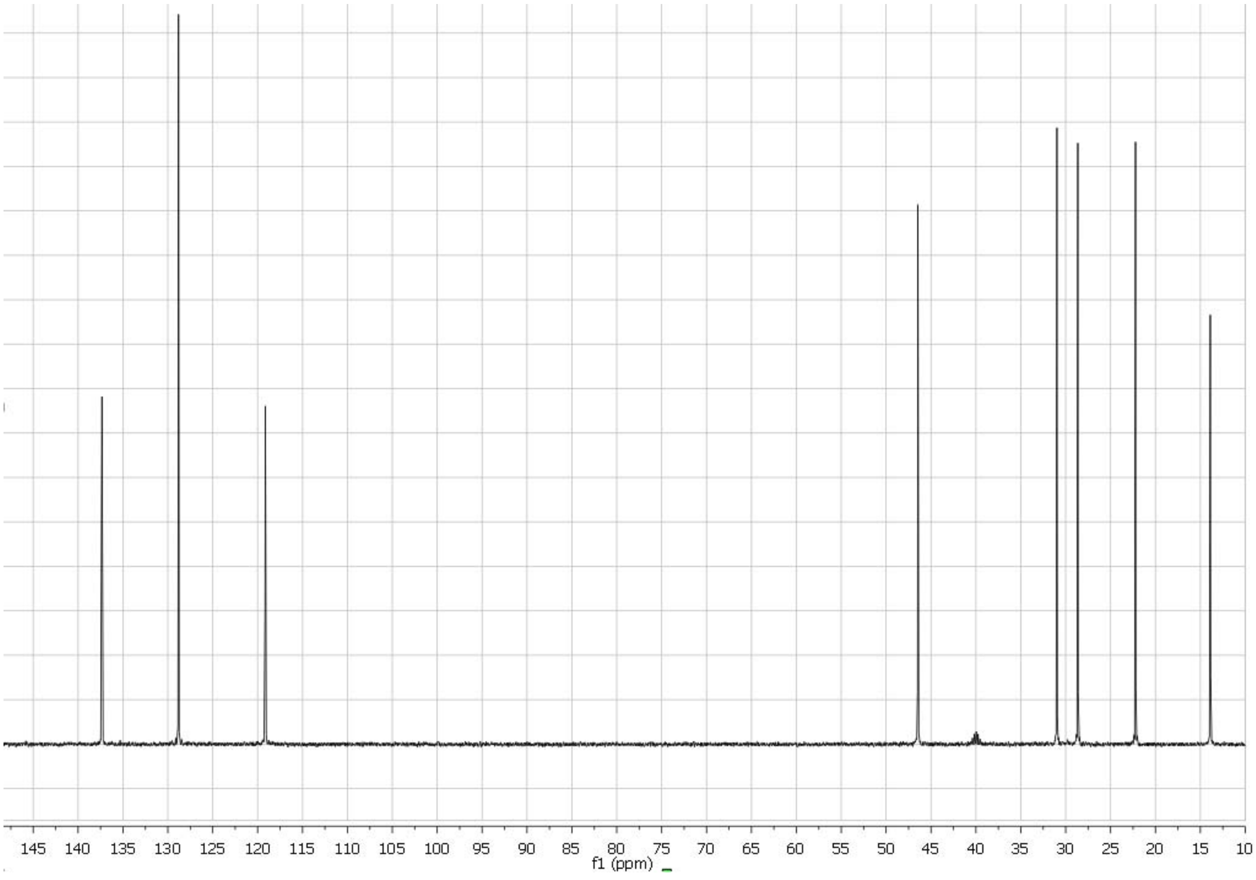
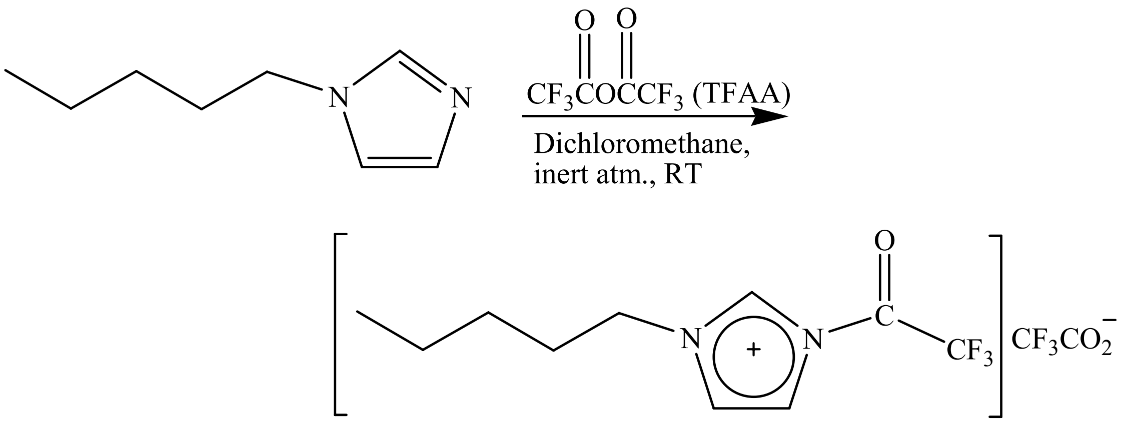


Figure 10. ^{13}C NMR of 1-pentylimidazole (distilled) in DMSO.

Synthesis of triflouroacetylated imidazole based ionic liquids

The ionic liquid based on triflouroacetylated imidazole was synthesized and obtained as in scheme 4. In the triflouroacetylation step, the formation of pentyl triflouroacetyl imidazolium triflouroacetate is supported by spectral data. The presence of the $COCF_3$ and CF_3CO_2 group was determined on the basis of short range $^{13}C–^{19}F$ coupling in CF_3 and long-range $^{13}C–^{19}F$ coupling of carbonyl carbon and CF_3 (Figure 11 and 12). Thus, the carbons of the $COCF_3$ group appear at around δ 115.96 ppm (quartet, $^{1}J_{C\text{-}F}$ =290.8Hz) and δ 160.75 ppm (quartet, $^{2}J_{C\text{-}F}$= 37—38 Hz) and the carbons of CF_3CO_2 at around δ 116.31 ppm (quartet, $^{1}J_{C\text{-}F}$ =290.0Hz) and δ 169.72 ppm (quartet, $^{2}J_{C\text{-}F}$ =35.9Hz). Thus these separate spectra for both trifluroacetyl group and triflouroacetate anion indicates that the triflouroacetylation has taken place.



Scheme 5. Synthesis of pentyl triflouroacetyl imidazolium triflouroacetate ionic liquid.

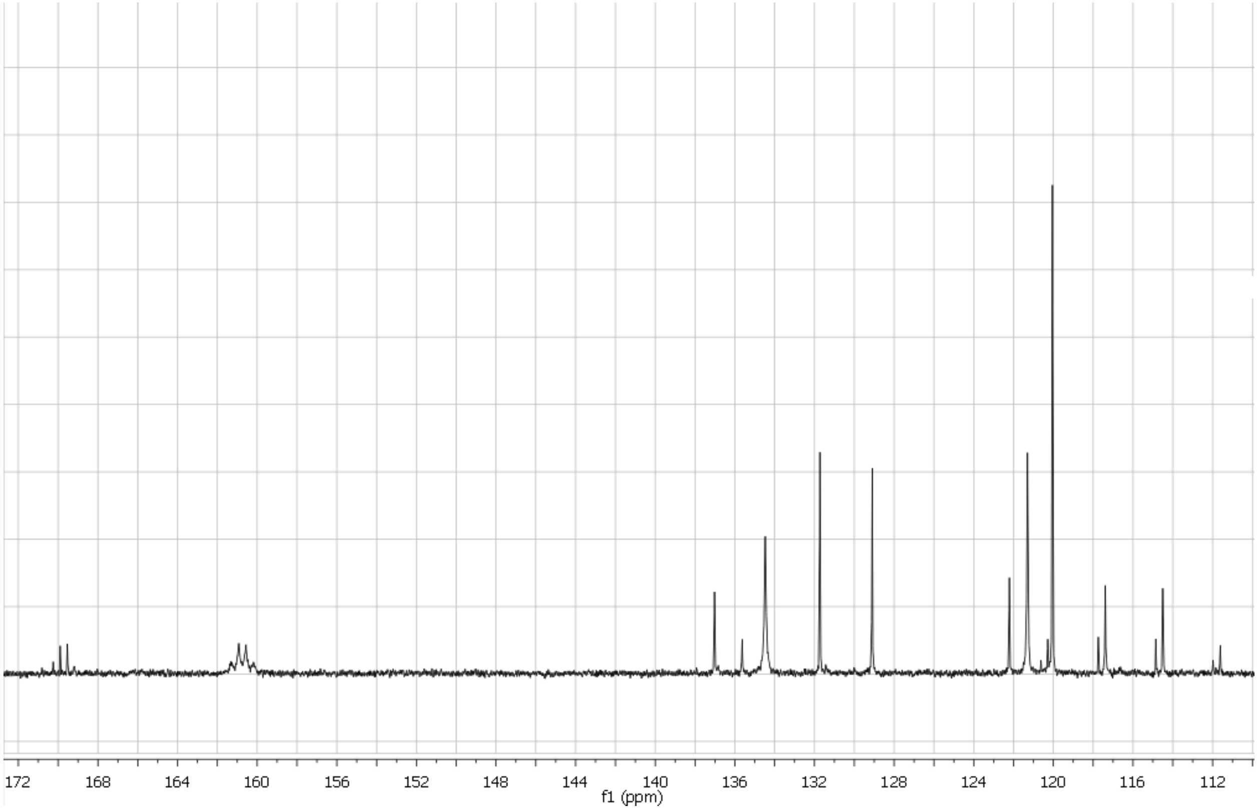


Figure 11. ^{13}C NMR portion of the two carbonyl and CF_3 groups of pentyl triflouroacetyl imidazolium triflouroacetate.

But the pentyl triflouroacetyl imidazolium triflouroacetate ionic liquid formed contained lots of unreacted pentylimidazole and of the dialkylated side products from the pentylimidazole. This is because an impure 1-pentylimidazole was used just to check the triflouroacetylation reaction as a first trial.

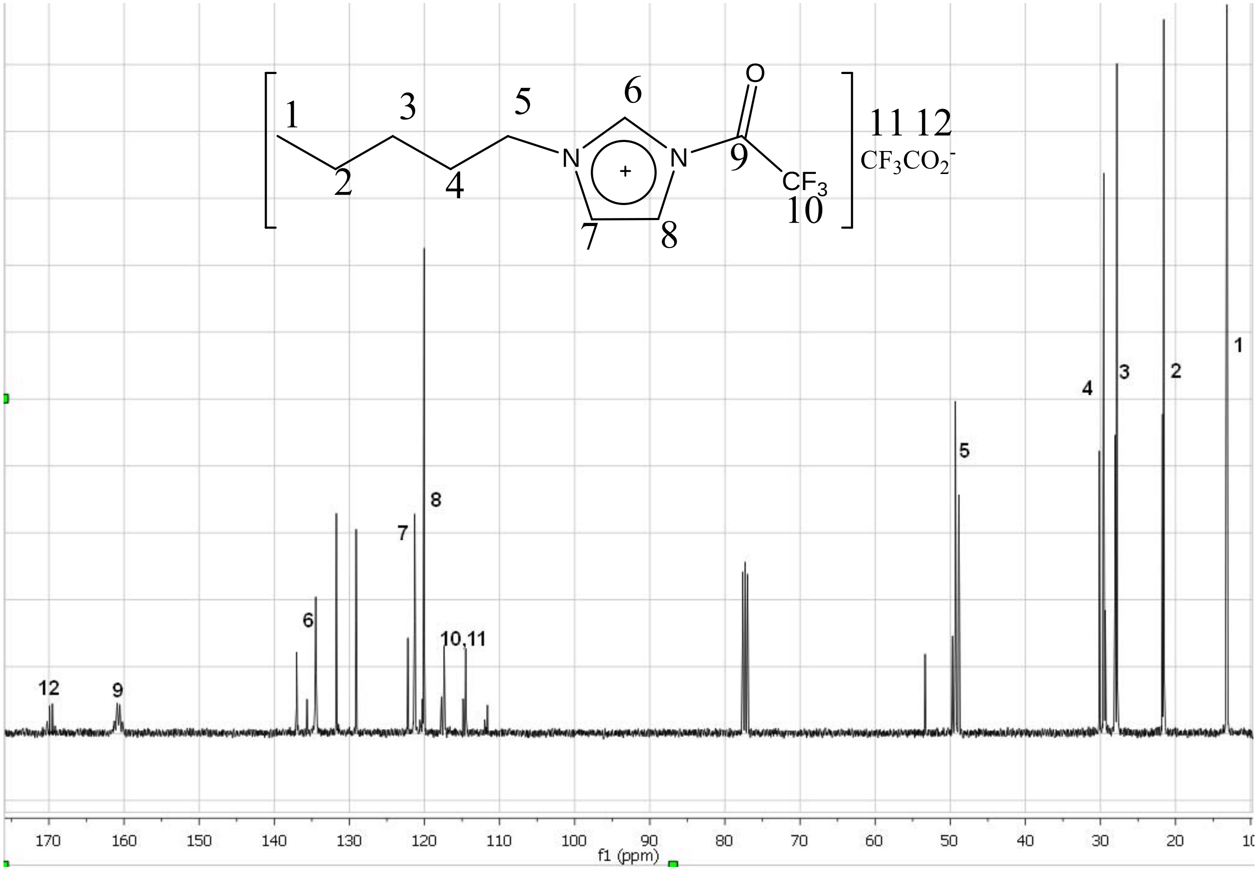


Figure 12. ^{13}C NMR of pentyl triflouroacetyl imidazolium triflouroacetate ionic liquid in $CDCl_3$.

In the second trial to synthesize a more pure pentyl triflouroacetyl imidazolium triflouroacetate ionic liquid, a compound with a very fine ^{13}C- and ^{1}H-NMR spectra of the type shown in figure 9 and 10 respectively was obtained, which is a different ionic liquid from the one expected of this synthetic procedure. The ^{13}C-NMR has shown that there is only one carbonyl carbon in the region above δ 150 ppm and one CF_3 group and the others are missing, which is most probably of triflouroacetate anion. From the ^{1}H-NMR spectra it is shown that there is an extra broad peak from the previous one at around δ 15.3 ppm. These all indicate that the counteranion of the ionic liquid has changed in some form.

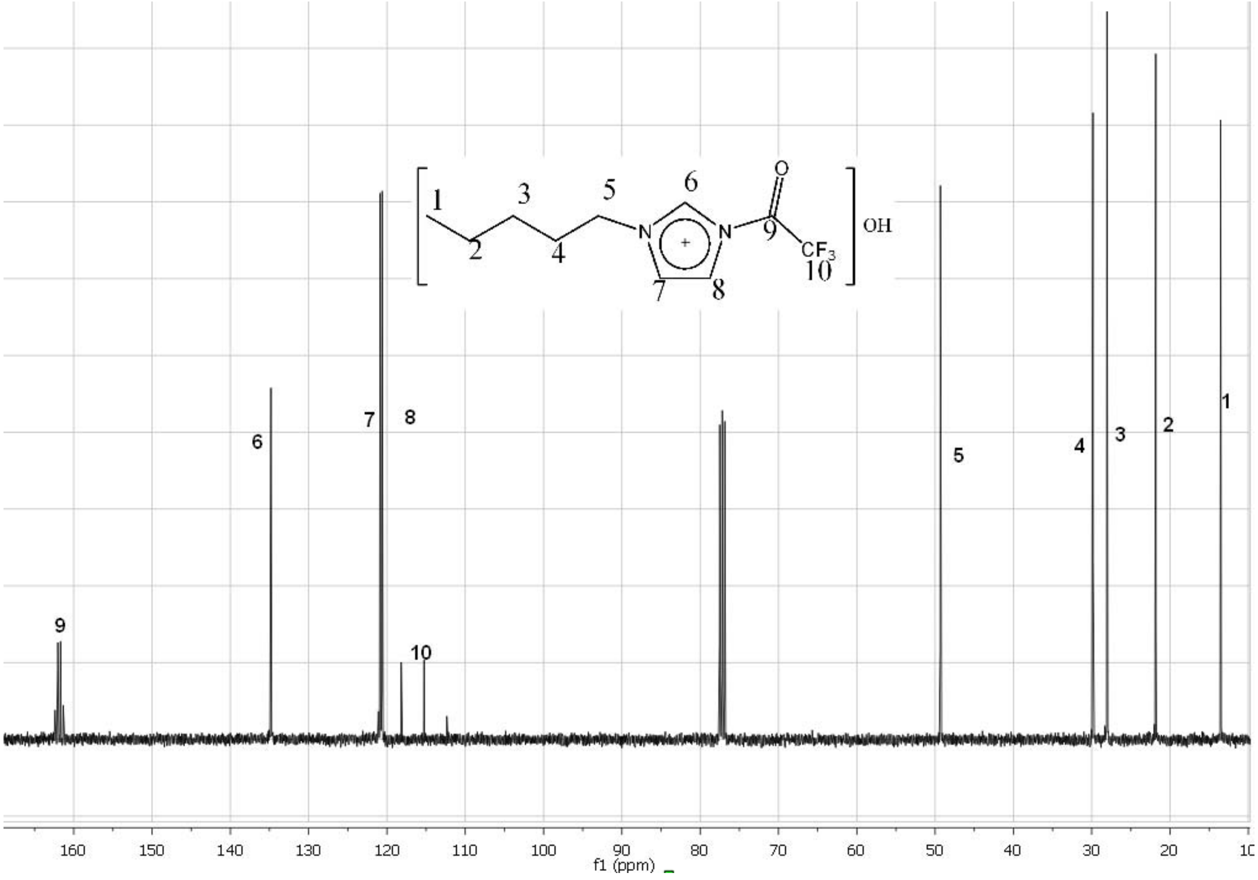


Figure 13. ^{13}C NMR of pentyl triflouroacetyl imidazolium hydroxide ionic liquid in $CDCl_3$.

Basically triflouroacetic anhydride is not a good triflouroacetylating agent because it has a low boiling point (39.5 °C), is moisture sensitive and thus forms trifluoroacetic acid as a by product which can initiate several side reactions and is also too reactive for some applications [4]. Thus the most probable explanation for the disappearance of the triflouroacetate anion in the ionic liquid is the moisture sensitivity of triflouroacetic anhydride and the basic nature of the triflouroacetyl anion which leads to a reaction to form triflouroacetic acid which has boiled off during distillation under vacuum which drives the reaction in scheme 5 to the right because it has a low boiling point (70 ^{0}C).

$$CF_3CO_2^- + H_2O \rightleftharpoons CF_3COOH + OH^-$$

Scheme 6. Reaction of the triflouroacetate anion with water.

And also extra time was given for the reaction so that the anion has changed sufficiently due to a possible moisture contamination in all the procedures and separated from the possible mixture of the two anions, $CF_3CO_2^-$ and OH^-, by distillation under vacuum as a hydroxide anion based ionic liquid.

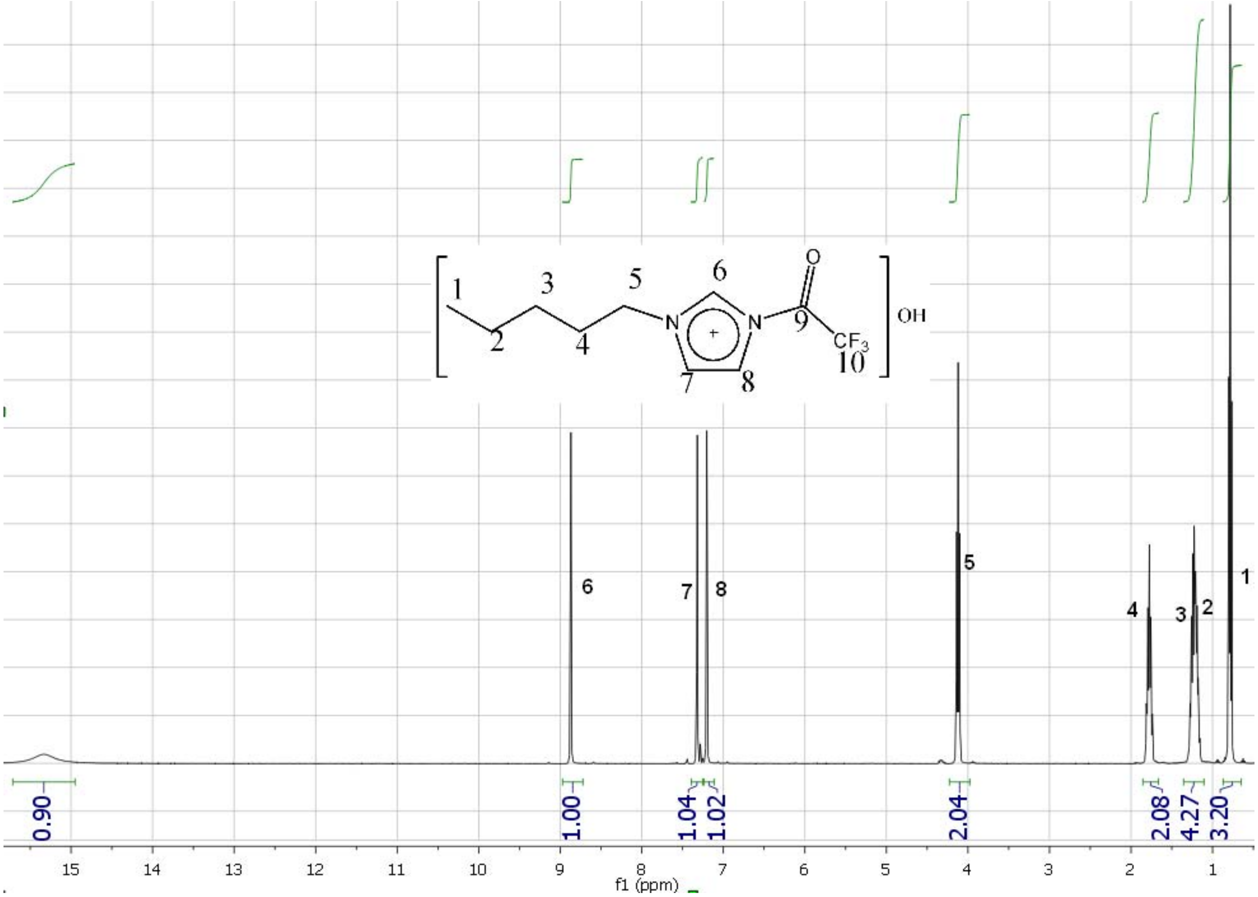


Figure 14. ^{1}H NMR of pentyl triflouroacetyl imidazolium hydroxide ionic liquid in $CDCl_3$.

Thus the counteranion has become a hydroxide rather than triflouroacetate. This is further explained and confirmed by the elemental analysis that fits the one calculated for the hydroxide anion based ionic liquid (Table 1).

	C	H	N
Theoretical (calculated) analysis for [C_5TFAIm]CF_3CO_2	41.38	4.02	8.04
Theoretical (calculated) analysis for [C_5TFAIm]OH	47.62	5.95	11.11
Experimental analysis for [C_5TFAIm]OH	46.74	6.11	10.79

Table 1. Calculated elemental analysis of pentyl triflouroacetyl imidazolium triflouroacetate and pentyl triflouroacetyl imidazolium hydroxide ionic liquids and experimental elemental analysis of pentyl triflouroacetyl imidazolium hydroxide liquid.

5. Conclusion

In conclusion, a new potential task specific, halide free pentyl triflouroacetyl imidazolium triflouroacetate ionic liquid was synthesized by simple alkylation of imidazole followed by triflouroacetylation using triflouroacetic anhydride. In the second trial of synthesis a different hydroxide anion based pentyl triflouroacetyl imidazolium ionic liquid was obtained using the same synthetic route under the same condition but prolonged time due to the high moisture sensitivity of the triflouroacetic anhydride which is evident from the NMR characterization and elemental analysis. Therefore, in order to obtain pure triflouroacetyl imidazolium triflouroacetate ionic liquids, reactions under inert atmosphere are recommended for future work.

This work can be helpful for further work in the future in devising a better triflouroacetylation reagents and methods to synthesize a new class of triflouroacetylated imidazole based ionic liquids which are a class of halide free ionic liquids and synthesis of hydroxide based ionic liquids which are the recently studied groups of ionic liquids. These hydroxide anion based ionic liquids can be derivatized by acid-base neutralization reaction with hydrochloric acid and then anion exchanged with bulky anions like bistriflouromethyl sulfonyl imide.

References:

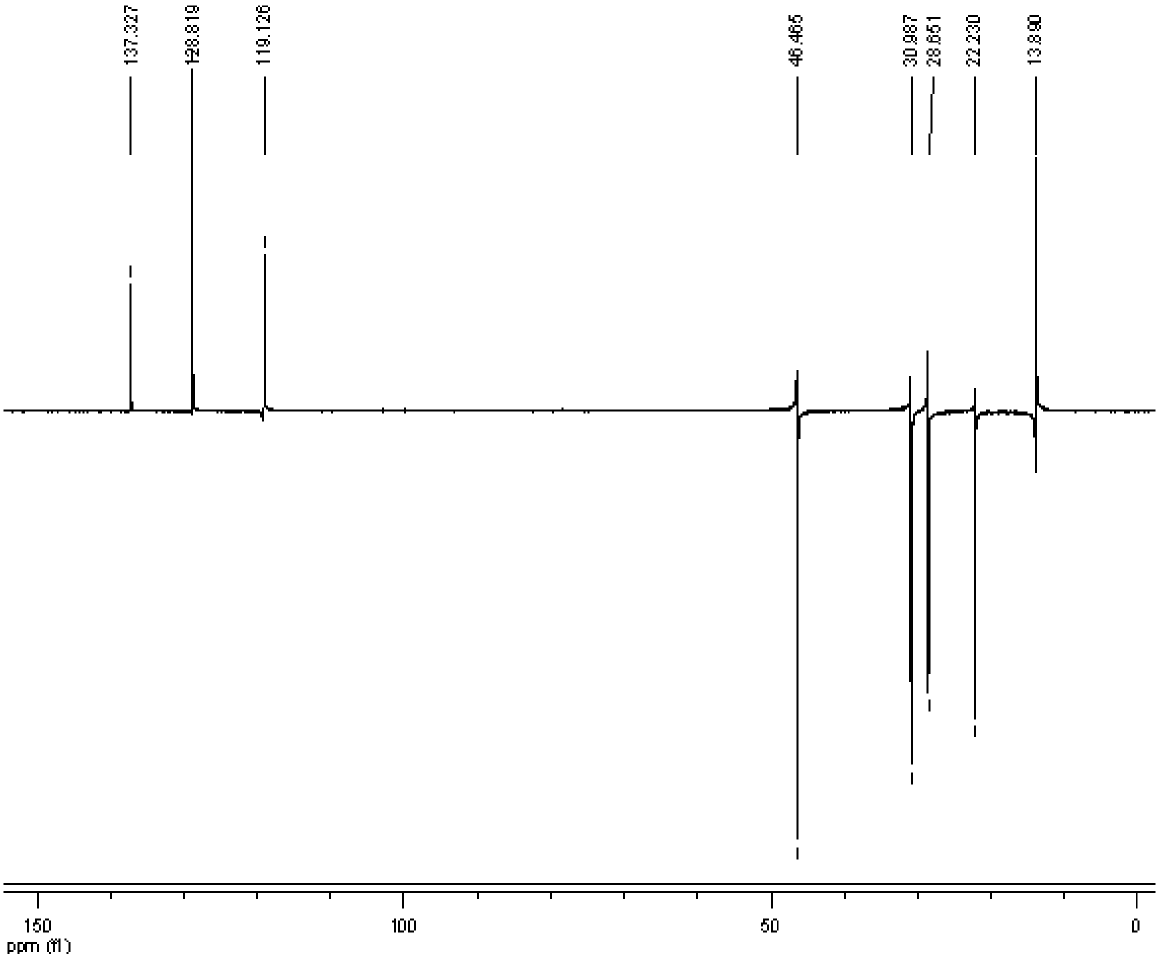
1. T. Welton, *Chem. Rev.*, **1999**, 99, 2071–2084.
2. M. J. Earle and K. R. Seddon, *Pure Appl. Chem.,* **2000**, 72, 7, 1391–1398.
3. D. Zhao, A thesis on Design, Synthesis and Applications of Functionalized Ionic Liquids, Lausanne, EPFL, **2007**.
4. E. E. Schallenberg, M. Calvin, *J. Am. Chem. Soc.* **1955**, 77, 2779.
5. P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, 35, 1168–1178.
6. J. S. Wilkes, *Green Chemistry*, **2002**, 4, 73–80.
7. M. Begtrup and P. Larsen, *Acta Chem. Scand.,* **1990**, 44, 1050-1057.
8. J. H. Davis, Jr.; K. J. Forrester; T. Merrigan, *Tetrahedron Lett.* **1998**, 39, 8955-8958.
9. S. Keskin, D. K-Talay, U. Akman, and Ö. Hortaçsu, *J. of Supercritical Fluids*, **2007**, 43, 150–180.
10. a) Charles M. Gordon and Mark J. Muldoon, Synthesis of ionic liquids, in Ionic Liquids in Synthesis, ed. P. Wasserscheid and T. Welton, Wiley-VCH, Berlin, **2003**, pp. 33–40. b) John D. Holbrey and Robin D. Rogers, Physicochemical Properties of Ionic Liquids: Melting Points and Phase Diagram, in Ionic Liquids in Synthesis, ed. P. Wasserscheid and T. Welton, Wiley-VCH, Berlin, **2003**, pp. 56–59. c) Rob A. Mantz and Paul C. Trulove, Physicochemical Properties of Ionic

Liquids, in Ionic Liquids in Synthesis, ed. P. Wasserscheid and T. Welton, Wiley-VCH, Berlin, **2003**, pp. 75–143.

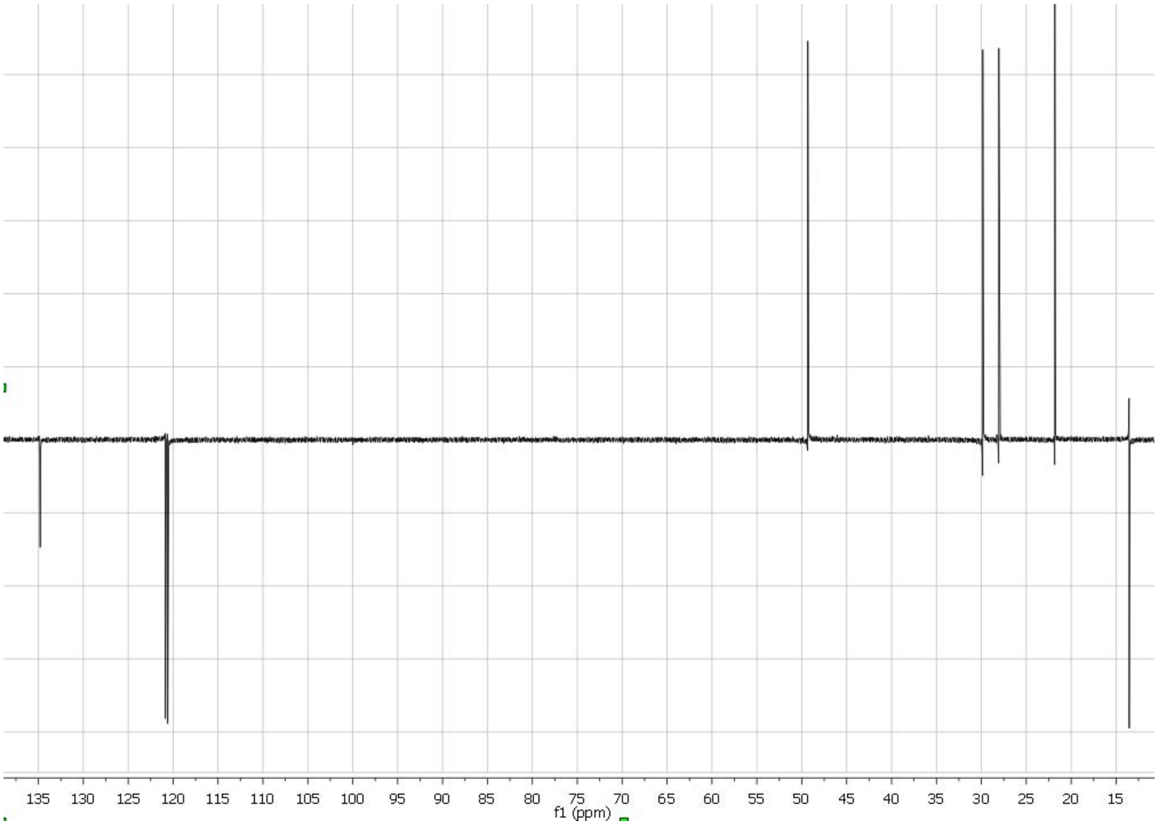
11. R. Hagivara and Y. Ito, *J. of Fluorine Chem.* **2000**, 2, 221.
12. S.N.V.K. Aki, J.F. Brennecke, A. Samanta, *Chem. Commun.* **2001**, 413–414.
13. P. Wasserscheid, R. van Hal, A. B¨osmann, *Green Chem.* **2002**, 4, 400–404.
14. K. R. Seddon, A. Stark, and M.-J. Torres, *Pure Appl. Chem.*, **2000**, 72, 2275-2287.
15. D. Fang, J. Cheng, K. Gong, Q.,R. Shi, X. L. Zhou, Z. L. Liu, *J. of Fluorine Chem.*, **2008**, 129, 108-111.
16. M. Deetlefs and K. R. Seddon, *Green Chemistry*, **2003**, 5, 181–186.
17. (a) R. J. C. Brown, P. J. Dyson, D. J. Ellis, T. Welton, *Chem. Commun.* **2001**, 1862; (b) A. S. Larsen, J. D. Holbrey, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2000**, 122, 7264.
18. M. D. Green and T. E. Long, *J. of Macromolecular Science*, *Part C*: *Polymer Reviews*, **2009**, 49,291–314.
19. V. K. Aggarwal, I. Emme and A. Mereu, *Chem. Commun.* **2002**, 1612.
20. a) Z. Fei, D. Zhao, T. J. Geldbach, R. Scopelliti and P. J. Dyson, *Chem. Eur. J.,* **2004**, 10, 4886 b) D. Li, F. Shi, J. Peng, S. Guo and Y. Deng, *J. Org. Chem.*, **2004**, 3582.
21. J. H. Davis, *Chem. Lett.* **2004**, 33 (9), 1072–1073.
22. R. J. C. Brown, P. J. Dyson, P. J. Ellis and T.Welton, *Chem. Commun.,* **2001**, 1862; P. J. Dyson, J. S. McIndoe and D. Zhao, *Chem. Commun.*, **2003**, 508.

23. S-G. Lee, *Chem. Commun.*, **2006**, 1049–1063 | 1049.
24. P. Wasserscheid, B. Driessen-Ho¨lscher, R. van Hal, H. C. Steffers, and J. Zimmerman, *Chem. Commun.,* **2003**, 2038.
25. D.M. Fox, W.H. Awad, J.W. Gilman, P.H. Maupin, H.C. De Long and P.C. Trulove ,*Green Chem.,* **2003**, 5, 724-727.
26. M. Badri, J-J. Brunet and R. Perron, *Tetrahedron Lett.* **1992**, 33, 4435-4438.
27. A.S. Larsen, J.D. Holbrey, F.S. Tham and C.A. Reed, *J. Am. Chem. Soc.*, **2000**, 122, 7264-7272.
28. G. Laus, G. Bentivoglio, H. Schottenberger, V. Kahlenberg, H. Kopacka, Thomas Röder and H. Sixta, Lenzinger Berichte 2005 , 84,71-85.
29. A.R. Hajipoura, and F. Rafiee, J. Iran. Chem. Soc., 2009, 6, 647-678.

Appendices



Appendix 1. DEPT spectrum of 1-pentyl imidazole in DMSO.



Appendix 2. DEPT spectrum of pentyl triflouroacetyl imidazolium hydroxide ionic liquid in $CDCl_3$.