THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Synthesis of protic ionic liquids

Challenges and solutions for the synthesis of pure compounds

Eduardo Maurina Morais

Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2022

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Licentiatuppsatser vid Institutionen för kemi och kemiteknik
Chalmers tekniska högskola
Nr 2022:07

Department of Chemistry and Chemical Engineering
Chalmers University of Technology
SE-412 96 Göteborg
Telephone +46 31 772 1000

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Abstract

The urgent need to diversify our energy matrix is responsible for a renewed interest in fuel cell technology, which can use hydrogen gas, a renewable green fuel, as an energy source. This technology is currently a commercially available option, however, it still requires technological improvements before it can be widely used for different applications. One way this technology could potentially be improved is by increasing its temperature range of operation by developing new, anhydrous proton conducting materials. Protic ionic liquids, which are organic salts with low melting temperatures, are interesting candidates for this application, since they can conduct protons in the operational conditions of fuel cells and without the need of water. These compounds can be synthesized by a simple acid-base neutralization reaction, but certain considerations must be taken in order to obtain high quality (dry and pure) protic ionic liquids.
In this thesis, a series of triazolium and imidazolium based protic ionic liquids were synthesized using a solvent-free method designed to address several limitations encountered with other commonly used methods. Using this method, pure (98-99% m/m) and dry (128-553 ppm of water) protic ionic liquids were synthesized (in a laboratory scale) without the need for purification methods that require heating the ionic liquid, hence avoiding the common issue of thermal decomposition. This method was also designed to allow for the accurate measurement of acid and base, and for the controlled mixing of both compounds, which is essential to avoid producing impure protic ionic liquids with excess of either acid or base. The system is consists of only glass and chemically resistant polymer (PTFE and PVDF) parts, which avoids other contaminants that can result from unwanted reactions involving the reagents with common laboratory tools (metallic objects, paper, plastic, *etc.*). The resulting ionic liquids were carefully analyzed by spectroscopic and thermal analysis methods designed to avoid water absorption, which is known to affect their properties. To complement this experimental characterization, computational chemistry tools were used to assess the ionic liquids' properties, as well as to assign vibrational modes.

Keywords: Protic ionic liquids, Fuel cells, Synthesis, DFT

List of Publications

This thesis is based on the following appended paper:

I. Solvent-free Synthesis of Protic Ionic Liquids. Synthesis, Characterization and Computational Studies of Triazolium based Ionic Liquids

Eduardo Maurina Morais, Iqbaal Abdurrokhman and Anna Martinelli

*A*ccepted for publication. *Journal of Molecular Liquids,* **(2022)**.

My Contributions to the Publication

Paper I

Shared first author. Designed and performed all experiments with the shared first author. Performed all of the computational experiments. Both first authors processed the experimental data, performed the analysis and drafted the manuscript. Was responsible for the submission process and the revisions after peer review.

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To my colleagues in the Division of Applied chemistry, thank you for your company during the many fika breaks, you guys make this place even better. To my examiner Magnus Skoglundh and director of studies Tiina Nypelö, thanks for all your time and dedication.

For all the hours of fun (inside and outside the climbing gym) and the beautiful places you took me to visit, I would like to thank my climbing friends. Snail boys forever!

Finally I would like to thank my family, the one I was born with and the one I've found along the way. You guys mean the world to me and I would not be here if it wasn't for you. You have made it all easier.

Eduardo Maurina Morais, Gothenburg, May 2022

Contents

List of Figures

List of Tables

List of Abbreviations

A
ATR Attenuated total reflectance. 11

D
DFT Density functional theory. 16–18, 21, 22
DSC Differential scanning calorimetry. 14, 15, 20

F
FTIR Fourier-transform infrared spectroscopy. 11, 12, 18, 21, 22

G
GC Gas chromatography. 13

I
IR infrared. 11, 12

K
KF titration Karl Fisher titration. 13

N
NMR Nuclear magnetic resonance spectroscopy. 9, 10, 19, 21

P
Δ**pKa** difference in pKa. 3

Q
qNMR Quantitative nuclear magnetic resonance spectroscopy. 10, 13

T
TfO trifluoromethanesulfonate anion. 6, 20, 21, 23, 24
TFSI bis(trifluoromethane)sulfonimide anion. 6, 20, 21, 23, 24
TGA Thermogravimetric analysis. 14, 15, 19

1 Introduction

It is a well established fact of life in the 21st century that there is an urgent necessity to diversify our global energy mix, since nowadays we heavily rely on dirty and non-renewable sources to power modern society (Figure 1.1).

This has thankfully been acknowledged by many nations, which are now committed to carbon neutrality at some point in the future. For example, the European Union is committed to reach this goal by 2050, and one of the strategies for reaching their objectives is the use of hydrogen fuel technologies. [2] Hydrogen gas is an interesting energy carrier option, since, when used to generate electricity, it emits no CO_2, producing only H_2O as a product.

Hydrogen can potentially fulfill many roles. It can be a fuel for light and heavy vehicles, be used to store excess energy from intermittent electricity generation sources (wind and solar for example) and even replace natural gas in the production of steel and cement. [3] Improvements in the fundamental technologies involved in the use and production of hydrogen, as well as the resolve of many nations to effectively tackle global climate change, have substantially increased the momentum and interest in hydrogen fuel cell technologies.

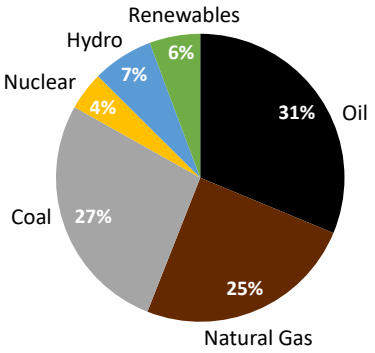

Figure 1.1: Global energy consumption by type in the year 2020. [1]

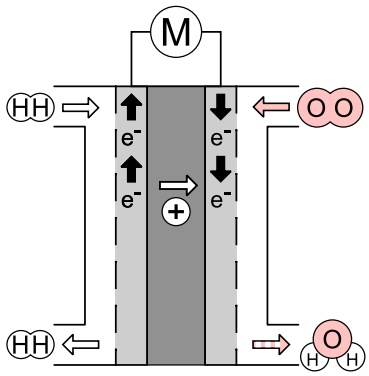

Figure 1.2: Scheme of a hydrogen fuel cell.

1.1 Hydrogen fuel cells

The fundamental concept of a hydrogen fuel cell (Figure 1.2) is quite simple, it is a device that allows for the controlled reactions of oxidation of H_2 and simultaneous reduction of O_2, generating H_2O. Since one of these redox reactions releases electrons (hydrogen oxidation) and the other requires electrons (oxygen reduction), if an insulator is placed in between the electrodes of the device where these two reactions are occurring, an electric potential can be formed, which can be used to drive a motor for instance. However, this insulator must be able to conduct protons from the anode side (where an excess of H^+ ions are being generated) to the cathode side (where the H^+ ions combine with O_2 to form H_2O). [1]

1:

$$H_2 \longrightarrow 2\,H^+ + 2\,e^-$$

$$\frac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \longrightarrow H_2O$$

$$H_2 + \frac{1}{2}\,O_2 \longrightarrow H_2O$$

One type of fuel cell, called proton exchange membrane fuel cell, commonly uses a hydrated polymeric membrane (*e.g.* Nafion®) as an electrolyte. This particular kind of fuel cell technology is quite attractive for use in vehicles, since it operates at low temperature (maximum of 80 °C) with high efficiency and high power density. [4] However, a clear limitation of this technology is that the use of water as a proton conducting species limits its temperature range of operation, due to evaporation, and it also increases the complexity of the device, since an additional water management system is necessary to make sure that the proton conducting membrane stays hydrated. At elevated temperatures, the catalytic activity also increases, improving the performance of the fuel cell. [5] To solve these problems, a proton conducting species that can function without the need of water would be ideal, although it must fulfill a series of requirements. It must be thermally stable, liquid within a broad temperature range, electrochemically stable, low flammability, low volatility and high proton conductivity. A class of compounds called protic ionic liquids (organic salts with a low melting point, read more on the Background chapter) have long been proposed to be candidates for this purpose [6], and have been receiving increased attention in the past few years (Figure 1.3).

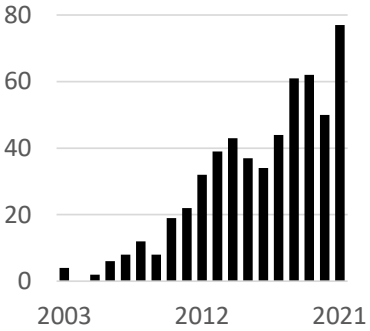

Figure 1.3: Number of publications per year (2003-2021). Search on Scopus using the keywords "Protic ionic liquids" and "Fuel cell".

1.2 Motivation of this work

The motivation of this work is the development and study of new materials for proton conducting membranes that do not require the use of water and offer similar or better performance than the currently used materials.

Background 2

2.1 Protic ionic liquids

Protic ionic liquids are compounds formed by the reaction between a Brønsted acid and a Brønsted base through the exchange of a proton during a neutralization reaction. [7] These compounds are distinct from regular inorganic salts (*e.g.* sodium chloride) in the fact that they present low melting temperatures, many times being liquids at room temperature (only being called ionic liquids, by an arbitrary definition, if liquids under 100 °C). Due to the strong intermolecular interactions (mainly by electrostatic interactions), these compounds tend to have low vapor pressures, when compared to common organic liquids (although higher when compared to aprotic ionic liquid counterparts).

2.1.1 Reversibility of the acid-base neutralization reaction

One fundamental characteristic of these compounds, is that they are formed by a reversible proton exchange reaction (Figure 2.1), hence, depending on the strength of the acid and the base used, fundamentally different properties are expected from the protic ionic liquid formed. For instance, if a strong acid and a strong base are used, the protic ionic liquid formed will consist in mostly ionic species, since there is a strong thermodynamic driving force pushing the reaction towards the products. On the other hand, if the difference in pKa (ΔpKa) of the two compounds is too small (*e.g.*, a weak acid and a weak base), a considerable amount of neutral species will be present. It is been estimated that a ΔpKa of ≈ 10 is necessary to accomplish full proton transfer, hence, forming a "true" protic ionic liquid. [8] So called pseudo-protic ionic liquids are found on the other side of the ionization spectrum, being composed of a large number of neutral species (free acid and base).

$$AH + B \rightleftharpoons A^- + BH^+$$

Figure 2.1: Generic acid-base neutralization reaction.

Keeping in mind the application, two fundamental properties of these compounds are extremely relevant, thermal stability and proton conduction, which are both related to the degree of ionization of the protic ionic liquid. In regards to thermal stability, if the ionic liquid contains many charged species and very few neutral species ("true" protic ionic liquid), the thermal stability is expected to be high. This can be explained by looking at the main decomposition mechanism of these compounds, which is the back proton transfer

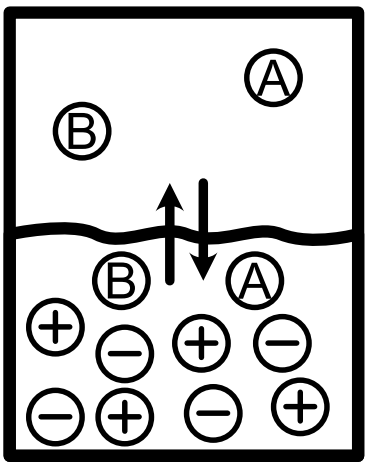

Figure 2.2: Schematic representation of the liquid-gas equilibrium of protic ionic liquids. A - free acid, B - free base.

mechanism, [9] in which the most acidic hydrogen of the cation is transferred back to the anion, forming the two corresponding neutral species (acid and base). Since these neutral species no longer interact through strong electrostatic interactions, they can now transition to the gas phase, which in practice results in the decomposition of the protic ionic liquid (Figure 2.2). Therefore, the less likely these neutral species are to form (*e.g.*, by using strong acids and bases), the more thermally stable will the protic ionic liquid be.

2.1.2 Proton conduction

On the other hand, the existence of neutral species can be beneficial to proton conduction. If we first look at the two main mechanisms of proton conduction (Figure 2.3), this observation becomes quite evident. Protons in protic ionic liquids can be conducted in two ways, by the vehicular and non-vehicular mechanism. [1]

1: Important to point out that two non-vehicular mechanisms exist, proton hopping and the Grotthuss mechanism. Even though many authors use these two terms interchangeably, they are two distinct mechanisms. An illustration of the differences between the two can be found in the supporting information material from Karlsson's work. [10]

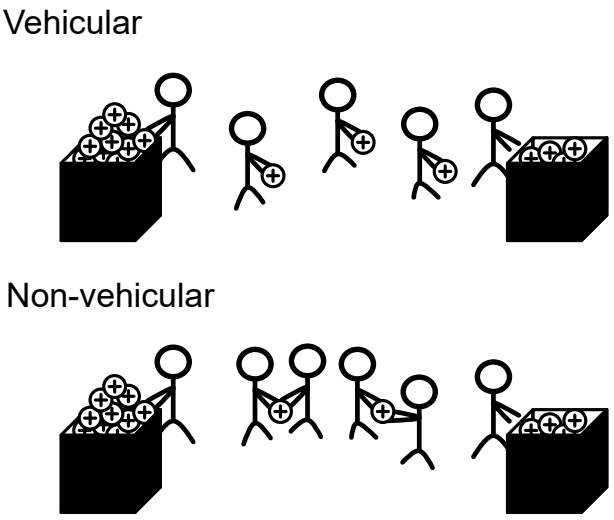

Figure 2.3: Schematic representation of the two proton conduction mechanisms for protic ionic liquids.

As the name suggests, in the vehicular mechanism protons are conducted from one point to another like passengers in a vehicle, through the diffusion of certain molecular species (protonated cations in the case of "true protic ionic liquids"). In the non-vehicular mechanism, protons are conducted by being transferred from one molecular species to another, and that is one of the reasons why the presence of neutral species can increase proton conduction, since the they can accept protons. The influence of neutral species has been demonstrated in different ways, for instance, by introducing neutral species to protic ionic liquids [11] or by analyzing pseudo-protic ionic liquids. [12, 13] It has been also proposed that many protic ionic liquids only present high proton conductivity because of the presence of neutral species introduced by improper synthesis (adding an excess of acid or

base by mistake) or thermal decomposition (causing an excess of the less volatile species, acid or base, to accumulate in the protic ionic liquid). [14] All of these studies highlight the importance of truly understanding and controlling the composition of the protic ionic liquid.

2.1.3 Synthesis of protic ionic liquids

The synthesis of these compounds is generally described in the literature as simply mixing acids and bases in a specific ratio (generally 1:1 mol ratio).[2] However simple it might sound, this must be done in a way that decreases the likelihood of unintentionally introducing impurities (mainly excess of acid or base and water), since as already discussed, these neutral species can considerably change the properties of these compounds (in the case of water, its content in protic ionic liquids has been shown multiple times to a relevant variable to be considered when analyzing their properties. [15]) To minimize the contamination by acid and base, the synthetic method must allow for the precise measurement of these two precursors. Not only that, but the process must not induce the decomposition reaction by back proton exchange (which in practice means keeping the reaction mixture and product at low temperatures). Avoiding water is also important, so the procedure must take into account all sources of water contamination (not only during the synthesis, but also when storing and analyzing). Additionally, since many of the acids and bases used are highly corrosive, the synthesis procedure must be designed taking this into consideration as well. In order to achieve this, a special synthesis procedure was developed. This procedure will be further discussed in the Methodology chapter of this thesis.

2: As far as the author of this thesis is aware, there are no publications discussing in detail all the problems involved in synthesizing these compounds, nor a way of avoiding these issues, which is one of the motivations for publishing such a detailed work as ours.

2.1.4 Triazolium protic ionic liquids

In this work, we choose to synthesize triazolium based protic ionic liquids and compare them to their more conventional counterparts (*i.e.* imidazolium based protic ionic liquids).

Triazolium based compounds (not strictly speaking protic ionic liquids, since many of the compounds described in the literature have melting points above 100 °C and some were nonstoichiometric mixtures) have been previously studied by other groups in the same [16, 17] or similar [10] context. These compounds were shown to have adequate thermal and electrochemical stability for use as proton conductors in fuel cells, as well as good proton conductivities. However, these studies mostly used the unmodified triazole molecule as a cation (with the exception of one study,

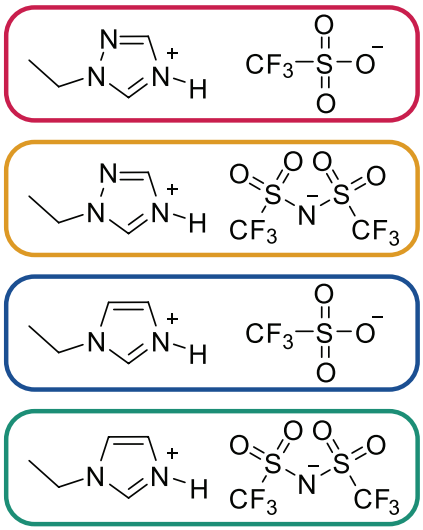

Figure 2.4: Molecular structure and color coding of all the protic ionic liquids considered in this study. From top to bottom: $[C_2HTr_{124}][TfO]$, $[C_2HTr_{124}][TFSI]$, $[C_2HIm][TfO]$ and $[C_2HIm][TFSI]$.

that used 1-methyl-1,2,4-triazole [10]), which keeps the melting point of the compounds quite high, due to the high symmetry of the cation. The studies also did not evaluate the use of the most commonly used anions, the trifluoromethanesulfonate anion (TfO) and the bis(trifluoromethane)sulfonimide anion (TFSI) (once again with the exception of one study that used TFSI [10]), which are well recognized for granting ionic liquids with high thermal and electrochemical stability as well as decreasing their melting point.

2.2 Objectives of this work

Our initial project goal was to obtain (either by purchasing or by synthesis) and characterize four protic ionic liquids, including two new ones based on the triazolium cation (Figure 2.4). Since two out of the four compounds could not be commercially sourced, we choose to synthesize them (including synthesizing a third compound which was available commercially, but at an unsatisfactory purity). While simple in theory, the synthesis of these compounds and their characterization have many peculiarities and presented serious challenges that had to be surpassed.

Methodology 3

Since Paper I was designed to serve as a sort of tutorial on how to synthesize and analyze protic ionic liquids, being very detailed and providing all of the information required to replicate our results, I choose not to unnecessarily repeat many of the experimental details (analysis conditions, temperatures, instrument settings, etc.). The objective of this thesis is to serve as a complement to the paper, specially for those with little experience in the field.

3.1 Synthesis

Two different types of synthesis were performed in our work, the synthesis of 1-ethyl-1,2,4-triazole and the synthesis of 3 ionic liquids ($[C_2HTr_{124}][TfO]$, $[C_2HTr_{124}][TFSI]$ and $[C_2HIm][TFSI]$.

3.1.1 Alkylation of triazole

To decrease the melting point of the resulting protic ionic liquids while keeping the size of the molecules small, we decided to add an ethyl group to 1,2,4-triazole. Due to the limited commercial availability of 1-ethyl-1,2,4-triazole, we decided to synthesize it. Our synthesis was based on the procedure published by Alpers *et al.* [18] The reaction is a simple nucleophilic substitution promoted by K_2CO_3 (Figure 3.1).

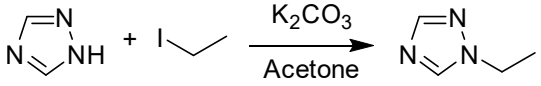

Figure 3.1: Alkylation of 1,2,4-triazole with 1-iodoethane.

A few modifications were done to the published procedure, since it was resulting in low yields of an impure product. We believe that the main issue with the reaction was the dialkylation of triazole, which most likely happened due to the excess of alkylating agent used (1:2 mole reaction between 1,2,4-triazole and 1-iodoethane) and low solvent volume, which resulted in high concentrations of the alkylating agent. We decided to reduce the ratio between reagents and increase the amount of solvent. Finally, in the original publication, the product was not purified to our satisfaction, so we decided to distill it using a Kugelrohr short-path vacuum apparatus. This, combined with purification using activated charcoal and molecular sieves, resulted in a product with 98.8% purity.

3.1.2 Synthesis of the protic ionic liquids

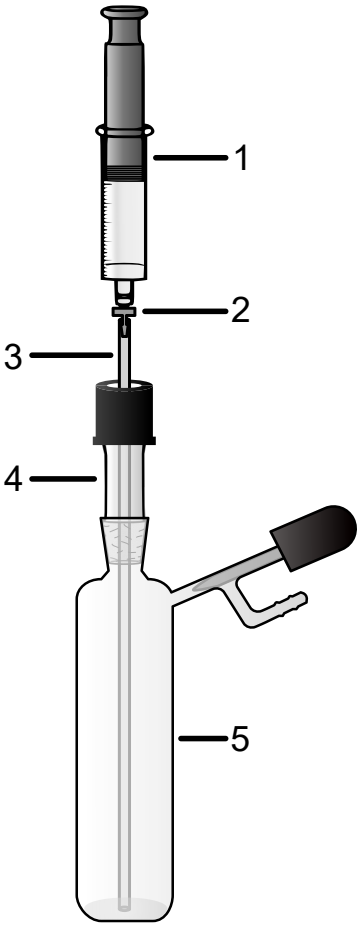

Figure 3.2: The setup for synthesizing protic ionic liquids. (1) 10 mL gas-tight glass syringe with PTFE plunger seal, (2) PVDF adapter, (3) PTFE tube, (4) Thermometer adapter (5) 25 mL Schlenk vial.

As previously discussed, the synthesis setup must allow for the accurate measurement of both reagents (acid and base), while reducing the likelihood of contamination. Many other factors were also taken into consideration while constructing this setup, like the commercial availability of parts, modularity, simplicity and reproducibility, just to name a few. In short, the setup (Figure 3.2) consists of two main modules, the syringe module (parts 1, 2 and 3) and the Schlenk module (parts 4, 5 and a stir bar). Liquids can be accurately and precisely measured (by weight) on the syringe module, while solids or liquids can also be precisely (accuracy being more difficult to achieve, specially for solids) measured (by weight) on the Schlenk module. This setup is assembled and filled with reagents inside a glovebox, which is necessary to avoid atmospheric moisture. Once both modules are filled with the appropriate amounts of reagents, they can be connected (through parts 3 and 4). The system is then removed from the glovebox and connected to a nitrogen Schlenk line. At this point, the Schlenk vial is cooled down with an ice bath (which is the reason why the reaction is not conducted inside the glovebox, since there were no reasonable cooling procedures that could be performed inside of it) and placed on top of a heating plate with magnetic stirring. Cooling is necessary to avoid heat decomposition and side reactions, since the neutralization reaction is very exothermic. The reagents can now be slowly mixed by pressing down on the syringe plunger. To make sure that no unreacted compounds are left on the walls of the system (or inside the PTFE tube for example), the liquid on the Schlenk vial is pulled back to the syringe and recirculated through the whole system multiple times, guaranteeing that both components (acid and base) are fully mixed. Now the protic ionic liquid is ready to be brought back to the glovebox, where a final purification procedure is performed before storage (activated charcoal and molecular sieves). This procedure resulted in pure protic ionic liquids with very low water contents (Table 3.1). More details on this procedure can be found in Paper I, as well as in a video in its supporting information.

Table 3.1: Purity assay and water content of the protic ionic liquids considered in this thesis.

Protic ionic liquid	Purity assay (% m/m from ^{19}F-qNMR)	Water content (ppm)
$[C_2HTr_{124}][TfO]$	98.0	345
$[C_2HTr_{124}][TFSI]$	98.3	553
$[C_2HIm][TfO]$[a]	99.7	bdl[b]
$[C_2HIm][TFSI]$	99.1	128

[a]From IoLiTec; [b]bdl: below detection limit

3.2 Instrumental techniques

Once the protic ionic liquids have been synthesized, a great deal of care was taken to make sure that all of the analysis results represented the true nature of the compounds, which means that for each analysis, a method of keeping atmospheric moisture away from the sample was developed. This guarantees that the sample is in the same state as it is in storage (anhydrous).

3.2.1 Nuclear magnetic resonance spectroscopy

Some atomic nuclei have a useful quantum property called nuclear spin (most notably ^{1}H,^{13}C and ^{19}F in the case of this work), which can be used to gather molecular chemical information. Nuclei with a spin $\neq 0$ (in other words, nuclei that have a spin), when under the influence of a strong magnetic field, interact with electromagnetic waves in different ways (by resonating at certain frequencies) depending on the electronic environment surrounding the nuclei, and this can be used to determine what is surrounding certain atoms (chemical environment).[1] In the context of this work, Nuclear magnetic resonance spectroscopy (NMR) was used to confirm the chemical structure of the synthesized compounds and to perform quantitative analysis (to be described in more detail in the following section). This structural analysis can be performed since the different hydrogens and carbon atoms in the molecules of interest have slightly different chemical environments (meaning that they are surrounded by electron clouds with different characters), which affects a property called chemical shift.[2] By combining the information provided by chemical shifts, peak splitting and relative peak areas, we can confirm the chemical structure of the synthesized compounds.
In regards to the practical aspects of preparing ionic liquid NMR samples for analysis, it is once again necessary to point out the importance of keeping moisture away from the NMR samples. Because of this, all samples were prepared and sealed inside the glovebox. Since we wanted to analyze the protic ionic liquids without the influence of a solvent, coaxial tubes (Figure 3.3) were used to physically separate the standard (DMSO-d_6 with TMS in the inner tube) and the protic ionic liquids (in the outer tube).

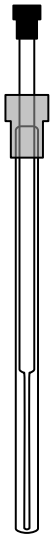

Figure 3.3: Coaxial NMR tube.

1: An excellent animation about the basics of NMR can be found in a website called "Quantum made simple", made by researchers from the Université Paris-Saclay. [19]

2: The chemical shift is a relative measurement, related to the difference between the resonance frequency of a nucleus in a sample and the one in a reference compounds, usually tetramethylsilane.

Quantitative nuclear magnetic resonance spectroscopy

Since the intensity of NMR peaks is related to the concentration of a certain atomic nucleus in the sample, it can be used for quantitative analysis (in our case, to determine the purity of a sample). This is done by comparing the intensity (by calculating the peak area) of a

peak originating from a certain nucleus from a reference sample to the intensity of a peak of the same type of nucleus from a different molecular species.

A good review on all aspects of Quantitative nuclear magnetic resonance spectroscopy (qNMR) was written by Bharti and Roy [20], hence, in this thesis, there will only be a short discussion on the most crucial aspects to consider when performing this type of analysis.

First of all, we must consider the reference molecule (internal standard), which must first fulfill certain requirements. Its NMR spectrum must be simple and have at least one peak (preferentially a singlet, since its integration is more simple and precise) that does not overlap with the analyte's peak of interest. The internal standard should be soluble in the solvent of choice, not react with any species present, non-hygroscopic, non-volatile, easy to handle (since the compound has to be precisely weighted, liquids with low volatility are quite well suited for this application) and of high purity. Having chosen an appropriate internal standard (4-fluoroacetophenone in our case), a known amount of this reference can be mixed with the analyte and a solvent. It is important to know the mass of both analyte and standard with high precision, and to make sure that they are fully mixed into the solvent. Multiple samples should also be prepared to account for small errors in the experimental procedure (in our case, triplicates were prepared). Once again, due to concerns about the effect of water on the results of the experiment, all sample preparation was performed inside the glovebox and samples were sealed. Now that multiple samples were prepared, they can finally be analyzed in an NMR spectrometer. However, there are a series of acquisition parameters to be considered, most notably, relaxation time, pulse angle, acquisition time, signal-to-noise ratio, number of points per peak (peak resolution), temperature and shimming. ^{19}F was chosen as the target nucleus (^{19}F-qNMR), since its natural abundance results in spectra with very well resolved and strong singlets, which simplify the task of peak integration. Once the data has been acquired, a few final steps must be conducted before peak integration, most notably, phase and baseline corrections. Now, the peaks of the analyte and the internal standard can be integrated, and the peak areas can be used to calculate the purity of the analyte using the equation:

$$P_x = (A_x/A_s)(N_x/N_s)(W_x/W_s)(M_x/M_s)P_s \tag{3.1}$$

where A_x and A_s are the peak areas of the analyte (x) and standard (s), N_x and N_s are the number of fluorine atoms of the analyte and standard molecules, W_x and W_s are the mass amounts of analyte and standard, M_x and M_s are the molecular masses of analyte

and standard, and finally P_x and P_s are the purities of analyte and standard. [3]

3: This is conveniently implemented as a script on the MestReNova software.

3.2.2 Vibrational spectroscopy

Vibrational spectroscopic techniques function based on the interaction between electromagnetic radiation (in the infrared (IR) region of the electromagnetic radiation spectrum) and matter. In this case, the result is the excitation of molecules to different states with distinct molecular vibrational modes. The nature of these molecular vibrations is dependent on the characteristics of each individual bond and the environment surrounding it, so they can be used to probe for molecular information. Two of the main techniques in the field are Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy. Both operate by different excitation mechanisms and result in spectra with different characteristics, but the fundamental molecular vibrational modes are the same. [21] [4]

4: While the vibrations are the same, depending on molecular symmetry, some are only visible on Raman for instance, being called Raman active. The same can happen on FTIR, being called IR active.

Fourier-transform infrared spectroscopy

In FTIR, the sample is irradiated with polychromatic IR radiation from an interferometer, being then transmitted through the sample and collected by a detector, forming what is called an interferogram. Using a mathematical operator called the Fourier transform, this interferometer can be used to build a spectrogram (which shows how much the molecule interacted with each individual wavelenght, as evidenced by its transmission). Many different sampling techniques can be used to expose the sample to the radiation, but one of the most common and simple ones is called Attenuated total reflectance (ATR). In this type of instrument, the sample is placed on top of a crystal (usually diamond) which is irradiated with IR. Most of this radiation is simply reflected inside the crystal, but part of it is absorbed by the sample material on top of the crystal. The result of this analysis is a FTIR spectrum, which can be used as a fingerprint, to uniquely identify a specific molecule, or as a tool to compare molecular characteristics of different molecules. In order to perform this type of analysis without the influence of atmospheric water, samples of the ionic liquids were collected from the glovebox in sealed syringes and placed on the ATR's diamond window under flow of dry nitrogen gas using a funnel (Figure 3.4).

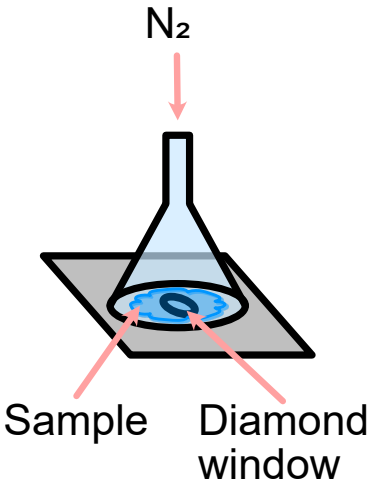

Figure 3.4: ATR funnel setup.

Raman spectroscopy

While the vibrational modes observed in FTIR and Raman spectroscopy are the same, the excitation mechanism that allows these

vibrations to happen is completely different. In Raman spectroscopy, a phenomenon called Raman scattering is used to generate the signal used to create the spectrogram. In order to create this Raman signal, the sample must be exposed to radiation with a higher energy than the one of the molecular resonant frequencies (IR in the case of vibrational spectroscopy). Lasers with visible wavelenghts are commonly used for this purpose, since they are much higher in energy compared to IR. Since high energy radiation is being used to excite the molecules, they are excited to a so called virtual state (a state that has a higher energy than the allowed vibrational states of the molecule), which quickly decays by a few different paths (Figure 3.5). Through some of these paths, Raman scattering radiation is generated, being then collected by a detector to form a spectrogram.

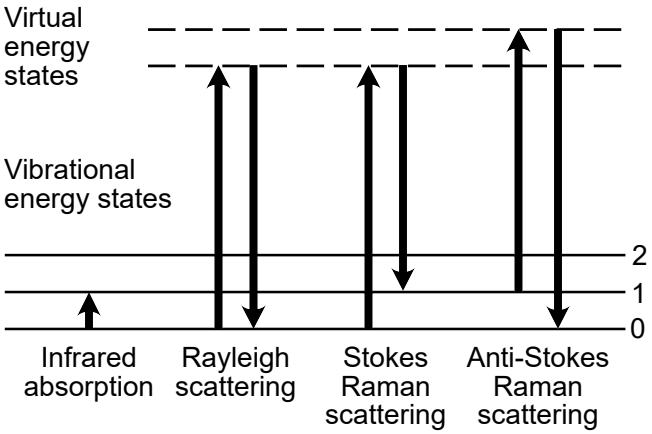

Figure 3.5: Jablonski diagram for different absorption and scattering modes on vibrational spectroscopy. Based on the work by Wikipedia user Moxfyre. [22]

To guarantee that the sample will not absorb water during analysis, which can take several minutes, all samples were prepared inside the glovebox and placed inside a specially designed (by Dr. Mohammad Hasani) apparatus (Figure 3.6).

The Raman spectra acquired by this method can also be considered to be a fingerprint of the molecule, in the same way as the FTIR spectra, but due to the different activities of certain vibrational

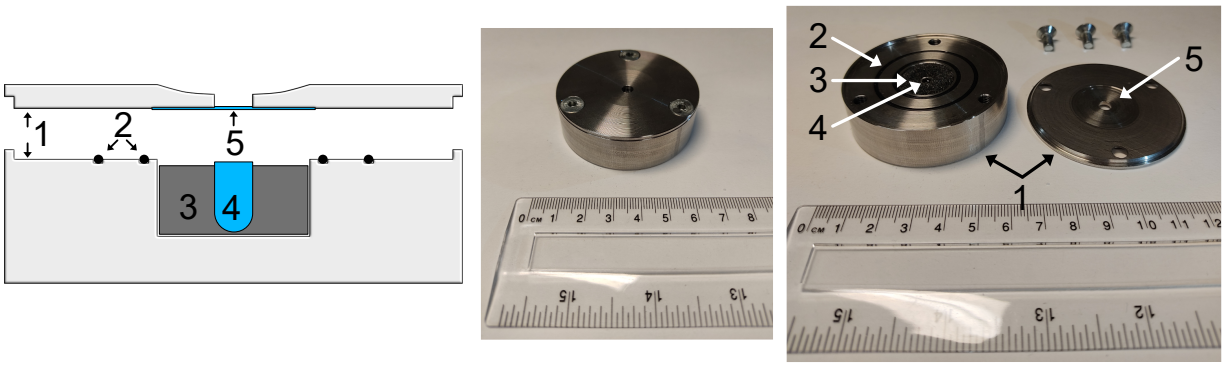

Figure 3.6: Custom made air-tight Raman cell. (1) Stainless steel body and lid, (2) rubber o-rings, (3) foam tube support, (4) glass tube (bottom of an NMR tube), (5) round glass coverslip (fixed to the lid with silicon grease).

modes in the two methods, different information can be obtained from Raman, specially in the fingerprint region.

3.2.3 Gas chromatography

As other types of chromatography, Gas chromatography (GC) is a separation technique that takes advantage of the different physico-chemical properties (mainly boiling point and the polarity) of compounds to separate them. The basic procedure consists in carrying a mixture of compounds (by using a gaseous mobile phase) through a heated capillary tube (with a modified internal surface as a stationary phase) which ends at some kind of detector. By doing this, compounds with high boiling points that interact strongly with the stationary phase will take a long time to get to the detector, while compounds with low boiling points and weak interactions with the stationary phase will arrive faster. Data from the detector can be used to generate a chromatogram, from where composition data can be extracted, such as the purity of a compound. In our work, GC was used to determine the purity of the synthesized 1-ethyl-1,2,5-triazole as well as the purity of 3-Fluoroanisole. The purities of all precursors (acids and bases) for the ionic liquids had to be determined in order to correctly measure the molar amounts to be mixed. Regarding 3-Fluoroanisole, this compound was used to validate the ^{19}F-qNMR technique, since we can cross-check the ^{19}F-qNMR purity results with the GC purity results while using 3-Fluoroanisole as a analyte of known purity (by GC). As was the case for many other sample preparation procedures, the triplicate samples were prepared inside the glovebox.

3.2.4 Water content analysis

The Karl Fisher titration (KF titration) technique is one of the most useful and easy techniques available for the determination of trace amounts of water in organic compounds. The technique is based on a chemical reaction[5] that consumes water and relates that consumption to an electrical current which can be quantified. This can be done, since one of the reagents, I_2, is electrochemically generated *in situ*. [23] In terms of the practical aspects of this technique, ideally, triplicate samples would be prepared to account for experimental errors in the water content determination, however, since the amount of water present in the ionic liquids is so low (in the order of a few hundred ppm), a large (in the context of the laboratory scale synthesis) amount of sample is required (up to 0.5 g of compound), hence, only a single measurement was performed for each analysis. Samples were prepared inside glovebox and quickly transported to the instrument (inside sealed

5: $H_2O + I_2 + [RNH]^+SO_3CH_3^- + 2\,RN \longrightarrow [RNH]^+SO_4CH_3^- + 2\,[RNH]^+I^-$

plastic syringes) in order to minimize water absorption during the analysis time.

3.2.5 Thermal analysis

The thermal properties of the protic ionic liquids are extremely important given their potential application as proton conductors in fuel cells. They must be capable of withstanding large variations in temperature without degrading and have a large liquidus range without any significant phase transitions. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) are two techniques that can be used to determine these thermal properties, but special concerns specific to these types of compounds must be taken into account.

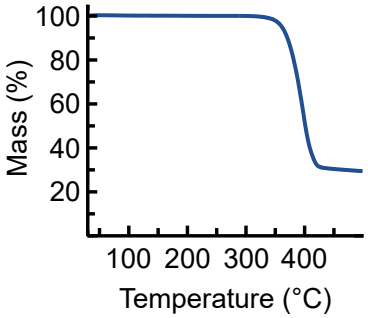

Figure 3.7: Example of a typical TGA thermogram. In this case, the thermogram for $[C_2HIm][TfO]$.

Thermogravimetric analysis

During TGA analysis, a sample of an analyte is place inside an inert container (most commonly a small aluminium crucible) on top of the arm of a precision scale. The crucible is then heated, which will cause the sample crucible to slowly lose mass (by evaporation or thermal decomposition of the sample material). The change of mass can be plotted as a function of time, forming a TGA thermogram (as an example, see Figure 3.7).

One crucial aspect of TGA analysis is to consider how the sample was analyzed, since different methods of analyzing the same sample can yield very different results. Variable like the atmosphere used in the oven, how the sample was prepared, which heating curves where used, must all be taken into consideration when interpreting the results. For instance, if a sample is found to be thermally stable by TGA analysis over a small period of time and under an inert atmosphere, it does not necessarily mean that the sample will be stable over long periods of time inside a fuel cell for instance, hence, it is important to take this into consideration when analyzing the results. Also, the way the samples are prepared is very important. It is a common practice in the field of ionic liquids research to subject them to a drying cycle before analysis, to make sure that most of the water absorbed by these compounds during sample preparation was removed (since the TGA crucibles have to be open, in order to allow for volatiles to escape the crucible during analysis). While this is reasonable for some aprotic ionic liquids, protic ones can decompose during this drying cycle, therefore, we decided to avoid this procedure by preparing the samples inside the glovebox, sealing them with a cap with a pin hole and blowing nitrogen over the crucibles until they are place inside the nitrogen filled TGA

oven. In this way, the samples can be analyzed without introducing water to the ionic liquids and avoiding thermal decomposition. To determine the effect of this method on the results of the TGA thermograms, a similar set of samples were also analyzed without the use of nitrogen flow, by simply allowing the samples to absorb atmospheric moisture for a period of approximately 1 h. This set of samples was also submitted to a drying cycle (heating the crucibles at 120 °C for 30 minutes inside the TGA instrument before analysis), for comparison.

Differential scanning calorimetry

The DSC technique consists in measuring the heat flow produced in a sample (commonly placed inside an aluminium crucible) when subjected to heating and cooling cycles. This is commonly used to detect phase transitions in ionic liquids, since these phase transitions are associated to exothermal or endothermal events (as well as changes in their heat capacities). The heat flow can be plotted as a function of the sample temperature, creating a DSC thermogram (as an example, see Figure 3.8).

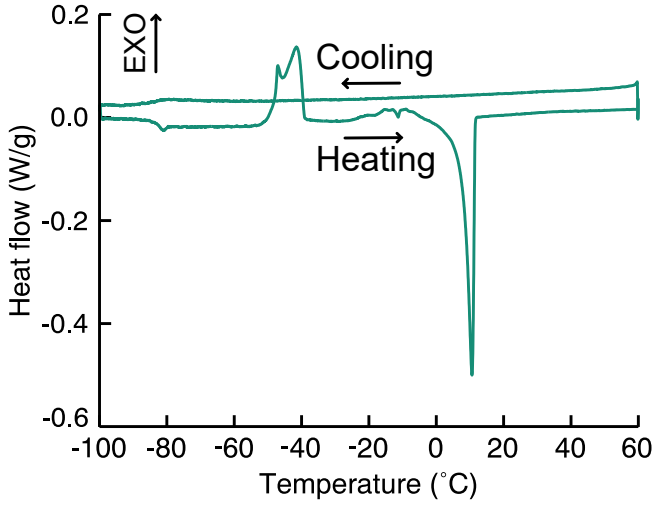

Figure 3.8: Example of a typical DSC thermogram. In this case, the thermogram for $[C_2HIm][TFSI]$.

Peaks on the thermogram can show the presence of phase transitions, like crystallization and melting, while other changes like the glass transition show as changes in the heat capacity of the sample (step around -80 °C). In order to perform this analysis, a few concerns have to be considered. As in TGA, the sample crucibles have to be prepared inside the glovebox, however, in this case they can be fully sealed, which simplifies the analysis procedure. In regards to the heating and cooling cycle, there are many ways to perform these, but we choose to perform 2 different types of cycles, the so called slow and fast methods. These methods were designed to induce or suppress crystal (or glass) formation, by tuning the heating/cooling rates, hence, allowing us to better spot

these transitions. It is important to point out that the data presented here and in Paper I was the result of the second cycle (multiple cycles of heating and cooling were performed for each sample), which is necessary to erase and equalize the thermal history of these compounds (especially relevant for solids and debatable for liquids).

3.3 Computational techniques

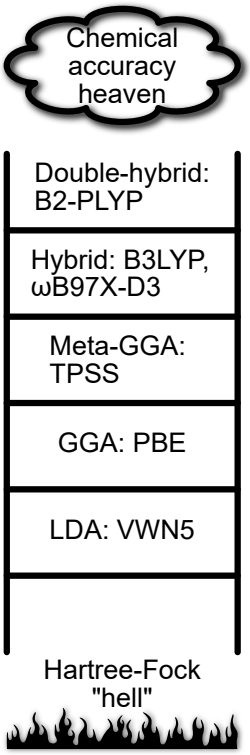

Figure 3.9: Jacobs ladder of DFT methods. For more details on the differences of these methods refer to the papers by Cohen [24] and Becke [25], as well as an excellent video by Prof. David Sherrill. [26]

In order to explore the fundamental physico-chemical properties of the protic ionic liquids in this work, computational chemistry methods were used, mainly molecular modeling using Density functional theory (DFT). Before discussing how these techniques were used, it is important to understand the fundamental theory behind it all and what are the limitations of it.
According to quantum mechanics, all of the information about an atom (and by extension a molecule) is contained in its wavefunction, as described by Schrödinger's theory. This means, that information about the reactivity of a molecule, its spectroscopical signatures and many other chemical properties could be perfectly described if we knew its wavefunction. However, in practice this can only be done for very small systems, like a single hydrogen atom isolated in space. If we want to apply these quantum chemical theories to larger systems, different approaches must be used, involving the use of some approximations. These different approaches are what I will refer to as levels of theory. Lower levels of theory make use of many approximations and are therefore further away from the "true" answer to the Schrödinger's equation. However, this means that they are computationally less intensive (requiring a lower number of individual mathematical operations), which in practice means that they can be used in larger molecular systems (thousands or even hundreds of thousands of atoms). This is the case for molecular mechanics, which uses classical mechanics in order to simplify molecular systems by using pre-established values for molecular parameters, like bond length and angles. This will of course come at a cost, by providing less accurate predictions. The next step is the use of quantum mechanical models, which are generally segregated by how they deal with the "many-body problem".[6]

6: Systems with multiple interacting entities are notoriously complicated to compute, since every variable in the system depends on all others.

One of the many ways of dealing with these issues while maintaining a certain level of accuracy is the use of DFT, which uses the electronic density as a sort of "substitute" for the wavefuncion, drastically reducing the complexity of the mathematics. This however introduces a new problem, how to mathematically describe this electron density. This gave rise to a hierarchy of DFT methods,

going from rough approximations to complete accuracy (which does not exist currently, and might never exist), many times represented by the so called Jabob's ladder of DFT functionals (Figure 3.9). [27]

A great resource to start learning about computational chemistry is the excellent book by Prof. Jeremy Harvey "Computational chemistry". [28]

This means that the user of DFT methods must determine which level of accuracy is required for a certain study, since we are simply limited by our computational resources and the size of the molecular model being used (number of atoms involved in the calculation). A good compromise between speed and accuracy is many times found in the form of hybrid functionals (one of the most popular being the B3LYP method). This accuracy can be determined by comparing calculation results from different functionals to a "gold standard" method (usually coupled cluster methods). [29] A few more decisions must be taken by the researcher before conducting the calculations (basis set, dispersion correction and solvation just to name a few), but maybe the most important is the choice of molecular model. In the case of pure protic ionic liquids, ideally, the model would be build by using multiple ion-pairs (maybe hundreds of thousands of ion-pairs), so that solvation effects and long range intermolecular interactions would be perfectly accounted for. This however is simply not possible while using highly sophisticated DFT methods. Commonly, single ion-pairs are used, and to account for some of the solvation effects, implicit solvation models are used.[7] Another important aspect to consider when building ion-pair models for protic ionic liquids is which conformer to select. Lower energy conformers are usually better representations of the bulk phase (since they are lower in energy, they will be the majority conformer according to the Boltzmann distribution), however, protic ionic liquid conformers can be quite close in energy (*i.e.*have a very "smooth" potential energy surface). To better understand this problem, lets look at the example of the two hypothetical dimer systems (Figure 3.10). Let us first consider dimer A. The puzzle pieces can easily fit in multiple different ways, therefore, their relative energies will be quite similar and the barriers to transition between the different dimer configurations (conformers) will be very low ("smooth" potential energy surface). On the other hand, if we look at the key and lock (dimer B), there is only one obvious way they can fit, making the other higher energy configurations less favorable and harder to access ("rough" potential energy surface).

7: In the implicit solvation model, the coulombic effects of the solvent on the molecules are approximated by simply surrounding the molecule with point charges

Ionic liquids are in the first category of compounds (same as dimer A), since their charges are very delocalized and their cations very asymmetrical. In practice, this means that finding the lowest energy conformer of an ionic liquid is not a trivial task and requires certain considerations. Ideally, a vast number of high level of theory geometry optimization calculations would be performed to find

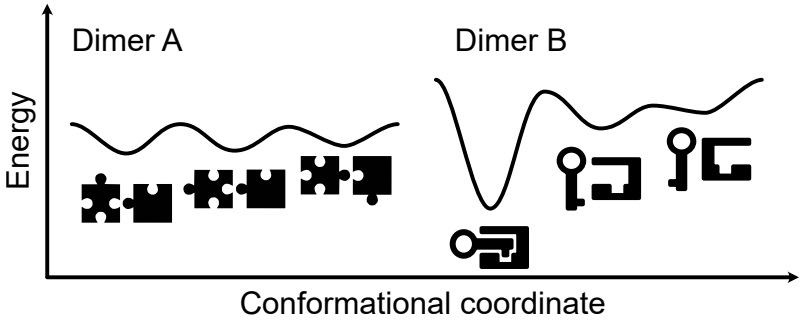

Figure 3.10: Scheme of two different one-dimensional potential energy surfaces for two different dimer systems.

a series of low energy conformers, but this is not practical, since it would take an unreasonable amount of time (several months). One solution to this problem is to manually build a few different reasonable conformers and optimize them with a low level of theory (molecular mechanics and semi-empirical methods for instance), next, a couple of these structures (the ones with the lowest energy) can be further optimized using high level of theory methods (like DFT). This was the procedure used in this work. However, it is important to point out that the exact procedure used could be simplified and improved.[8] Once the optimized structures of the ion-pairs are found, several other molecular properties can be calculated. In the case of this work, vibrational spectra were calculated and compared to the experimental ones (allowing us to suggest assignments of vibrational modes to experimentally determined peaks in the FTIR spectra), and molecular descriptors (like bond lengths, charges, electrophylicity) were calculated and used to compare the differences in acidity between the different compounds. Finally, it is important to discuss some considerations about the use of computational techniques. When analysing the results, one must consider that models have their limitations. In the case of this work, as discussed previously, the molecular model used (an isolated ion-pair with implicit solvation) is not a true representation of the bulk phase of protic ionic liquids, but an approximation. Also, the quantum chemical model itself is not perfect, not achieving the "chemical accuracy heaven". Although these methods are not usually capable of perfectly predicting experimentally determined quantities (such as bong lengths and vibrational frequencies for example), they can certainly get extremely close, making them useful tools to determine general trends between a series of compounds. In short, computational results should always be taken with a grain of salt.

8: The optimization steps using HF and B3LYP could have been skipped with little to no effect on the final result. Also, better low level of theory methods became available since this work was performed. For instance, the CREST software [30] can be used to easily generate multiple low energy conformers with geometries quite similar to the ones resulting from DFT calculations.

Results and discussion 4

The results discussed here are a summary of the ones presented in Paper I, since a detailed discussion is already presented there.

4.1 Synthesis of the protic ionic liquids

As stated previously, the initial objective of our project was to obtain the four protic ionic liquids (Figure 2.4) and to compare their properties. However, it became obvious that a new method of synthesizing these compounds was necessary, hence, this was our first priority. This was successfully accomplished by the use of the system illustrated in Figure 3.2. The system fulfilled all requirements (more details on the "Practical constraints" section of Paper I), and allowed for the controlled mixing of highly corrosive and hydroscopic materials, producing dry and pure protic ionic liquids (Table 3.1). The ionic liquids have the expected structure and did not exhibit signs of major contaminants, as confirmed by NMR (hydrogen, carbon and fluorine. More details on the "Synthesis of the ionic liquids" section of Paper I). As always, there is room for improvement, so a new system is being developed in order to allow all steps of the synthesis to occur inside the glovebox. This could not be done before, since we did not have any reasonable cooling methods that could be used inside the glovebox, however, we purchased an instrument (a magnetic stirrer with heating and cooling functions) that will hopefully allow us to do so. We also expect this new method to allow us to eliminate the use of molecular sieves, since the ionic liquid will not have any opportunities to be exposed to atmospheric moisture, meaning that if the precursors are dry, the ionic liquid will be dry. The next step is to finally analyze the physico-chemical properties of the protic ionic liquids. Once again it is important to point out that each technique has special sample preparation precautions that were developed to guarantee that the analysis represents the true nature of the protic ionic liquids (as stored in the glovebox).

4.2 Thermal analysis

Starting with TGA, it became clear that the commonly used method of analyzing these compounds (pre-heating them in the TGA oven to drive out moisture) should not be used, since it considerably changes the results and conclusions of the analysis (Figure 4.1).

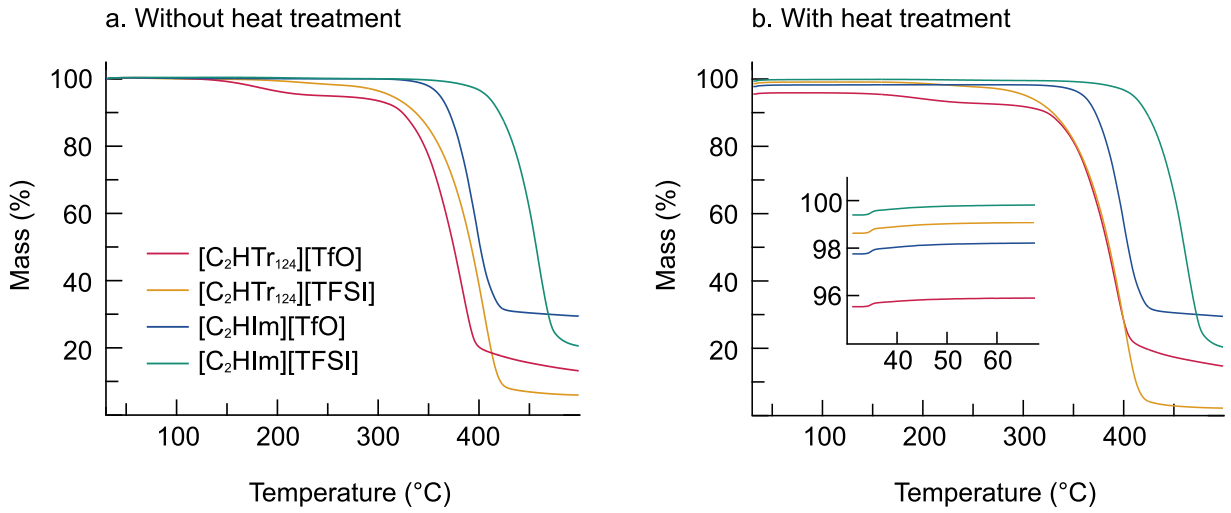

Figure 4.1: Thermogravimetric curves of $[C_2HTr_{124}][TfO]$, $[C_2HTr_{124}][TFSI]$, $[C_2HIm][TfO]$ and $[C_2HIm][TFSI]$ recorded under N_2 atmosphere, without (a) and with (b) a heat treatment. Inset in b) is a zoom in of the top left region of the graph.

The results clearly point to triazolium based protic ionic liquids as being less thermally stable when compared to imidazolium ones, and TfO based ones being less stable when compared to TFSI ones. We suspect that one of the reasons for this reduced thermal stability of triazolium and TfO based protic ionic liquids is most likely due to their increased acidity, which means that back proton transfer decomposition is more likely. The triflic acid (HTfO) formed is also more volatile when compared to trifluoromethanesulfonimide (HTFSI), which once again would result in a lower thermal stability. This acidity trend is a repeating pattern throughout many other analysis in this work.

In regards to DSC (Table 4.1), it appears to indicate that triazolium ionic liquids have a tendency to form glasses, while imidazolium ones form crystals. This could be due to the decrease in symmetry of the triazolium cation, but we also cannot exclude the possibility that it might be related to the lower purity of the triazolium based protic ionic liquids (resulting from the fact that we could only achieve 98.8% purity for the 1-ethyl-1,2,4-triazolium base). Important to highlight $[C_2HIm][TfO]$ as having a strong tendency to crystallize, most likely due to its purity (99.7%) and strong coordination of the TfO anion.

Table 4.1: Results from the thermal analysis by DSC of all protic ionic liquids. Values are extracted from the 2nd cycle. Multiple values indicate a set of proximate peaks.

Method	Protic ionic liquid	T_g (°C)	T_c (°C)	T_m (°C)
Fast method (10 °C/min)	$[C_2HTr_{124}][TfO]$	-65.27	-	-
	$[C_2HTr_{124}][TFSI]$	-62.60	-	-
	$[C_2HIm][TfO]$	-	-18.26	22.27/29.11
	$[C_2HIm][TFSI]$	-81.83	-	-
Slow method (2 °C/min)	$[C_2HTr_{124}][TfO]$	-67.47	-	-
	$[C_2HTr_{124}][TFSI]$	-64.31	-	-
	$[C_2HIm][TfO]$	-	-8.512	19.52/22.55/28.91
	$[C_2HIm][TFSI]$	-84.23	-47.03/-41.59	10.61

4.3 NMR results

As previously stated, the ^{1}H-NMR results confirm the expected structure of the protic ionic liquids (Figure 4.2). The ^{13}C and ^{19}F-NMR results also are as expected (in the supporting information for Paper I).
A very interesting trend can be seen in the chemical shifts of the N-H hydrogens of the cations (region between 9-14 ppm), with triazolium N-H hydrogens being shifted downfield (higher ppm) when compared to the imidazolium peaks. The same is observed when comparing TfO to TFSI. It has been previously shown that the chemical shift of this type of hydrogen is associated with acidity [31], hence, our data seems to indicate that triazolium protic ionic liquids and TfO protic ionic liquids have a more acidic character.

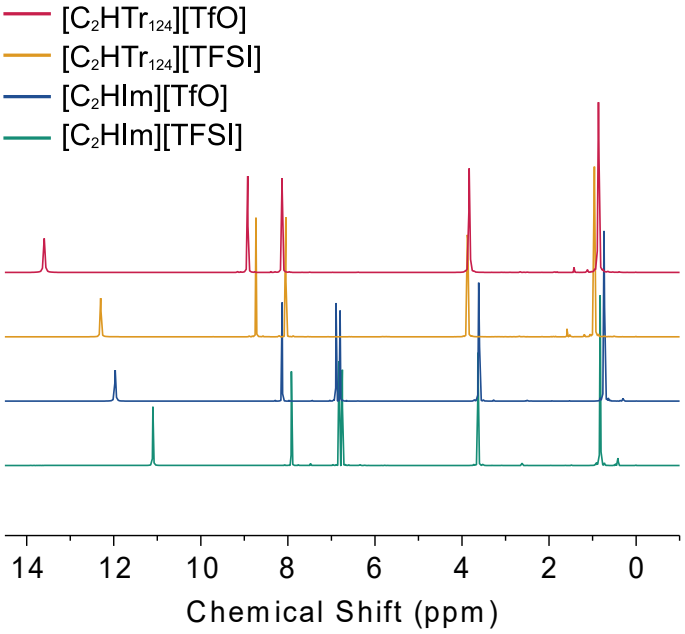

Figure 4.2: ^{1}H-NMR of the ionic liquids. From the top to the bottom, $[C_2HTr_{124}][TfO]$, $[C_2HTr_{124}][TFSI]$, $[C_2HIm][TfO]$ and $[C_2HIm][TFSI]$.

4.4 Vibrational spectroscopy

FTIR results show good agreement with DFT calculated spectra, meaning that the molecular model is a quite decent representation of the bulk phase of the protic ionic liquids. The experimental and calculated FTIR results were compared to provide assignments for the vibrational modes of all four protic ionic liquid. As discussed before, since these are quite complex systems, one should not expect DTF results to perfectly match with experimental data. With that in mind, we only provided assignments for peaks that we have a certain level of confidence. Since this process can be quite subjective, the software vibAnalysis [32] was used in conjunction with the visual inspection of the animated vibrational modes in the Avogadro software. [33] By analyzing the assignments, it becomes

clear the the spectra are divided in two regions, with the cation mainly contributing with the high wavenumber region and the anion contributing with the fingerprint region (low wavenumbers). One interesting piece of information that can be taken from the high wavenumber region, the acidity of the N-H group (Figure 4.3).

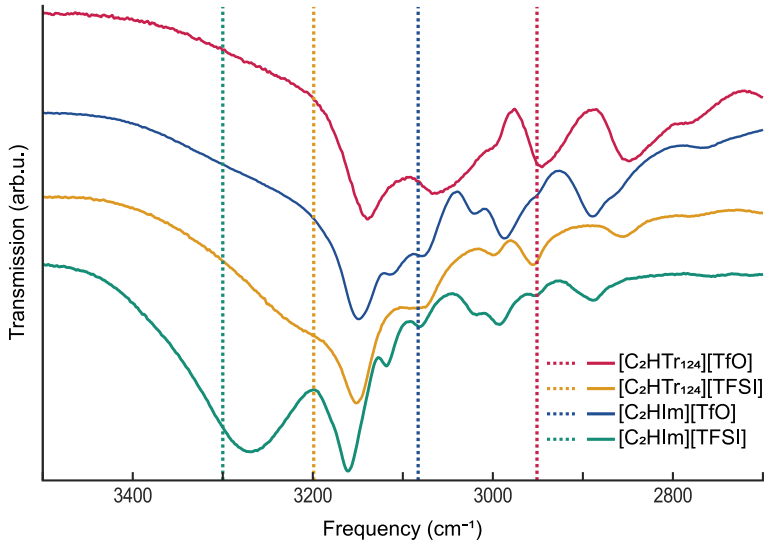

Figure 4.3: Experimentally recorded FTIR spectra, of all four ionic liquids, in the frequency region of the N-H stretching mode. Dashed lines correspond to the calculated frequencies for the N-H stretching.

It appears that the N-H stretching band is shifting towards lower wavenumbers when comparing the spectra of $[C_2HIm][TFSI]$ with $[C_2HTr_{124}][TfO]$, once again suggesting that triazolium ionic liquids are more acidic when compared to imidazolium. Calculated values seem to indicate the same trend. However it is important to highlight that computational values for this particular vibrational mode are quite hard to accurately calculate, since they are highly influenced by their surroundings. Additionally, only the position of the $[C_2HIm][TFSI]$ N-H peak could be clearly determined, since the other N-H peaks are merged with the other features in the region. Raman spectra was also acquired, at this point serving only as a complement to FTIR data.

4.5 Computational results

The DFT computational studies all seem to point to the same direction, with triazolium protic ionic liquids as being more acidic. This is evidenced by a few different descriptors. The N-H bond lengths of the triazolium compounds are longer than the ones of their imidazolium counterparts, the polarization of the N-H bond (as evidenced by the differences in charge between the N and H atoms) is larger and they have higher electronegativity and electrophilicity (two descriptors of Lewis acidity). This can be explained due to the differences in electronic structure between the two cations (Figure 4.4).

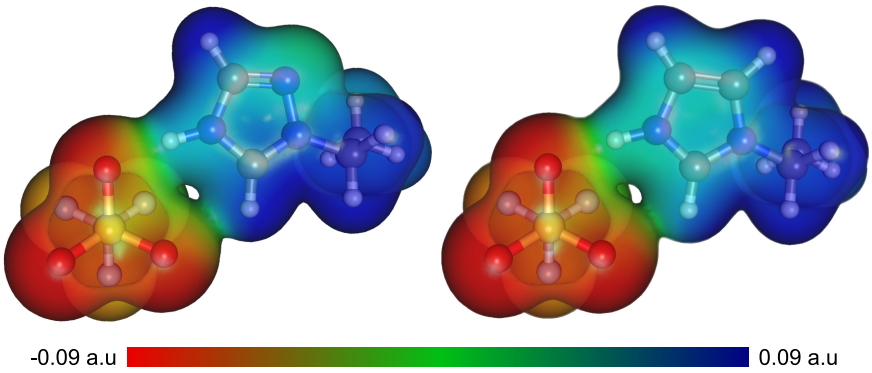

Figure 4.4: Electrostatic potential map (plotted on the electron density iso surface with a value of 0.007) for the $[C_2HTr_{124}][TfO]$ and $[C_2HIm][TfO]$ optimized ion pairs in the ωB97X-D3BJ/cc-pVTZ level of theory.

When comparing two protic ionic liquids with the same anion but different cations ($[C_2HTr_{124}][TfO]$ and $[C_2HIm][TfO]$), it becomes clear that the presence of an extra nitrogen on the triazolium ring causes electron density to pool around it, reducing the electron density around the N-H bond, increasing its acidity. This is similar to the electron-withdrawing effect that a nitro group would exert in an aromatic ring.

The effect of the TfO group in increasing the acidity of the ionic liquids can also be seen in the lengthening of the N-H bonds and their increased polarization, when compared to TFSI. This can be explained by the increased coordination of the TfO anion with the N-H bond (by forming a stronger hydrogen bond), which weakens it. One can imagine this increased acidity as being the effect of the two ions competing for the hydrogen in a sort of molecular tug of war, with TfO being a stronger competitor when compared to TFSI. As discussed before, one should always take these results with a grain of salt, hence, additional studies (both computational and experimental) would be required to definitively prove these hypotheses.

Conclusions and future work 5

The methods presented in this thesis allowed the synthesis of pure and dry protic ionic liquids and to analyze them in their unmodified state (without absorbing substantial amounts of atmospheric moisture). This is crucial, since it gives us more confidence in the results of the analyses. These objectives were accomplished while keeping the complexity of the system to a minimum, which will hopefully allow other research groups to make use of it. In regards to the results of the analyses performed in the four protic ionic liquids, they seem to indicate a trend on their acidity, with triazolium based compounds being more acidic when compared to imidazolium, and TfO based compounds being more acidic when compared to TFSI ones. Triazolium and TfO compound are also less thermally stable, which is most likely a consequence of their increased acidity (due to back proton transfer).

Future outlook

Since our synthesis procedure is by no means perfect, we hope that we can find new solutions to further simplify it in the future. One of the most important ways it could be simplified, is by having a cooling system inside the glovebox. This would allow the entire synthesis to happen in a water-free environment, which means that the only way water can be introduced into the ionic liquid is by its presence in the precursors (acid and base). This would also drastically simplify the synthesis process, since it removes one of the many constraints of the synthesis setup, which is fitting inside the glovebox antechamber (the entire synthesis setup from Figure 3.2 must be able to fit sideways inside the small antechamber, since it must be transferred to the Schlenk line outside of it, where the mixing of the acid an base happens). Another constraint that would be eliminated is the need of the system to be airtight, since this would now be irrelevant, due to the absence of atmospheric moisture. Schlenk vials would also not be necessary, since there is no need to pressurize the system with nitrogen gas. All of these factors allow for the development of new systems, which could for instance enable the synthesis of larger amounts of ionic liquid.
The next step is to take advantage of this system to make new protic ionic liquids that might be useful proton conductors. Currently, this system enables the solvent-free synthesis of a variety of protic ionic liquids, as long as at least one of the components (acid or base) is a liquid at room temperature. Four new compounds (protic ionic liquids based on nitro and cyano functionalized imidazole, furfural based amine and histamine) are currently being considered and preliminary synthesis work has already been conducted.
Now that we have a method for making these compounds, we can finally analyze their

transport properties and determine how different structural features impact proton conductivity. This is commonly done by analyzing their conductivity and self diffusion, but these properties must be measured in a way that does not modify these compounds, by using the same sample preparations and analysis principles described in this thesis (the compounds must be analyzed in the same state as they are in storage). Ideally, these compounds would also be introduced into a suitable polymeric membrane and tested in real fuel cell systems.
In regards to the theoretical calculations, better and more time efficient computational techniques can be used. As previously suggested, the CREST software can be used to find low energy conformers and a single optimization at the DFT level should suffice. Explicit solvation methods should also be explored in the future, since they might better represent the true nature of the bulk ionic liquid. It would also be interesting to validate our hypotheses in regards to acidity by studying a larger set of protic ionic liquids, while also performing experimental studies.
Finally, its important to point out that we expect this work to serve as a stepping stone for other researchers interested in making protic ionic liquids; by using our system, they will hopefully find ways to further improve it and make it more accessible for groups with less economic resources.

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