Abstract

Ionic liquids are continuously finding more and more applications, both in research and in the industry. Many attempts have been made to find parameters that could be used to describe all ionic liquid systems. Five years ago a Japanese group [1] applied the work of Gutmann [2] on ionic liquids to use ionic association to describe solvation effects. The group calculated ionic association from conductivity and diffusion measurements. This report presents a direct approach through electrophoretic NMR to measure ionic association in ionic liquids.

The report contains a brief introduction to ionic liquids and their properties as well as a short explanation of Nuclear Magnetic Resonance (NMR) spectroscopy, diffusion NMR and a more detailed explanation of electrophoretic NMR (eNMR). Experimental setups, taken from previous work [3, 4] by the NMR group at Physical Chemistry KTH, have been modified to allow for measurements in ionic liquid systems. The report discusses the issues that can arise when measuring eNMR in ionic liquids and suggests solutions. The method developed is principally built upon experiments on 1-butyl-3-methyl-imidazolium trifluoroacetate and is directly applicable to other ionic liquid systems. For more viscous systems than the one investigated here, slight changes will need to be made, as explained in the report.

In order to evaluate the method developed during the project the degree of association for 1-butyl-3-methyl-imidazolium trifluoroacetate has been calculated from experimental results and results in similar values as reported by Tokuda et al. [1]. Furthermore, the temperature variation due to Joule heating during a complete eNMR experiment was also investigated by observing change in chemical shift.

Keywords

Ionic liquid, ion charge, association, electrophoretic NMR, diffusion NMR.
Contents

Abstract ii
  Keywords .................................................. ii

Contents iii

Introduction iv

1 Background 1
  1.1 Ionic liquids ........................................... 1
    1.1.1 Introduction ........................................ 1
    1.1.2 Why use ionic liquids ............................... 2
    1.1.3 Nomenclature and classification of ionic liquids .... 2
    1.1.4 Green solvents ....................................... 3
    1.1.5 Physicochemical properties .......................... 4
    1.1.6 Dissociation of ionic liquid ......................... 6
  1.2 NMR ..................................................... 7
    1.2.1 General principles ................................... 7
    1.2.2 Diffusion NMR ....................................... 9
    1.2.3 Electrophoretic NMR (eNMR) ......................... 10

2 Summary of research 14
  2.1 Methodology .......................................... 14
    2.1.1 Samples ............................................ 14
    2.1.2 NMR ............................................... 16
    2.1.3 Electrodes .......................................... 17
  2.2 Problems encountered ................................. 18
  2.3 Results ............................................... 22
    2.3.1 Diffusion ........................................... 22
    2.3.2 eNMR ................................................ 23
    2.3.3 Calculations ........................................ 24

3 Conclusions 26

Acknowledgements 27

Bibliography 28

List of Symbols and Abbreviations 32

List of Figures 33
Introduction

Ionic liquids is a very broad term comprising several millions of possible systems with more than 1500 systems reported to date. Ionic liquids were first used back in 1914 by Walden [5] and have been the subject of increasing research for the past 30 years with the industrial applications being readily available since 1998 with the introduction of ionic liquids as designer solvents [6]. With such a large number of available systems the task of finding a set of parameters to describe them for comparison has been daunting. No one parameter thus far has proven applicable to every situation until the introduction of the concept of degree of association as a solubility parameter [1] based upon the work by Gutmann [2]. The difficulty lies with finding a way to measure association in an ionic liquid. Thus far, the only available method has been to combine conductivity and diffusion measurements to measure the degree of association indirectly. This report shows that eNMR can be used to measure the degree of association of an ionic liquid more directly and with accurate and reproducible results.

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful and widely used technique. The foundation of NMR was laid by Rabi [7], Purcell [8], Bloch [9] and Hahn [10] between 1938 and 1950. NMR is used in many applications, from process control in industry to research. It is able to distinguish between chemical entities by subtle differences.

Diffusion NMR allows for the study of self-diffusion for different chemical entities with a high degree of accuracy. Self-diffusion is central to chemical reactions, considered together with activation energy and molecular orientation. This stems from the fact that molecules typically need to collide before they can react with one another. The study of diffusion can give information about molecular size and shape as well as kinetics for low activation energy reactions.

eNMR was introduced three decades ago and builds upon the principle of electrophoresis where charged particles can be separated based on drift velocities as they migrate to one of two electrodes supplying a constant electric field. eNMR combines electrophoresis with diffusion NMR to give information on electrophoretic mobility and effective charge distribution of the investigated sample.

The goal of this project has been to develop a way to use eNMR to directly measure the ionic association of ionic liquids, specifically of 1-butyl-3-methyl trifluoroacetate that has been chosen as the system to be investigated. The method could then be used to provide a set of parameters to systemize ionic liquids.
Chapter 1

Background

1.1 Ionic liquids

1.1.1 Introduction

Ionic liquids constitute a fairly new term in the world of science and refer to systems that consist solely or almost solely of ions. For the past 20 years the term ionic liquid has mainly been used for systems that are liquid below 100 °C, sometimes referred to as Room Temperature Ionic Liquids (RTIL). The origin of what is now known as ionic liquids (then molten salts) can be traced to the works of Paul Walden [5] and his article Über die Molekulargrösse und elektrische Leitfähigkeit einiger geschmolzener Salze, published 1914. Walden reported using molten salts that were liquid at low temperatures which were used to carry out his experiments in a water-free environment. After this, the work on molten salts took a backseat in the minds of chemist’s world-wide and it wasn’t until 1982 that work began anew on ionic liquids. Wilkes et al [11] introduced ionic liquids with an AlCl$_4^-$ anion and 1-alkyl-3-methyl-imidazolium cations. These ionic liquids were however air and water sensitive and it would take another decade until a more robust system was devised. In 1992 Seddon et al., Hussey et al. and Chauvin et al. reported ionic liquid systems based on other anions, mainly BF$_4^-$, that were less sensitive to moisture than AlCl$_4^-$. The next significant step was taken in 1998 by Davis et al. [6] who introduced the ionic liquids that today are sometimes known as designer solvents or third generation ionic liquids.

With the introduction of third generation ionic liquids, chemists got access to a new range of solvents for a wide variety of applications. Whilst the term ionic liquid can seems to suggest that we are dealing with systems that should be similar, this is generally far from the norm. The physical and chemical properties of ionic liquids vary and it has thus far proved to be impossible to provide a systematic classification for every ionic liquid that can be synthesized. For instance, most ionic liquids have negligible vapor pressure but there exists ionic liquids that can be distilled [12].

Whilst there is currently no way to provide a systematic classification system for ionic liquids there are still some definitions that are true for all ionic liquids. For those seeking a more thorough description of ionic liquids there has been several books published on the subject [13, 14].
1.1.2 Why use ionic liquids

Ionic liquids offer a wide array of options and benefits for use as solvents. Depending on what parameters that are important to the situation, different anions and cations can be chosen to give the ionic liquid the sought properties. Currently, one issue is that there are still a lot of unknown combinations and non-investigated systems. This is something that through continued investigation is becoming less and less of a concern. Presently one typically chooses an ionic liquid that is close enough to the needs of the process from previously reported anion/cation combinations rather than going through the tedious process of trial and error that is a necessity when the available systems do not fit the requirements.

There are a number of reasons to use ionic liquids over more traditional solvents. Whilst there are ionic liquids that do not have all of these properties, the sheer amount of both theoretical (numbering in the millions) and reported (approximately 1500 to date) ionic liquid systems will allow for almost any combination of characteristics to be available in one or more of these systems. If one were to include the advanced ionic liquid systems that are a combination of several simple ionic liquids the possibilities become almost endless. The major advantages of using ionic liquids as solvents include that:

- they have negligible vapor pressure and do thus not evaporate. This can be of significant use in the regeneration of the ionic liquid after use
- they are generally non-flammable and are thus also more temperature stable than most organic solvents
- they have a far wider liquid range than most organic solvents
- they can be used for separations from organic or aqueous systems

1.1.3 Nomenclature and classification of ionic liquids

A simple ionic liquid consists of one cation and one anion. The anions are generally small and the cations bulky with alkyl chains. Some commonly used anions for simple ionic liquid systems are:

- $\text{Cl}^-$
- $\text{Br}^-$
- $\text{BF}_4^-$
- $\text{CF}_3\text{SO}_3^-$ abbreviated $[\text{OTf}]^-$
- $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ abbreviated $[\text{NTf}_2]^-$

There are a few different commonly used cations for ionic liquids, the most commonly studied ones are the 1-alkyl-3-methyl-imidazolium cations. Other cations are phosphorus or nitrogen containing organic ions with attached alkyl chains of varied length.
1.1. IONIC LIQUIDS

Figure 1.1: A few examples of common ionic liquid anions.

Figure 1.2: A few examples of common ionic liquid cations.

The name of an ionic liquid first states the cation followed by the anion. For the most commonly studied systems (imidazolium based cations) the cations are named according to the alkyl chains lengths followed by imidazolium. A 1-butyl-3-methyl-imidazolium cation are sometimes abbreviated as C$_4$C$_1$Im, BMIm, BMIM, bimim or ByMeIm. Throughout this report the notation BMIM will be used. The anions are generally named in accordance to general principles, e.g. Ac meaning Acetate. The ionic liquid studied in this report is thus named BMIM TfAc (1-butyl-3-methyl-imidazolium trifluoroacetate).

1.1.4 Green solvents

Green chemistry is concerned with removing the impact of industrial chemical processes on the environment. The application of ionic liquids for green chemistry was recognized by Seddon [15] in a paper where he wrote: Clean technology is concerned with reducing the waste of an industrial chemical process to zero. Its implementation will lead to a cleaner environment and more cost-effective use of starting materials. Ionic liquids are described as neoteric (ground breaking) solvents with seven desirable properties for clean technology:

- Higher liquid range compared to water
- Thermally stable up to 200°C
- They exhibit Brønsted, Lewis and other types of acidity
- They have negligible vapor pressure
- Good solvents for organic, inorganic and polymer materials
- Water sensitivity does not affect industrial applications
- Inexpensive and simple to prepare
Earle and Seddon [16] also noted that ionic liquids can be recycled and can result in high product yields, both which are properties desirable in a green solvent. At that point, ionic liquids were viewed as green solvents. Soon though chemists realized that the label *green solvent* could not be applied to all ionic liquids. Some are toxic, others, like imidazolium-based ionic liquids, are synthesized from non-renewable petroleum, and little is known what happens if a spill should occur into the environment. The term *green solvent* is applicable to some ionic liquids, but not to all of them.

### 1.1.5 Physicochemical properties

Compared to most fields of chemistry, the study and synthesis of ionic liquids is still very new, and as such, our knowledge of the properties of these systems are incomplete. The knowledge base is, however, growing at a fast rate as more and more ionic liquids are synthesized and investigated. One of the more interesting aspects of ionic liquids is the wide range of properties they exhibit. With few exceptions, there are, however, a few properties that they all share.

The ionic liquids that are currently being investigated are almost without exception so called room temperature ionic liquids. Ionic liquids remain liquid in a temperature range that is broader than that of other liquids. Most 1-alkyl-3-methyl-imidazolium ionic liquids have a glass transition temperature between -10°C and -60°C and are chemically stable up to between 250°C and 400°C depending on the alkyl chain length and the choice of anion. They thus have a liquid range of over 300°C whereas water has a liquid range of 100°C. Ionic liquids generally form glasses when below their melting point and also show a strong tendency for supercooling [17]. The high temperatures needed for thermal degradation along with negligible vapor pressure makes ionic liquids ideal for reactions at high temperatures as they do not boil or evaporate at increased temperatures.

When looking at the melting point of ionic liquids one can see some trends. The melting point of ionic liquids tends to decrease with increasing alkyl chain length and increase with increasing degree of symmetry. The heat capacity for some commonly used imidazolium based ionic liquids were reported in 2003 [18] and range from 1.17 to 1.80 J/°K at 100°C which is comparable to most liquids except water which has a heat capacity of 4.18 J/°K at 100°C. Wilkes et al. [19] have also shown that ionic liquids could be superior to currently used liquids for heat transfer in that they have negligible vapor pressure and are temperature stable over a wider range of temperatures and thus are able to store large amounts of heat. They suggested the use of ionic liquids as heat transfer fluids in large scale solar energy collectors.

The lack of vapor pressure for most ionic liquids is a result of the strong Columbic forces between the anions and cations of the liquid. It has however been shown that when operating at high temperature and low pressure some ionic liquids are distillable [12].

Ionic liquids are generally more viscous then organic solvents, sometimes by several orders of magnitude. The viscosity is highly correlated to the size of the ions of the ionic liquid, mainly the cation as those tend to be larger. The viscosity of an ionic liquid is also highly dependent on the temperature. A temperature increase from 20°C to 25°C for BMIM PF₆ results in a 30% decrease in viscosity.
1.1. IONIC LIQUIDS

Per definition, an ionic liquid will consist of ions, capable of transporting charges and all ionic liquids are thus conductive with the ions acting as charge carriers. The degree of conductivity depends, as usual, on the viscosity of the ionic liquid and is thus highly dependent on temperature.

The wide variation of the physicochemical properties of ionic liquids and the ease with which the design of the ionic liquid can be changed gave ionic liquids the name designer solvents in the latter part of the 1990s. Whilst this is true in theory, reality paints a different picture. Due to the vast amount of possible ionic liquids, basically any combination of properties can be incorporated into an ionic liquid. This does however require the painstaking trial and error process of synthesis and investigation until a suitable anion / cation combination can be found. As only about 1500 simple ionic liquids have been investigated to date there are still a lot of unknowns. In practice the industry currently chooses an ionic liquid that is close enough to the sought properties when designing a new process. With time the available material matrix will increase and will give more credence to the name designer solvents.

Generally speaking, ionic liquids are seen as polar solvents due to the fact that they consist of ions. Ionic liquids can, however, dissolve both polar and non-polar solutes. The main factor that determines the ability of a solvent to dissolve a solute is the polarity of the solvent. Solvent polarity is not an easily determinable factor; it is actually often defined as the overall solvation capability of the solvent, that is to say, the ability for solvent molecules (or ions) to associate with solute molecules (or ions). In ionic liquids solvation can occur due to ion-ion interaction, dipole interaction, van der Waals forces as well as $\pi - \pi$ interactions.

One way to measure relative solvent polarity is through measuring the dielectric constant of the solvent. In general, liquids consisting of non-polar molecules have low dielectric constant whilst polar molecules lead to high dielectric constant. Measuring the polarity directly requires a non-conducting medium and as such one needs to employ alternate methods for measuring the dielectric constant indirectly. One such method was reported by Reichardt [20] who set the polarity of tetramethylsilane at 0.00 and the polarity of water at 1.00. On that scale ionic liquids were reported to have a polarity ranging from 0.35 to 1.10 with imidazolium based ionic liquids having polarities between 0.50 and 0.75, similar to that of ethanol.

A good solvent has a high degree of solubility for the solute of interest and a high immiscibility for any byproducts and impurities. One interesting feature of ionic liquids is the wide range of possible solubilities and miscibilities that are available by changing between different ionic liquids. They can for instance dissolve both ionic and non-ionic species. The ability to dissolve a material in an ionic liquid depends mainly on two factors, the polarity of the ions and the possible degrees of coordination.

An ionic liquid’s miscibility with water is of great interest for biphasic reactions where the ionic liquid replaces the usual organic solvent. The degree of miscibility of water in an ionic liquid depends mainly on the degree of coordination possible with the ions. Basic ions ([NO₃]⁻) can strongly coordinate with water, whilst acidic ions are non-coordinating and pH neutral ions ([BF₄]⁻) and ([NTf₂]⁻) are weakly coordinated with water. The length of the alkyl chains on the cation also affects the miscibility of water in an ionic liquid. Longer chains result in a more hydrophobic ionic liquid.
Ionic liquids can also be chosen to be miscible or immiscible in organic solvents. How miscible the ionic liquid is depends largely on the polarity of the ionic liquid. Generally speaking ionic liquids are miscible in polar organic solvents and immiscible in non-polar organic solvents. For any given ionic liquid the solubility of an alkene decreases with increased alkyl chain length on the alkene [21].

Gases can be soluble in ionic liquids to a variable extent and is depending on both cation and anion [22, 23, 24]. The solubility of gases in a given ionic liquid can be important for gas separation in a mixture of gases, for storing gases in ionic liquids for carrying out reactions such as oxygenation. Highly soluble gases decrease in solubility with increased temperature, the reverse being true for gases with low solubility [25].

1.1.6 Dissociation of ionic liquid

When discussing ionic species one must also discuss ion dissociation at some point. The degree of disassociation for an ionic liquid shows how large a fraction of the nominally neutral species has separated into cations and anions. Some degree of dissociation must exist as shown by the non-zero conductivity of ionic liquids.

There exist several empirical solvent polarity scales to describe solvents and their physicochemical properties, one of which is Gutmann’s donor and acceptor number. Gutmann [2] showed that the strength of the Lewis base and the Lewis acid can be used to describe solvent effects. Numerous groups have experimentally [17, 26, 27, 28, 29] studied and related physicochemical properties of ionic liquids to their structure. In general it appears that ionic liquids typically behave as weak Lewis bases and weak Lewis acids. This in turn will lead to a weak coordination between ions and the surrounding molecules. The degree of disassociation can thus be seen as one parameter to characterize ionic liquids as it will directly affect the solvatization capabilities and polarity of the ionic liquid. There are, however, many problems with measuring the dissociation of ionic liquids and not many studies has thus far been made on the subject. In one publication [1] Tokuda et al. combine conductivity measurements with diffusion NMR to obtain information on the degree of association of the investigated ionic liquids. In this work, electrophoretic NMR is used to directly measure the effective charge of the anions and cations in an ionic liquid and thus characterize the association of the ionic liquid.
1.2 NMR

Nuclear Magnetic Resonance spectroscopy or NMR is today one of the more commonly used techniques for structure determination and studies of molecular dynamics. NMR is sensitive enough to distinguish between different isotopes and allows for quantitative and qualitative measurements on a molecular level. As such, it is one of the more important techniques used by chemists today.

The foundation for NMR was laid by Isidor Rabi [7] in 1938 which was followed up by Purcell et al [8] and Bloch et al. [9] in 1946 (for which they both received the Nobel Prize in Physics in 1952). The two groups approached the problem differently; Purcell et al. measured the magnetic resonance absorption of protons in solid paraffin whilst Bloch et al. studied the induced signal from the precession of a water sample’s nuclear magnetic momentum. Both systems worked by slowly sweeping a radiofrequency (r.f.) field or a magnetic field and are examples of what is now known as continuous wave (cw) NMR.

A third approach, and the basis of what is used today, were introduced by Hahn [10] in 1950. Rather than applying a continuous r.f. field, Hahn used short pulses at discreet frequencies and measured the precession of the induced magnetic moment after the pulse had been turned off. This is known as pulsed NMR.

Until 1966 most NMR spectrometers used cw systems, until Ernest and Andersson [30] showed that Fourier Transform theory could be applied to the Free Induction Decay (FID) from pulse NMR to provide the spectrum faster and better. Since then, NMR has almost exclusively used various pulse methods with Fourier transformation of the resulting FID.

1.2.1 General principles

NMR is a form of spectroscopy and like all other types of spectroscopy, it is analyzed by plotting intensity of absorption (and/or emission for the general case) versus frequency. An NMR spectrum will have frequencies between 10 and 1000 MHz, which are in the radiofrequency range. As a typical NMR spectrometer has a fixed magnetic field strength, and thus a fixed frequency for a specific nucleus, comparing NMR spectra from different spectrometers could be difficult if a Hz scale would be used. It is therefore common practice to use a ppm (parts per million) chemical shift scale. This makes sense with the knowledge that each nucleus of a given isotope (say $^1$H, the most commonly used nucleus in NMR) will have a slightly different resonance frequency depending on how shielded it is by its chemical surrounding.

By using a chemical shift axis rather then a frequency axis one gets spectral interpretation that is independent of the field strength and thus is comparable between different spectrometers. As we are talking about chemical shift, this has to be in reference to something. For $^1$H and $^{13}$C NMR the normal reference, designated at zero ppm, is the spectral peak of TMS. The chemical shift is then easily calculated by:

$$\delta(\text{ppm}) = \frac{\nu - \nu_{\text{ref}}}{\nu_{\text{ref}}} \times 10^6$$

where $\nu_{\text{ref}}$ is the resonance frequency of the reference compound and $\nu$ is the resonance frequency of the peak of interest.
NMR is built on the principle that almost every nucleus has at least one (sometimes several) isotope with a non-zero quantum spin number. Nuclei with a non-zero quantum spin number will, when placed in an external strong magnetic field $B_0$, align themselves either parallel or opposite to the magnetic field. There is a small difference in energy between these two states, $\Delta E$, where the difference depends on the interaction between the nuclei and the static magnetic field. By supplying an r.f. pulse of the correct frequency $\nu$ the nuclei can be forced to change their orientation if the resonance condition is roughly fulfilled:

$$\Delta E = h\nu$$  \hspace{1cm} (1.2)

where $h$ is Planck’s constant. The r.f. pulse supplied during an NMR experiment is typically broad enough to excite all nuclei of one type, regardless chemical shift, in a sample and its center frequency is generally set in the middle of the resulting spectrum. The difference in resonance frequency between different types of nuclei or indeed different isotopes is generally too large to allow for more than one type of nuclei to be detected during a single experiment.

![Figure 1.3: $^1H$ spectrum of 10 mM TMA Br in D$_2$O. The peak at 1.1 ppm is TMA$^+$ and the peak at 2.2 ppm is residual $^1H$ signal from D$_2$O.](image)

Once a sample has been placed within the NMR magnet, the individual spins align themselves along the orientation of the magnetic field. This takes a non-zero time which is referred to as longitudinal relaxation time or $T_1$. A second type of relaxation is $T_2$, the spin - spin relaxation time of a sample which reflects relaxation due to interactions with closely connected nucleus. Once an r.f. pulse is supplied, the spins will be forced out of alignment and (if nothing more is done to the sample) they will start to oscillate and an induced signal can be detected. This is know as a free induction decay, FID. The FID is then Fourier transformed from the time domain to the frequency domain and analyzed. An example of a resulting NMR spectra is shown in figure 1.3.

As the r.f. pulse is operating at a set frequency dependent on the field strength, the power supplied to the sample will depend on the length and amplitude of the r.f. pulse. The typical length of an r.f. pulse is in the order of $\mu$s and during an experiment one typically uses what is known as 90° and 180° pulses. The angular notation refers to the flip angle the pulse exacts on the spins.
Depending on what is sought, the sequence of r.f. pulses required can vary greatly and normally the experiment is repeated several times. Should the sample be diluted several scans will be required, as the signal to noise ratio increases as $\sqrt{N}$ where $N$ is the number of scans. A single run of pulses is referred to as a pulse sequence and is typically displayed graphically (see Figure 1.4) with boxes along a time axis with a FID displayed to represent data acquisition at the end of the sequence. There are several ways to explain what happens to the spins of a sample during a pulse sequence, the two most commonly used are a classical vector-based model and a quantum mechanical operator based model. For anything but the most basic NMR experiment, some form of quantum mechanical approach is required. The interested reader may read through one or more of the well written course literature in NMR [31, 32, 33, 34].

### 1.2.2 Diffusion NMR

Central to most chemical reactions and their kinetics is self-diffusion. Self-diffusion is the thermal random motion of a molecule and is characterized by the self-diffusion coefficient $D$ (m$^2$s$^{-1}$). Throughout this report the term diffusion will be used as a synonym for self-diffusion (there are a number of different types of diffusion). Ionic conductivity can be seen as dependent on diffusion of the charge carrier species [35] and is described by the Nernst- Einstein equation:

$$\Lambda = \frac{zF^2}{RT}(D_{cation} + D_{anion})$$

(1.3)

where $z$ is the charge, $F$ is the Faraday constant, $R$ the ideal gas constant, $T$ temperature in kelvin and $D_{cation}$ and $D_{anion}$ is the diffusion coefficient for cation and anion respectively. The diffusion coefficient can be calculated through the Einstein-Sutherland equation:

$$D = \frac{k_BT}{f_{friction}}$$

(1.4)

where $k_B$ is Boltzmann’s constant. Almost all diffusion NMR measurements use some form of spin-echo pulse-sequence coupled with a magnetic gradient used for spatial encoding. Evaluation of NMR diffusion pulse sequences requires following spin coherence changes with either density matrix or product operator formalism.
As explained by Price [36], diffusion can be measured through the signal attenuation as a function of applied magnetic gradient strength. The effect of flow (note the difference from random motion) can be interpreted as a phase shift. The signal attenuation in a diffusion measurement is typically described as:

$$\frac{S}{S_0} = e^{-\gamma g^2 \delta^2 D (\Delta - \frac{\delta}{2})}$$  \hspace{1cm} (1.5)$$

where $\gamma$ is the gyromagnetic ratio, $g$ the magnetic gradient field strength, $\delta$ the magnetic gradient pulse length, $D$ the diffusion coefficient and $\Delta$ the diffusion time.

Diffusion measurements are typically done by stepwise increasing $g$ and then plotting the signal attenuation and fitting the exponential decay.

Depending on the experimental situation, a suitable diffusion NMR pulse program is required in order to acquire a good result. One example is the Pulsed field Gradient Double stimulated Spin Echo (PGDSTE) shown in figure 1.5 which helps to compensate for flow effects, for example due to convection, in the sample.

![Figure 1.5: A PGDSTE pulse sequence.](image_url)

An extensive review of diffusion NMR and its applications has been written by Price [36] and is suggested to the reader interested in a deeper understanding of diffusion NMR.

### 1.2.3 Electrophoretic NMR (eNMR)

In order to understand eNMR and its applications one first needs to have a working understanding of electrophoresis. Electrophoresis is the movement of a charged particle when subjected to an electric field, $E$, between two electrodes. The electric field strength is defined as:

$$E = \frac{U}{l}$$  \hspace{1cm} (1.6)$$

where $U$ is the potential difference between two electrodes separated by the distance $l$. For a charge $ze$ the force experienced is:

$$F = \frac{zeU}{l}$$  \hspace{1cm} (1.7)$$
If $F_{\text{friction}}$ is defined as:

$$F_{\text{friction}} = f v$$

(1.8)

where $v$ is the speed of the charged particle (the steady-state drift velocity), $v$ can be written as a function of $f$ and $E$:

$$v = \frac{zeE}{f}$$

(1.9)

Alternatively, the drift velocity can be seen as dependent on the electrophoretic mobility, $\mu$, and the applied electric field strength, $E$:

$$v = \mu E$$

(1.10)

The principle of electrophoresis is used as a separation method in for instance biochemistry as a means of separating proteins depending on their size and charge. The use for electrophoresis in NMR comes from combining equation 1.9 and equation 1.4, yielding the Einstein relation:

$$D = \frac{\mu k_B T}{ze}$$

(1.11)

Equation 1.11 shows that the charge of a particle can be calculated from $D$ and $\mu$. $D$ can be obtained through diffusion NMR measurements and eNMR provides a way to measure $\mu$ directly.

eNMR is not a commonly used NMR method. Indeed, only a few research groups currently work with it and each group has its own way of setting up eNMR experiments. eNMR was introduced by Packer in 1969 [37] and experimentally proven by Packer et al. [38] in 1972. It would take a decade before Holz et al. [39] were to measure drift velocities of small ions. Since then eNMR has been developed further.

The NMR group at the Division of Physical Chemistry, KTH, uses the setup and methods that will be described below and which were latest improved upon by Hallberg et al. [3]. Throughout this report the methods employed by the NMR group will be referred to simply as eNMR methods, ignoring other implementations. eNMR experiments are built upon diffusion NMR pulse sequences with two significant changes; the magnetic gradient is kept constant, and an electric field is increased stepwise between two electrodes in the sample NMR tube throughout the experiment.

During an eNMR experiment, an electric field is applied between two palladium electrodes isolated from the sample by glass capillaries. The electrode ends are situated outside of the sensitive volume of the NMR spectrometer, above and below it, with one electrode’s wire running through the sensitive volume. This setup provides some difficulties with shimming of the samples but allows for eNMR to be run using conventional built probes; typically a standard Bruker Biospin 5mm BBI probe were used. The sample cell is thus approximately cylindrical and the coherent displacement induced by electrophoresis (and other macroscopic flows) can be seen as a signal phase shift in PGDSTE experiments. The experimentally detected phase shift, $\phi$, is dependent on the drift velocity according to:

$$\phi = \gamma g \delta \Delta v$$

(1.12)
CHAPTER 1. BACKGROUND

As \( v \) depends on the electric field strength, \( E \) (see 1.10) \( \phi \) also depends linearly on \( E \) when all other variables are held constant, as they are during an eNMR experiment. As discussed above, the goal of eNMR is to measure electrophoretic mobility, \( \mu \), and by combining equation 1.12 and 1.10 one arrives at the central equation of eNMR:

\[
\mu = \frac{\phi}{\gamma g \delta \Delta E}
\]  

(1.13)

There are two important issues that need to be addressed when performing eNMR experiments, both concerned with induced flow in the sample as it is indistinguishable from electrophoresis.
The first one is thermal convection and is a result of the heating when supplying a current to the electrodes. This will create a temperature gradient in the sample which leads to convection. As the sample is allowed to cool down between scans a radial thermal gradient can be induced as the sample cools off at the edges of the sample tube.

The second concern is called electroosmosis and is a result of ion solvation. When the ions move towards the oppositely charged electrode they drag solvent molecules with them, resulting in liquid motion [40]. Electroosmosis require a charged surface in order to manifest but as most surfaces are charged to at least some extent (glass walls consisting of SiO$^{-}$ ions) this is quite commonly the case. Electroosmosis can be countered by coating the glass walls with a non ionic polymers. In practice, however, it is far from straightforward to create a layer of polymer that will remain unaffected during an experiment.

The solution to convection problems in eNMR was, at least to a significant extent, developed by Hallberg et al. [3]. Currently employed by the NMR group at KTH is a convection compensated pulse sequence. The sequence is taken from diffusion NMR, with the polarity of the electrodes switched between the two parts of the double stimulated echo, and compensates for moderate convection induced flows. Electroosmosis is not suppressed by this directly but as electro-osmotic flow takes relatively long time to build up. Whilst the pulse sequence does compensate for some convection induced flows, it does not do so to the extent that eNMR typically requires. In order to compensate for convection a non-charged reference is also used. This reference has to be chosen with care as it can not be allowed to preferentially bind to either cation or anion. As the reference will not be affected by electrophoretic movement but only by the flows in the system the convection compensated $\phi_{\text{sample}}$ can be calculated as:

$$\phi_{\text{sample}} = \phi_{\text{sample, observed}} - \phi_{\text{reference}}$$  \hspace{1cm} (1.14)

Figure 1.8: The pulse sequence with convection compensation used in the eNMR experiments.
Chapter 2

Summary of research

2.1 Methodology

2.1.1 Samples

The ionic liquid that is central to this report, BMIM TfAc, was chosen from amongst several other candidates through a two-step initial screening process. With knowledge of physicochemical properties [41] of a large number of ionic liquids a smaller selection was chosen. The selection was based on viscosity, diffusion coefficients, conductivity and availability from manufacturers. In the first step, six ionic liquids were chosen, a combination of two cations and three anions. The cations chosen were EMIM and BMIM whilst the chosen anions were TfAc, OTf and NTf$_2$. With initial studies of the two ionic liquids, EMIM Ac and EMIM BF$_4$, providing information on problems to be expected, BMIM TfAc was selected as the ionic liquid to be investigated and subsequently ordered from Sigma Aldrich. Before any measurements were taken, the entire sample of BMIM TfAc was placed in a freezer at -18°C for 72 hours and then placed in vacuum for 24 hours in order to remove any water present in the sample upon delivery. In order to evaluate eNMR experiments one needs a non-charged reference in order to compensate for flow effects in the sample. As was quickly discovered, finding a eNMR reference can be far from straightforward. Several $^1$H and $^{19}$F references were ordered from Sigma Aldrich and evaluated. As $^1$H reference hexamethyldisilane was chosen in the end. Samples were prepared in volumes of 2 - 4 ml ionic liquid with 5 volume % reference and smaller samples were then taken from these to be analyzed. $^{19}$F measurements are currently not possible due to problems with finding a $^{19}$F reference. $^{19}$F references yielded irreproducible results. Either these resulted in a change in chemical shift for the imidazolium ring peaks or were completely immiscible in the ionic liquid, one even reacted at the electrodes. The $^{19}$F references that was investigated were:

- Monofluorobenzene - *non reproducible results, chemical shift*
- 1,4 - difluorobenzene - *non reproducible results, chemical shift*
- Hexafluorobenzene - *reacted with sample under applied voltage*
- 2,2,2 - trifluoroethanol - *non reproducible results, chemical shift*
- Heptacosfluorotributylamine - *immiscible*
2.1. METHODOLOGY

Figure 2.1: The system studied, BMIM TfAc with hexamethyldisilane as $^1$H reference.

Figure 2.2: Spectra of BMIM TfAc with 5 volume % hexamethyldisilane for peak identification.

With the proton assignment in figure 2.1 and the spectrum in figure 2.2 the peaks in all eNMR and diffusion NMR experiments can be identified. Here the reason for using 5 volume % reference can be seen; below this amount the reference peak (peak marked 1. in figure 2.2) could not be used for convection compensation due to low signal-to-noise ratio. As the study concerned neat ionic liquid systems it was also considered important to keep the amount of reference to the minimum level.
2.1.2 NMR

All diffusion experiments were run using a double stimulated echo experiment with step-wise increasing gradient strength. The system used consisted of a 500MHz Bruker Spectrospin spectrometer combined with a 5 mm diffusion probe with a maximum gradient strength of 1800 G/cm. All processing was done using Topspin 2.1. Diffusion measurements were done with the reference added to the sample using a PGDSTE sequence for convection compensation at the elevated temperature of 60 °C.

All eNMR experiments were performed using the system developed by Hallberg et al. [3, 4] and the eNMR experiments were performed in a 500MHz Spectrospin spectrometer with a 5mm BBI probe, processing was done using Topspin 1.3. The system uses the sample cell described in section 1.2.3.

By first measuring T$_1$, (∼1.1s for BMIM TfAc) most of the project’s experimental time was spent performing experiments at various settings. The total electrophoretic voltage was alternated between 100V and 400V and the constants in equation 1.12 were varied in order to find a system that would allow for measurements. Different probes and gradient amplifiers have been tried, resulting in the need to create LED pulse sequences (see section 2.2) and changes to $\Delta$ as well as $\delta$ have been investigated. The results of this and the final chosen values can be found in section 2.2. The eNMR experiments finally used in this report were run with voltage increasing from 0 to 200 V in 22 V steps with 16 scans per step. Results from the first 6 first steps (110V) were used for phasing as beyond this point Joule heating resulted in too large signal losses due to convection. In order to evaluate the accuracy of the results both eNMR and diffusion experiments were repeated three times.

Voltage for the eNMR experiments was generated through auxiliary outputs from the NMR console which in turn was routed to a custom built pulse generator which fed a high voltage amplifier. In turn, the high voltage was routed through an r.f. filter box and into the eNMR cell electrodes. Amplifier voltage input and output were monitored using an oscilloscope. eNMR sample tubes were cut down to suitable length and used without any coating to reduce electro-osmotic flow. All phasing was done by a single person in order to avoid systematic errors. A second and sometimes third person also phased the experiments in order to ensure reproducibility. All eNMR measurements were done using a double stimulated echo pulse sequence with convection compensation.

The eNMR cell was constructed according to the design by Hallberg et al. [4] using palladium wire and thin glass capillaries to isolate the wires from the sample. Leading one of the wires through the NMR sensitive volume causes concern for shimming, though not as large as one might expect. In most cases peak widths of 5 - 6 Hz were obtained. Several ways of sealing the bottom part of the capillaries were tried, firstly with silicone as described by Hallberg, secondly by melting the ends around the wire to seal them and finally to leave them open. All measurements presented in this report were performed using the open capillary electrodes. Between experiments the electrodes were removed from the connector and cleaned with de-ionized water and dried using compressed air.
2.1. METHODOLOGY

2.1.3 Electrodes

When running eNMR experiments an issue exists when using silicon sealed capillary electrodes. The silicon reacts with the ionic liquid and is irreversibly damaged during the course of an eNMR experiment. There are at least two other options available, both of which have been evaluated.

One alternative is to melt the ends of the capillaries and allow the glass to seal the electrode in. An issue with doing this is that palladium expands when heated and once it cools off the seal is no longer tight, resulting in leaks and contamination of future samples. If a low enough temperature were to be used this problem should be negligible; this has thus far been difficult to achieve in practice and some small leakage is generally always found with melted electrodes.

The second alternative investigated was to use non-sealed electrode capillaries. The major concern with using open capillaries is the capillary rise of the sample and its affect on the NMR spectrum. By weighing a sample before of water, inserting electrodes into the sample and weighing the remaining water after removing the electrodes a sample/capillary volume ratio of 30 was found and the effect have subsequently been ignored. Using open capillaries is more time consuming than using sealed capillaries as they require thorough cleaning and drying between each experiment. Open capillaries however show the most reproducible results and, as long as they are cleaned thoroughly between each experiment, showed no cross-sample contamination which was the main concern with melted glass capillaries.

Once the eNMR cell was built, the exact distance between the resulting two electrodes needed to be established. As previously described by Hallberg et al. [4], this was done by running eNMR experiments on 10 mM sample solutions with known electrophoretic mobility, in this case that of Tetramethylammonium Bromide, TMA Br. Three experiments were made on different samples of the same concentration and the difference in electrophoretic mobility from the eNMR experiment and literature data gives a length calibration factor that was used to normalize all eNMR results obtained with the eNMR cell. For the electrodes used in the measurements presented in this report, the length calibration provided an effective electrode-electrode distance of 40.0 mm.
2.2 Problems encountered

A significant amount of project time has been devoted to investigating different solutions to the problems that might occur when running eNMR experiments on ionic liquids. The difficulties lie with the low diffusion coefficient for ionic liquids, their relatively high conductivity and finding a non-charged reference for phasing. In the process of developing a method for determination of the degree of dissociation of an ionic liquid these problems have been addressed.

The high conductivity of ionic liquids compared to the samples routinely investigated by eNMR presents a significant problem with Joule heating. Two significant problems can occur, the first is the introduction of convection in the sample due to temperature gradients, and the second is the continued accumulation of heat in the sample during the experiment.

Convection in the sample results in signal attenuation which, if it becomes large enough, will result in a spectrum that can not be phased. Convection is such that the flow will strive to remove any temperature gradients and will thus assist in dealing with the second issue, heat accumulation. In order to reduce the induced convection and its effect one can first use a pulse sequence with convection compensation, such as the one used in this report. Another partial solution is to reduce Joule heating, one of the concerns with running eNMR. Luckily, in some systems that are sensitive to temperature variation, the change in chemical shift can be used as an internal thermometer. This is the case for BMIM TfAc and thus a study of chemical shift changes over the course of an eNMR experiment was carried out in order to investigate the extent of Joule heating.

Firstly, changes in chemical shift resulting from changes in the sample temperature were detected. The sample was heated to 55°C, allowed to stabilize, and then a 1D spectrum was obtained. This was repeated at 60°C and 65°C. By plotting the chemical shift change of the singlet peak close to 9.8 ppm versus temperature, the shift-temperature relation was obtained from the linear fit of data.

![Figure 2.3](image)

Figure 2.3: The spectra show that increased temperature results in lowered chemical shift for BMIM TfAc with 5 volume % of hexamethyldisilane.
2.2. PROBLEMS ENCOUNTERED

Secondly, an eNMR experiment at 110 V applied voltage at 60°C was carried out with a single scan per experiment and with 16 repetitions. This voltage was selected since it corresponds to the voltage at the final point in previously performed eNMR experiments (with δ, Δ and g taken from the successful eNMR experiments). By studying the chemical shift of the ionic liquids in the performed eNMR experiments, the temperature variation in the sample during an eNMR experiment could be plotted. Using the obtained calibration curve (chemical shift vs. temperature), the temperature variation in a complete eNMR experiment could be calculated.

As can be seen from the temperature calibration in figure 2.5, there is some heating of the sample during a single scan. The temperature profile in figure 2.5 obtained whilst doing the temperature calibration can be explained by convection. When the sample is heated, a temperature gradient is created. Until the gradient becomes large enough no convection is induced. Once the gradient becomes large enough, convection is induced
and the temperature in the sensitive volume decreases and at the end reaches a point where the temperature stabilizes. Increased time between individual scans and increased air flow over the sample will further reduce convection.

Heat accumulation in the sample during an eNMR experiment is the second possible result due to Joule heating. With 30 second delays between individual scans no discernable heat accumulation could be found, indeed the sample shows a tendency to cool down as the experiment progresses due to increased convection. This was investigated by use of the chemical shift change in the sample during the three eNMR experiments for BMIM TfAc. Run 1 - 3 are the same run 1 - 3 reported in the result section of this report (see figure 2.9, figure 2.10 and figure 2.11).

![Figure 2.6: Temperature variation during eNMR experiments on BMIM TfAc with 5 volume % hexamethyldisilane.](image)

The high viscosity and low diffusion coefficient of ionic liquids in general presents another set of problems. High viscosity increases the chance of heat accumulation in the sample during an eNMR experiment whilst the low diffusion coefficients that are typical of ionic liquids present the main concern. As can be seen by equation 1.11 a small diffusion coefficient will result in a small electrophoretic mobility. This in turn (see equation 1.12) will result in a small phase shift if no other constants are changed from what is typically used for eNMR when investigating other samples. By increasing the constants in equation 1.12 the theoretical observed phase shift can be increased. When doing this several things need to be kept in mind. The signal attenuation of an eNMR experiment, discounting flow effects, is given by equation 1.5 on page 10.

As can be seen, increasing any parameter will result in more signal attenuation. \( \Delta \) also needs to be smaller then \( T_1 \) by a significant margin, preferably no larger then 0.5 \( T_1 \). Another important thing to consider when increasing \( \Delta \) is that it will directly affect Joule heating. \( \delta \) also has a upper limit, governed mainly by \( T_2 \). The supplied electric field, \( E \), can also be increased. The limit of how far \( E \) can be increased stems from both joule-heating and the sample itself. For sufficiently high voltage electrode reduction can take
place; their absence must be verified by comparing 1D spectra before and after eNMR experiments. One other possibility to increase the phase shift of the eNMR experiment is to increase the gradient strength used for encoding and decoding.

There are two limitations when increasing \( g \). One is the signal attenuation that will grow as \( g^2 \) and the second is the limitation of the NMR probe and gradient amplifier. In order to use larger gradients, alternate setups with a micro-imaging probe and a diffusion probe were used together with a stronger external gradient amplifier (40A). Unless the probe-amplifier system is well set issues with eddy currents arise when the gradient strength is increased. The effect is significantly larger for unshielded probes as is common in micro-imaging probes. This can be countered in several ways. First one needs to create a set of pre-emphasis settings for the setup [42]. The next step is to add a Longitudinal Eddy current Delay (LED) to the pulse sequence as proposed by Gibbs and Johnson [43], where the signal acquisition is delayed. Another possibility is to increase the gradient recovery time, up to half a millisecond can be used should the system require it.

This leaves \( D \) as the best candidate to increase. This can be done by heating the sample and running experiments at higher temperatures. For our purposes it has been found that 60 °C gives a significant enough increase in \( D \) to allow for eNMR measurements. Increasing temperature from 25 °C to 60 °C resulted in a change in \( D \) from 1.8 \( \times \) 10\(^{-11}\) \( m^2 s^{-1} \) to 7.7 \( \times \) 10\(^{-11}\) \( m^2 s^{-1} \). Increasing temperature and thus \( D \) of the sample has the significant drawback of also increasing the conductivity of the sample as this depends on the viscosity.

Investigation and evaluation of changes to these parameters has been in large part what this project has concerned. By a combination of theoretical work and the equations mentioned above as basis and trial and error a set of parameters were chosen. Coupled with increased temperature to 60 °C the parameters that found to give reproducible results were:

\[
\begin{align*}
E &= 200V \\
\Delta &= 300ms \\
\delta &= 3ms \\
g &= 0.45T/m
\end{align*}
\]

Finding a reference for convection compensation in eNMR proved to be a far from easy task when working with neat ionic liquids. One requirement is a large number of chemically identical protons (or whichever nucleus is being investigated) as the sample cannot be diluted too much with a reference. Another requirement is that the reference and the ionic liquid are miscible and that they do not coordinate. During the course of this project, no \(^{19}\)F reference could be found that did not either coordinate to a significant extent to the cation’s imidazolium ring as shown by chemical shift change for the imidazolium peaks or were immiscible in BMIM TfAc. Hexamethylidisilane proved to be a good choice for \(^1\)H reference.
2.3 Results

2.3.1 Diffusion

Diffusion experiments were run and evaluated and the resulting fits to the signal decay gave $D_{cation}$ at 60 °C for each run as:

$$7.70 \pm 0.03 \cdot 10^{-11} (m^2s^{-1})$$
$$7.68 \pm 0.03 \cdot 10^{-11} (m^2s^{-1})$$
$$7.50 \pm 0.03 \cdot 10^{-11} (m^2s^{-1})$$

Figure 2.7: 13 of the 24 steps (every second step) of the first diffusion measurement on BMIM TfAc with 5 volume % hexamethyldisilane.

Figure 2.8: The exponential fit for peak 2 (see figure 2.2 and figure 2.1 on page 15) from the diffusion experiment shown in figure 2.7.
2.3. RESULTS

\( D_{\text{anion}} \) was also measured with the same settings and found to be:

\[
\begin{align*}
8.09 \pm 0.03 \cdot 10^{-11} (m^2 s^{-1}) \\
7.97 \pm 0.03 \cdot 10^{-11} (m^2 s^{-1}) \\
8.21 \pm 0.03 \cdot 10^{-11} (m^2 s^{-1})
\end{align*}
\]

This results in the following average and variance:

\[
\begin{align*}
D_{\text{cation}} &= 7.6 \pm 0.08 \cdot 10^{-11} (m^2 s^{-1}) \\
D_{\text{anion}} &= 8.9 \pm 0.10 \cdot 10^{-11} (m^2 s^{-1})
\end{align*}
\]

2.3.2 eNMR

\(^1\)H eNMR results are reported with reference compensation and were run at 60 °C. For clarity the reference phase shift is also reported.

As can be seen in figure 2.9, signal attenuation increases with each step due to convection-induced flows; indeed, the small phase shift of ionic liquids is not visible on the last spectrum with this magnification and further increase in applied voltage was not practical.

The phase shifts measured from eNMR with phase compensation from the reference were plotted and the data fit was used to calculate \( \mu \) (see equation 1.13 on page 12).

As can be seen from figure 2.11 on page 24 and figure 2.5 on page 19 the second runs deviation in temperature variation from the other two runs can also be seen as a significant difference in convection compensation from the reference compound.
Figure 2.10: Plot of eNMR data for BMIM TfAc with 5 volume % hexamethyldisilane. The plot shows the convection compensated phase shifts (reference shifts taken from figure 2.11) with linear fits.

Figure 2.11: Plot of reference phase shifts that were used to convection compensate the eNMR results for BMIM TfAc with 5 volume % hexamethyldisilane in figure 2.10.

2.3.3 Calculations

Equation 1.13 on page 12 relates phase shift to electrophoretic mobility, \( \mu \). With \( \delta \), \( \Delta \), \( D \) and \( g \) taken as constant and \( \phi / E \), given by the fit for the eNMR data in figure 2.10 as the slope \( (k_1, k_2 \text{ and } k_3) \), \( \mu_{\text{cation}} \), can be calculated as the average of \( \mu_1 \), \( \mu_2 \) and \( \mu_3 \). For the three experiments, the resulting electrophoretic mobility is then:
2.3. RESULTS

\[
\mu_1 = \frac{k_l}{\gamma g \Delta} = \frac{0.17853 \times 0.040}{1.533 \times 10^{-6} \times 0.451 \times 0.003 \times 0.300} = 1.277 \times 10^{-9} \frac{m^2}{Vs} \\
\mu_2 = \frac{k_l}{\gamma g \Delta} = \frac{0.18409 \times 0.040}{1.533 \times 10^{-6} \times 0.451 \times 0.003 \times 0.300} = 1.317 \times 10^{-9} \frac{m^2}{Vs} \\
\mu_3 = \frac{k_l}{\gamma g \Delta} = \frac{0.20733 \times 0.040}{1.533 \times 10^{-6} \times 0.451 \times 0.003 \times 0.300} = 1.483 \times 10^{-9} \frac{m^2}{Vs}
\]

Thus $\mu_{\text{cation}}$ is taken as $1.36 \pm 0.09 \times 10^{-9}(m^2V^{-1}s^{-1})$. Once $\mu_{\text{cation}}$ and $D_{\text{cation}}$ were both known, the effective cation charge of BMIM TfAc could be calculated through equation 1.13 on page 12 as:

\[
z_{\text{cation}} = 0.51 \pm 0.03
\]

As the nominal charge of the BMIM cation is +1 this gives a degree of dissociation of $z_{\text{cation}}$ or 0.51. The acquired result coincides well with those reported by Tokuda et al. [1] who reported $z_{\text{cation}}$ as 0.52.
Chapter 3

Conclusions

As shown in this report BMIM TfAc has an effective charge for its cation of +0.51. This coincides well with the reported value of 0.52 [1]. As the system is in principle neat it is assumed that the anion charge should be the opposite that of the cation, or -0.51. This is however a point that requires further investigation. The most reasonable path to proceed along is to measure anion electrophoretic mobility through $^{13}$C eNMR. As shown by equation 1.12 on page 11 one needs to keep $\delta \cdot g \cdot \gamma$ constant in order to achieve the same phase shift during an experiment. If $\gamma$ is then reduced by a factor of 4, by changing nucleus from $^1$H to $^{13}$C, $g$ and/or $\delta$ need to be increased by a factor 4 to acquire the same phase shift during the experiment. As the system is at 85% of maximum $g$ without changing probe and increasing $\delta$ to above 5 ms is not recommended this will in turn require a change to a high-gradient strength diffusion probe. Running $^{13}$C eNMR would also require altering the pulse sequence to incorporate $^1$H decoupling.

As shown in the calibration section of this report, the temperature increase due to Joule heating during eNMR experiments on ionic liquids presents a problem in terms of convection and thus signal attenuation. No continuous build up of heat was measurable, only induced convection due to temperature gradients. The effects of this could without changing input parameters be reduced by further increasing the air flow in the spectrometer to allow for faster temperature stabilization. Preferably the delay time between scans should also be increased in order to suppress convection. As can be seen from the plots of temperature variation during the eNMR experiments and the resulting reference phase shifts and cation phase shifts, the convection compensation through added reference gives excellent results.

eNMR provides a more direct approach of measuring the degree of dissociation of ionic liquids then reported elsewhere. As shown the results are reproducible and in good agreement with the report by Tokuda et al. [1]. eNMR provides quick and accurate measurements of dissociation and with proper control of parameters, this method should be applicable to any ionic liquid of interest.

Presented in this report is a method of measuring ionic dissociation directly through eNMR. In order to be of benefit, more ionic liquids need to be investigated and categorized if ionic association is to be used as a parameter for systematic categorization of ionic liquids. This is most suitably done initially on previously investigated systems where other physicochemical properties are already known.
There are several people who deserve being mentioned, without whom this diploma work would not have happened. I would like to thank my supervisor, prof. István Furó, for allowing me to do the diploma work at physical chemistry and for his input and ideas throughout the project, prof. Peter Stilbs and ass.prof. Sergey Dvinskikh for their help with problems that has occurred, both practical and theoretical.

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List of Symbols
and Abbreviations

<table>
<thead>
<tr>
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<th>Description</th>
<th>Definition</th>
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<td>$F_{\text{friction}}$</td>
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<td>Electrophoretic mobility</td>
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</tr>
<tr>
<td>$\phi$</td>
<td>Phase shift in eNMR spectra</td>
<td>11</td>
</tr>
</tbody>
</table>
List of Figures

1.1 A few examples of common ionic liquid anions. .................................................. 3
1.2 A few examples of common ionic liquid cations. .................................................. 3
1.3 $^1$H spectrum of 10 mM TMA Br in D$_2$O. The peak at 1.1 ppm is TMA$^+$ and the peak at 2.2 ppm is residual $^1$H signal from D$_2$O. ........................................... 8
1.4 A standard 1D experiment, used to obtain the spectra in figure 1.3. ......................... 9
1.5 A PGDSTE pulse sequence. ....................................................................................... 10
1.6 The eNMR sample cell used for experiments. .......................................................... 12
1.7 An example of an eNMR experiment on 10 mM TMA Br in D$_2$O. .......................... 12
1.8 The pulse sequence with convection compensation used in the eNMR experiments. .......................................................... 13
2.1 The system studied, BMIM TfAc with hexamethyldisilane as $^1$H reference. ............ 15
2.2 Spectra of BMIM TfAc with 5 volume % hexamethyldisilane for peak identification. .......................................................... 15
2.3 The spectra show that increased temperature results in lowered chemical shift for BMIM TfAc with 5 volume % of hexamethyldisilane. .......................................................... 18
2.4 Magnification of the peaks at 9.8 and 7.9 ppm from figure 2.3 to better illustrate the change in chemical shift due to temperature change. .......................................................... 19
2.5 Plot of temperature versus scan number during an eNMR experiment on BMIM TfAc with 5 volume % hexamethyldisilane. Run at 110V supplied voltage. .............................. 19
2.6 Temperature variation during eNMR experiments on BMIM TfAc with 5 volume % hexamethyldisilane. .......................................................... 20
2.7 13 of the 24 steps (every second step) of the first diffusion measurement on BMIM TfAc with 5 volume % hexamethyldisilane. .......................................................... 22
2.8 The exponential fit for peak 2 (see figure 2.2 and figure 2.1 on page 15) from the diffusion experiment shown in figure 2.7. .......................................................... 22
2.9 The 6 steps of the third reported eNMR experiment on BMIM TfAc with 5 volume % hexamethyldisilane. .......................................................... 23
2.10 Plot of eNMR data for BMIM TfAc with 5 volume % hexamethyldisilane. The plot shows the convection compensated phase shifts (reference shifts taken from figure 2.11) with linear fits. .......................................................... 24
2.11 Plot of reference phase shifts that were used to convection compensate the eNMR results for BMIM TfAc with 5 volume % hexamethyldisilane in figure 2.10. .......................................................... 24