Variable Pressure Nuclear Magnetic Resonance Studies of Ionic Liquids and Electrophoretic Probe Design

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Variable Pressure Nuclear Magnetic Resonance Studies of Ionic Liquids and Electrophoretic Probe Design

by

Armando Rúa

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York 2014
This manuscript has been read and accepted for the Graduate Faculty in Physics

In satisfaction of the dissertation requirement for the degree of Doctor of Philosophy

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July 24, 2014

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THE CITY UNIVERSITY OF NEW YORK
Abstract

Variable Pressure Nuclear Magnetic Resonance Studies of Ionic Liquids and Electrophoretic Probe Design

by

Armando Rúa

Advisor: Prof. Steve G. Greenbaum

Energy storage materials play a key role in, efficient, clean, and versatile use of energy, and are crucial for the exploitation of renewable energy. The improve efficiency of energy use stimulates the development of energy storage such as batteries or super capacitors, toward higher power and energy density, which significantly depends upon the advancement of new materials used in these devices. The new materials need better understanding and description in the electrochemical properties. Nuclear Magnetic Resonance (NMR) has been an important tool in the characterization of ionic liquids and solids. The measurements of the relaxation times and the diffusion coefficient are of great importance in understanding the dynamics at micro and macro scale and are performed as a function of temperature and pressure to obtain parameters such as activation energies and activation volumes respectively. In this work, studies of ionic liquids and polycarbonates are presented and the design and fabrication of cells used in the study of NMR under an electric field.
For Linnette, Adrian, and Cristian for always believe in me, unconditional love, and support throughout the years. Without it, this thesis would never have been possible.
Acknowledgement

I would like to thank to all my nice NMR Group at Hunter College, who has created a warm and inspiring work atmosphere.

Many thanks for my advisor Dr. Steve Greenbaum for encouraging me to start a PhD. Also thanks for your inspiration, good advice and patience during my dissertation research.

I am grateful to Dr. Phil Stallworth for always finding the time to help me with the high pressure system. Your pedagogic assistance in the designs and the NMR fundamental concepts is much appreciated and for giving critical comments on my research and dissertation.

Very special thanks to my friend Joel De Jesus for his valuable help, great support and many discussions for about things that really matter, and things that don’t.

Dr. Mallorie Gobet, for your inspiring discussions and useful advice.

The legion of clandestine angels: Andi Shehu, Maria Isabel Sanchez, Tetiana Nosuch, Marc Berman, Laura Sermasan, Nastasiia Segiienko, Lisa Cirrincione, Kartik Pilar, Peng Jing, Jorge Colon, for making my graduate life joyful, what will I do without them.

Finally, I thank the Research Initiative for Scientific Enhancement program (RISE) for providing financial support on my Ph.D. studies.
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Introduction

The world’s demand for electricity is projected to double by 2050\(^1\). This poses two challenges to society: The depletion of fossil fuel and the negative impact of fossil fuel combustion on the environment (global warming and environmental pollution). These issues must be addressed in two ways: 1) development of renewable clean energy technologies (solar, hydropower, wind, etc.) , and 2) improve the efficiency of energy use (electric vehicles, materials for house insulation, etc.). Currently, renewable energy technologies are being developed for intermittent use and therefore require highly efficient energy storage systems. Advances in battery, fuel cell and super capacitor technologies promise to address these issues.

A lithium-ion battery basically is composed of a graphite anode, a transition metal oxide cathode and an electrolyte. Alternative anode materials have been studied including Li–Sn, and Li–Si alloys\(^2\). Some examples of cathode compounds are\(^3\) LiTi\(_2\)O\(_4\), LiCoO\(_2\), LiMn\(_2\)O\(_4\), LiMnCoO\(_4\), and LiFePO\(_4\). The electrolyte, usually a mixture of a lithium salt (LiPF\(_6\) for example) and anhydrous organic solvents, should be electronically insulating as well as a good ionic conductor.

From the point of view of battery safety, it is important that the electrolyte be non-volatile (negligible vapor pressure), have high ionic conductivity and possess a high thermal stability and breakdown strength (electrochemical window). In recent years, ionic liquids (ILs) have been studied extensively in order to understand and improve their electronic and related properties. They may be used as solvents for many processes as well as electrolytes in electrochemical devices as they possess both anion and cation components.\(^4\) In fact, it is a most outstanding feature of ILs that their physical and chemical properties can be tuned by altering the
anion and cation component structures. It has been pointed out that there may be as many as $10^{18}$ variations in the possible number of ionic liquids.\textsuperscript{5} Considering this; the IL Thermo database contains information for just 169 pure ionic liquids\textsuperscript{6}. Much of this information concerns data gathered at atmospheric pressure and ambient temperature conditions. It is pointed out that one of the main barriers for the development of ionic liquids for industrial application is rather limited database of their thermophysical and electronic properties\textsuperscript{7}.

Transport properties (viscosity, electrical conductivity, thermal conductivity, and self-diffusion coefficient, etc.) are among the most relevant considerations for chemical process design and development\textsuperscript{8}. Nuclear Magnetic Resonance (\textit{NMR}) spectroscopy has been used to measure self-diffusion coefficients of several \textit{IL}s\textsuperscript{9-14}. Noda et al\textsuperscript{10}, for example, using a spin echo approach, showed that their ionic liquids obey the Vogel-Fulcher-Tamman equation. The pressure-temperature effect on electrical conductivity using $^1$H and $^{19}$F self-diffusion in several ionic liquids were reported by Kanakubo et al.\textsuperscript{15,16} Electrophoretic NMR (eNMR) is another extremely useful technique for the study of transport mechanisms in \textit{IL}s. ENMR, which measures the driven electrophoretic mobilities and transference numbers of charged cations and anions separately, was initially conceived by Packer\textsuperscript{17}, experimentally worked out by Holz et al\textsuperscript{18}, and later refined by Johnson et al.\textsuperscript{19} Umecki et al.\textsuperscript{20} presented for first time eNMR measurements of ionic mobilities for several \textit{IL}s: EMI-BF$_4$, EMI-FSI, EMI-TFSI, and BMI-TFSI. Their data revealed higher ionic mobilities than expected using predictions from diffusion coefficient data. Similar results were obtained by Kikuko Hayamizu and Yuichi Aihara.\textsuperscript{21} Other groups, using eNMR, determined transference numbers in lithium ion-conducting polymer electrolytes\textsuperscript{22} and electroosmotic drag coefficients in Nafion membranes.\textsuperscript{23} However eNMR measurements of \textit{IL}s present a challenge, due to irreproducible nonelectrophoretic bulk flow
effects from both electroosmosis and thermal convection. In this thesis, new experimental eNMR sample cell are presented. These include a design to suppress bulk flow effects. The developments improved the signal-to-noise ratio compared to the U-tube setup previously used for eNMR.
Chapter 1

1.1 Batteries

An electrical battery is a device that converts stored chemical energy directly into electrical energy. The battery is typically composed of one or more electrochemical units called cells. A cell, being the working chemical unit, has three main parts: a positive electrode (cathode), a negative electrode (anode), and a liquid or solid separating them called the electrolyte. The energy conversion from chemical to electrical occurs inside the cell in the form of a reduction-oxidation (redox) reaction. When the battery discharges, the redox reaction commences in such a way that reduction processes occur (electrons are added) at the cathode, while oxidation processes occur (electrons are removed) at the anode. The electrodes do not touch each other but are in chemical contact through the electrolyte. Charge transport between electrodes takes place within the electrolyte. Some cells use two half-cells with different electrolytes. A separator between half cells allows ions to flow, but prevents mixing of the electrolytes. There are two types of batteries: primary batteries (disposable batteries), which are designed to be used once and discarded, and secondary batteries (rechargeable batteries), which are designed to be recharged and used multiple times.

Primary batteries are intended to be used once and discarded. These are most commonly used in portable devices that have low current drain, used intermittently and used well away from an alternative power source, such as in alarm and communication circuits where other electric power is only intermittently available. Since the chemical reactions are not easily reversible and active battery components do not completely return to their original forms, disposable primary cells cannot be reliably recharged. Zinc-carbon batteries and alkaline batteries are common types in this category.
Secondary batteries must be charged before use and they are usually assembled with active materials in the discharged state. Rechargeable batteries or secondary cells can be recharged by applying electric current, which reverses the chemical reactions that occur during its use. There are a vast number of battery types in the rechargeable category such as lead-acid and Li-ion battery types. A brief description of lithium batteries is given in the following section as they are more related to the projects discussed in this thesis.

1.2 Lithium Batteries

The lithium-ion battery (LIBs), first commercialized by Sony in 1991, owes its name to the exchange of the Li$^+$ ion between the graphite anode and layered-oxide cathode. Actually the materials used for cathodes are typically Li-containing metal-oxides with layered structures (such as LiCoO$_2$) or tunnel structured materials (such as LiMn$_2$O$_4$). The negative electrode (anode) materials include insertion-type materials (such as carbon, LiTi$_5$O$_{12}$, TiO$_2$, etc.), conversion-type materials (such as Si, Sn, etc.).

During charging or discharging, Li-ions are transported between the two electrodes via the electrolyte. Associated with the cation insertion/deinsertion mechanism are the chemical oxidation and reduction of the transition metal Co(III) $\leftrightarrow$ Co(IV) in the cathode. Upon completion of the circuit, the active negative electrode material becomes oxidized (Li$^0$ $\rightarrow$ Li$^+$ + $e^-$) and Li$^+$ extraction from the anode begins. Simultaneous Li$^+$ insertion occurs at the active positive electrode material and the transition metal becomes reduced (Co(IV) + $e^-$ $\rightarrow$ Co(III), Figs. 1.1 and 1.2). The opposite takes place during charging.
Figure 1.1 Basic operation mechanism and components of a Li-ion battery, where $M=Mn$, $Co$, $Ni$.

![Diagram](image)

**Figure 1.1** Basic operation mechanism and components of a Li-ion battery, where $M=Mn$, $Co$, $Ni$.

**Figure 1.2** Electrode reactions in Li-ion cell, where $x$ and $y$ selected based on the molar capacities of the electrode materials of the lithium ($x/y \approx 3$).

![Diagram](image)

The electrolyte, as mentioned previously, should be a good ionic conductor and electronic insulator. Therefore appropriate liquid electrolytes for lithium-ion batteries consist of lithium
salts, such as LiPF$_6$ or LiBF$_4$ dissolved in an organic solvent. Organic solvents with the sufficient requirements include dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylene carbonate (EC) and propylene carbonate (PC) or inorganic solvents such as thionyl-chloride (SOCl$_2$). Beyond the redox couple, additional chemical reactions within the cell can occur. As these tend to compromise battery performance, efforts are made to eliminate them. To protect the components from reactions with air and water, lithium cells are hermetically sealed. The choice of electrolyte is naturally a consideration because of the possibility of electrically induced decomposition. Of the most important and complex set of issues related to cell performance are the factors governing the solid-electrolyte interphase (SEI) layer formation. The electrolyte components can in principle be reduced/oxidized at the electrodes thereby forming a variety of surface-film breakdown products called the SEI. The SEI may seem detrimental since it increases the cell’s internal resistance. On the other hand, there are some benefits, as in the case of the anode, the SEI protects the electrode from decomposition and exfoliation. Currently, this is a very active area in battery research.

1.3 Safety in Li-Batteries

Safety is an important issue for lithium battery technology. For instance, the present LiPF$_6$-organic carbonate electrolytes: exhibit 1) a narrow stability domain, thereby preventing the use of high voltage cathodes, and 2) high vapor pressures, which while giving a higher flammability risk, are incompatible with environment and health standards. One way to address item 1) is to develop electrode materials that operate within the stability window of the electrolyte (i.e. Li$_4$Ti$_5$O$_{12}$ or LTO). Various efforts are underway to improve the fire safety like the implementation of: redox shuttles to protect from overcharge, shut-down separators to
prevent thermal runaway, additives to help build a stable SEI and, to reduce toxicity, other lithium salts as alternatives to LiPF₆.

Other approaches involve the development of solid-state electrolytes or free lithium conducting membranes. The solid electrolyte offers a more inert system and greater cell reliability in a more modular design with easier handling. Membranes based on homopolymers, such as polyethylene oxide (PEO), hosting a lithium salt (i.e. LiCF₃SO₃), appear to be promising options. The drawback with this material is that the ionic conductivity remains low even at temperature as high as 70°C. There is a large research investment in fabricating PEO-Liₓ membranes that can be used under ambient conditions in batteries.

The unique combination of favorable properties with ionic liquids (i.e. non-flammable, high thermal stability, high ionic conductivity, large electrochemical window and environmentally compatible) encourages their development as stable and safe electrolytes in electrochemical devices. One drawback in pursuing ionic liquids is the prohibitively high cost of development, although price reduction is expected if and when production is scaled up. In the meantime, in spite of the high cost, it is likely that ILs, will be used as additives to the common organic liquid electrolyte solutions. In this work, special attention will be paid two ionic liquids of the imidazolium family.
References


Chapter 2

2.1 NMR Principles

Protons and neutrons possess intrinsic angular momentum, denoted as spin \( I = I/2 \), and correspondingly possess magnetic moments. Atomic nuclei, being combinations of protons and neutrons, also have spin and magnetic moments, for example, \( I = 1/2 \) (\(^1\text{H}, ^{19}\text{F}\)), \( I = 1 \) (\(^2\text{H}\)), \( I = 3/2 \) (\(^7\text{Li}\)), etc. Nuclei with \( I = 0 \) do not interact with magnetic fields because they don’t have magnetic moments. Nuclear magnetic resonance (NMR) is a spectroscopic technique that works within the magnetic energy levels of nuclear moments.

The nuclear magnetic moment \( \mu \) and the angular momentum \( I \) are related by:

\[
\mu = \gamma I
\]  
(2.1)

Where \( \gamma \) is the gyromagnetic ratio specific for each nucleus, for example, \( \gamma = 42.58 \) (\(^1\text{H}\)), 6.54 (\(^2\text{H}\)), and 40.08 (\(^19\text{F}\)) in rad-MHz/T units. In the presence of an external magnetic field a nuclear moment will interact with the field \((B_0 = B_0 \hat{e}_z)\) with energy given by:

\[
E = -\mu_z B_0 = -\gamma \hbar m_I B_0
\]  
(2.2)

where \( \mu_z \) is the component of the magnetic moment along \( B_0 \) (\( z \)-axis) and \( m_I \) is the magnetic \((m_I = I, I-1, \ldots, -I)\). The energy difference between two consecutives energy levels is therefore,

\[
\Delta E = \gamma \hbar (m_I - m_{I-1}) B_0 = \gamma \hbar B_0
\]  
(2.3)

A nuclear moment can be raised in energy from a lower energy level by absorbing \( \Delta E \) amount of energy. Conversely, a nuclear moment in a higher energy level can lose (to the surroundings) \( \Delta E \) of energy and find itself in a lower level. The energy supplied to the moment is an electromagnetic radiofrequency (RF) field. If the energy is supplied at a rate at or below the characteristic time required for the moment to lose energy to the surroundings, then a resonance
condition can be maintained. In this way, the frequency satisfying the resonance condition $\hbar \omega_0 = \Delta E = \gamma \hbar B_0$, is:

$$\omega_0 = \gamma B_0 \tag{2.4}$$

This frequency, $\omega_0$, called the Larmor frequency, is proportional to the applied field. It is the frequency at which the nuclear magnetic moment precesses about the $B_0$ field.

Instead of a single magnetic moment, now consider the equilibrium magnetization that is established for an ensemble of non-interacting nuclear spins inside a magnetic field $B_0$, where $I=1/2$ and $m=1/2,-1/2$. In this case, the ratio of the populations (number of spins in each energy level) at equilibrium is given by:

$$\frac{N_\beta}{N_\alpha} = e^{-\frac{\Delta E}{k_BT}} \tag{2.5}$$

$N_\beta$ is the population of the highest energy level, $N_\alpha$ is the population of the lowest energy level, $\Delta E = \gamma \hbar B_0$, $k$ is the Boltzmann constant and $T$ is the temperature. Therefore, since $N_\beta > N_\alpha$ in this system, there will be a net magnetization at equilibrium ($M_0$) in the direction of magnetic field $B_0$ (z-direction) as shown in Fig. 2.1.

![Figure 2.1 Net magnetization vector $M_0$](image)

$\textbf{Figure 2.1}$ Net magnetization vector $M_0$
Also from Fig 2.1, it can be seen that the magnetization components in the x and y directions ($M_x, M_y$) are 0.

Most modern NMR spectrometers manipulate nuclear spin ensembles (i.e. the sample being studied) through the application of RF pulses. The sample is placed inside an inductor that can deliver the RF pulse of a particular frequency and power. For solid-state NMR, the inductor is most often a solenoid oriented with its symmetry axis perpendicular to the applied field direction. An RF pulse is most easily imposed on the sample when transmitted by a coil. Since the pulse is simply an oscillating magnetic field of appropriate duration, frequency, and intensity $B_1$, it is generated by applying an RF voltage to the coil leads. The duration of the pulse, called the pulse width, is on the order of $\mu$s. The pulse frequency is generally near the Larmor value, which considering typical laboratory magnetic field strengths, is on the order of MHz. The pulse intensity or amplitude, being much smaller than $B_0$, is on the order of a few Gauss or milliTesla.

Under the action of the $B_1$ field, the bulk magnetization $M_0$ is rotated away from the z-direction towards the x-y plane (Fig. 2.2).

![Figure 2.2. Effect of $B_1$ on the magnetization vector](image-url)
The angle of rotation or flip angle is given by:

\[ \theta = \gamma \tau B_1 \]  

(2.6)

where the duration of the pulse is given by \( \tau \). A \( 90^\circ \) pulse is one which rotates the sample magnetization by \( \pi / 2 \) onto the x-y plane. Note that immediately after the \( 90^\circ \) pulse, the longitudinal magnetization component, \( M_z \), is identically zero (Fig. 2.3). The effective non-zero magnetization in the x-y plane is called the transverse magnetization.

\[ \text{Figure 2.3. Effect on the net magnetization by a } 90^\circ \text{ rf pulse} \]

The sample magnetization after the pulse will, over time, come to equilibrium with the external field \( B_0 \) field again. The time constant which describes how \( M_z \) returns to its equilibrium value is called the spin-lattice relaxation time, \( T_1 \). An experiment can be designed to measure \( T_1 \). For instance, if the spin populations over the energy levels are made equal (i.e. by applying many pulses quickly), the bulk magnetization vanishes and is said to be “saturated.” \( M(t) \) will evolve from this initial saturated condition to its equilibrium value \( (M_0) \) over time such that the expression for its z-component \( M_z \) is:

\[ M_Z = M_0 \left( 1 - e^{-\frac{\tau}{T_1}} \right) \]  

(2.7)

Similarly, the x and y-components can be formalized. The time constant \( T_2 \) which describes the decay of the transverse magnetization, is called the spin-spin relaxation time.
\[ M_x = M_0 \cos(\omega_0 t) e^{-\frac{t}{T_2}} \]  
(2.8)

\[ M_y = -M_0 \sin(\omega_0 t) e^{-\frac{t}{T_2}} \]  
(2.9)

Figure 2.4 The exponential curves for \( T_2 \) and \( T_1 \) measurements.

2.2 \( T_1 \) Measurements

One of the most common pulse sequences to measure spin-lattice relaxation (\( T_1 \) process) is the inversion recovery sequence\(^2\). The sequence consists of two RF pulses, \( \pi \) and \( \pi/2 \) respectively, separated by a recovery time \( \tau \). (Fig 2.5)

Fig. 2.5: Recovery inversion pulse sequence and magnetization vector evolution.
The first pulse is applied along the +x-axis, which rotates the magnetization vector by $\pi$ from the +z-axis to the –z-axis. In the delay $\tau$ between the pulses, the magnetization vector recovers along the z-axis towards its equilibrium value $M_0$ along the +z-axis. A second pulse is applied along the +x-axis after the delay time $\tau$. The pulse rotates the magnetization vector by $\pi/2$ onto the y-axis, where its free induction decay is detected. The second pulse allows the spectrometer to detect the magnetization, since the spectrometer can only measure magnetizations in the x-y plane.

In the inversion recovery sequence, the magnetization intensity is monitored as it evolves with respect to $\tau$. The characteristic time for the system to achieve equilibrium, the spin-lattice relaxation time, $T_1$, is a dynamic time reflecting the efficiency of the various thermodynamic interactions governing the spin system. To prevent saturation of the spin system, the magnetization needs to be at equilibrium before a pulse sequence is applied. Therefore, knowledge of $T_1$ has practical importance because the time delay between successive pulse - signal acquisition periods necessarily has to be long enough for the system to reach equilibrium. Usually, this delay time is at least $7T_1$.

2.3 Diffusion NMR

In absence of external forces, the motions of particles within an ensemble results from their thermal agitation. The magnitudes and directions of the displacements are stochastic and can occur over a range of times scales depending on the particle and its environment. The phenomenon is known mostly as Brownian motion, but in the event of chemical interactions (at zero chemical potential gradient), this process is denoted as self-diffusion. NMR is a very good method for the measurement of self-diffusion coefficients because the experimental simplicity
and isotope selectivity in observation of the diffusing species. The limitations become more pressing, however, in those cases of strong interactions, low abundance spins and very small diffusion coefficients (<10^{-13} m^2/s). Typically, the NMR diffusion measurements are made employing some type of modified echo pulse sequence. The echo intensity or signal is dependent on its amplitude and its corresponding phase, given by \(^6\):

\[
S(t_e) = S_0(t_e) \exp(i\Phi(t_e))
\]

where \(t_e\) is the time at which the echo occurs, \(S_0(t_e)\) is the spin dephasing by homogeneous spin-spin interactions (pure T\(_2\) process) and \(\exp(i\Phi(t_e))\) accounts for the dephasing caused by the magnetic field gradient (inhomogeneous T\(_2\) process). \(S_0\) is given by the solution of the M\(_{xy}\) Bloch equation for a system with no magnetic field gradient (2.8 and 2.9) where \(t_e = 2\tau\) for the \(\pi/2 - \tau - \pi\) (Hahn) echo pulse sequence.

\[
S_0(t_e) = M_0 \exp[-2\tau / T_2]
\]

The second term is the sum of all the spin phase contributions and can be simplified using a cumulant expansion:

\[
\exp(i\Phi(t_e)) = \exp(i\Phi(t_e)) - 1/2(\Phi^2(t_e)) - \Phi(t_e)^2 \pm \ldots
\]

(2.12)

For free diffusion \(\Phi(t_e)\) is normally distributed, and thus has a mean equal to 0. Therefore equation (2.10) reduces to:

\[
S(t_e) = S_0(t_e) \exp(-1/2\Phi^2(t_e))
\]

(2.13)

Now we need to evaluate \(\Phi^2(t_e)\). The spin phases are dependent on \(\gamma\), the gradient \(g\) and the position of the nuclei \(z\) (along the gradient direction). Therefore:
\[ \Phi(t_e) = -\gamma \int_0^{t_e} g(t') z(t')dt' \]  \hspace{1cm} (2.14)

The phase integral can be expanded by integration by parts, resulting in:

\[ \Phi(t_e) = - \int_0^{t_e} G(t) v(t) dt \]  \hspace{1cm} (2.15)

where \( v(t) \) is the velocity of the nuclei, \( G(t_e) = 0 \) and

\[ G(t) = \gamma \int_0^t g' (t') dt' \]  \hspace{1cm} (2.16)

With this result, the expression for the inhomogeneous dephasing could be derived as follows:

\[ \langle \Phi(t_1) \cdot \Phi(t_2) \rangle = \int_0^{t_e} \int_0^{t_e} G(t_1) G(t_2) < v(t_1) \cdot v(t_2) > dt_1 dt_2 \]  \hspace{1cm} (2.17)

Assuming simple diffusion:

\[ \langle r(t_1) \cdot r(t_2) \rangle = 2D \delta (t_2 - t_1) t_1 \]  \hspace{1cm} (2.18)

Therefore:

\[ \langle v(t_1) \cdot v(t_2) \rangle = 2D \delta (t_2 - t_1) \]  \hspace{1cm} (2.19)

Combining equations 2.11, 2.13, 2.17, and 2.19 results in:

\[ S(t_e) = M_0 \exp[-2\pi/T_2] \exp(-D\int_0^{t_e} G^2(t_1) dt_1) \]  \hspace{1cm} (2.20)

Equation 2.20 is the general expression for the echo intensity decay as a function of the applied magnetic field gradient \( G(t_1) \), which can have a variety of expressions, depending on the
application. By measuring the echo intensity decay as a function of $\tau$ it is possible to measure the diffusion coefficient for a sample.

2.4 Diffusion Measurements.

The principle to NMR self-diffusion measurements is to encode spatial information about the nuclei, atoms, molecules, etc. by applying magnetic field gradients during the spin-echo pulse sequence.

![Diagram of pulsed field gradient spin echo](image)

**Fig. 2.6.** Schematic of the pulsed field gradient spin echo.

The pulsed field gradient (PFG) spin echo NMR pulse sequence used in this thesis is shown in the figure 2.6. The resulting echo attenuation using this sequence is:

$$S(2\tau) = M_0 \exp\left(-\frac{2\tau}{T_2}\right) \exp[-Dq^2\left(\Delta - \frac{\delta}{3}\right)]$$  

(2.21)

where $q = \gamma g \delta$, $\gamma$ is the magnetogyric ratio, $g$ is the gradient strength ($dB/dz$), $\delta$ is the duration of gradient pulses, $\tau$ is the time between pulses for dephasing and refocusing, $\Delta$ is the time
between the two gradient pulses. From this equation the value of $D$ can be obtained. In practice the work presented here, the value of $\tau$ is fixed (thereby keeping the $T_2$ contribution to the decay constant) and echo data are gathered with respect to the gradient amplitude.

### 2.5 High Pressure NMR

Even without knowing the state of a system, it is generally understood that a temperature variation at atmospheric pressure produces a concurrent change in the thermal energy and volume of the system. To gain insight into the behavior of molecular motion it is important to separate these effects. The motivation for using pressure as an experimental variable is to gain further understanding, on a molecular level, of the nature of the dynamic processes occurring in the ionic liquids. This approach provides information not obtainable by variable temperature measurements alone. Compression causes reduction of interatomic distances and increased intermolecular interactions, thereby affecting liquid viscosity and ion transport. High pressure measurements of viscosities, ion self-diffusion coefficients and electrical conductivities have previously been made on ionic liquids; and the properties have been analyzed in terms of the empirical Stokes–Einstein, Walden and Nernst–Einstein equations.\textsuperscript{4-14} Kanakubo and Harris for example,\textsuperscript{4,6-14} used a phenomenological approach of velocity correlation coefficients (VCC), which are time and ensemble averages of integrals of Kubo velocity cross-correlation functions, just as self-diffusion coefficients are time and ensemble averages of integrals of velocity auto-correlation functions. The VCCs results for ionic liquids show consistent regularities when plotted against the viscosity. They show that the deviation of the Nernst–Einstein parameter, $\Delta$, is a function of differences between the VCCs ($f_{ij}$).
\[ \Delta = \frac{c(2f_{++} - f_{+-} - f_{--})}{(D_+ + D_-)} \] (2.22)

Where \( c \) is the molarity. The results suggest that \( \Delta \) is, if not constant for a given ionic liquid, only a very weak function of temperature and pressure.

In this thesis we use the activation volume (\( \Delta V \)) to quantify the effect of \( P \) pressure on the relaxation time and diffusion in ionic liquids. This dynamic parameter is defined by:

\[ \Delta V = -kT \left[ \frac{\partial (\ln(A))}{\partial P} \right]_T \] (2.23)

where, \( T \) is the temperature of the sample, \( P \) is the pressure and \( A \) could be either the diffusion coefficient or the spin lattice relaxation.

### 2.6 Diffusion Measurements in the fringe field of Superconducting Magnets

The magnetization intensity decay for the gradient field diffusion experiment is governed by two effects, spin-spin relaxation, \( T_2 \), and diffusion (Equation 2.21). In order to measure the diffusion coefficient, it would be convenient to have the exponential function containing the diffusive term dominate the intensity decay process. This is hardly universally true, especially when measuring very small diffusion coefficients. To help in this regard, experiments can be performed in a static field gradient (SFG), i.e. placing the probe (sample) within the inhomogeneous region of the magnet, and carrying out the NMR spin-echo experiment as usual. SFGs can be an order-of-
magnitude greater (~ 10kG/cm) than the largest gradients produced by anti-Helmholtz coils in custom NMR probes (~1kG/cm).

SFG measurements can give root-mean-square molecular displacements as small as 200 Å and self diffusion coefficients, D, as small as $10^{16}$ m²/s. The sample has to be rather thin (a “slice”) since the gradient is a function of position (along the z-axis). On the other hand, one doesn’t have to consider long eddy current relaxation times since the gradients are not pulsed. The SFG approach in this thesis lends itself nicely to high pressure diffusion measurements since the sample_rf-coil enclosure (high pressure containment cell or bomb) can be positioned conveniently to run experiments at specific fields and gradients. The probe assembly consists of an upper part: the high-pressure bomb containing the sample and rf-coil; and lower part: rf-electronics including the matching and tune capacitors.

Prior to the $T_1$ and $D$ pressure dependences elaborated in this thesis, the gradient was mapped as a function of height (z) from the base of the magnet (Figure 2.7). For sub-millimeter precision control of the field/gradient, the sample_rf-coil (bomb/probe) was positioned appropriately along the z-axis using a computer controlled home built motorized stage (“elevator”).

![CMX Magnet B Field and Gradient](image)

**Figure 2.7.** Magnetic field strength and gradient as a function of position.
The sample within the rf-coil was isostatically pressurized by hydraulic fluid (Fluorinert, oil, etc.) all inside a bomb. The was hermetically sealed in a polyethylene bag to separate it from the hydraulic fluid and the fluid was fed to the upper probe assembly using an Enerpac™ 11-400 manual pump. The data acquisition was performed using a Chemagnetics ™ CMX 300 spectrometer. More details about the experiments can be found in reference 15 and are discussed in the next chapters.

2.7 References


Chapter 3

Multi-Nuclear Variable Temperature and Pressure NMR Studies of EMIM/BMIM TFSA:

Effect of Pressure on Deuteron Spin-Lattice Relaxation Times and the Self-Diffusion Coefficients in Ionic Liquids.

3.1 Introduction

There is great interest in studying ionic liquids (ILs) on a fundamental level as models for the transport properties of complex liquid systems, as well as for possible applications in several industries, including textile, energy and nuclear waste recycling. With regards to energy, ILs comprised of imidazolium based cations and their counter anions have formed the basis of many research projects geared towards the development of alternative electrolyte materials for energy production devices such as batteries\cite{1-4} and supercapacitors.\cite{5-8} This is because of their excellent chemical, thermal and physical properties such as non-volatility, non-flammability and relatively high ionic conductivity. Another attractive feature of ILs is their tunability. Depending on the application, improved performance can be achieved by combining the right cation and anion, thereby producing the desired properties. For example, if one desires greater transport properties, the choice should be ions of small size, greater charge delocalization and multiple conformations which differ slightly in energy.\cite{9-11} In spite of this unique feature, at present there is no method to determine what properties will result from particular pairings for many cations and anions. In terms of charge delocalization, the bis((trifluoromethyl)sulfonyl)amide (TFSA, (CF$_3$SO$_2$-N-SO$_2$CF$_3$)) anion offers both, and when combined with an imidazolium cation, can produce fluid room temperature ILs with high ionic conductivity.\cite{11}

Various techniques have been used to understand the fluid properties of ILs, including molecular dynamic simulations,\cite{12-14} conductivity,\cite{15,16} viscosity,\cite{15-17} Raman spectroscopy\cite{18-20} and
nuclear magnetic resonance (NMR).\textsuperscript{12, 16, 21-26} As a tool, NMR is able to provide nucleus-specific microscopic and macroscopic translational and rotational dynamics through determination of the spin-lattice relaxation time $T_1$ and the self-diffusion coefficient $D$, over a wide temperature and frequency range. Most NMR studies have been done as a function of temperature, which causes both changes in energy and density. However, when done as a function of pressure, NMR allows separation of the density from energy-related effects, which oftentimes control the transport dynamics of mobile systems, especially ones in which viscosity effects play a role. In this study we report multi-nuclear NMR ($^1$H, $^2$H, and $^{19}$F) $T_1$ and ($^1$H and $^{19}$F) $D$ data as a function of temperature and pressure for the deuterated isotopologue ILs of the 1-ethyl-3-methylimidazolium (EMIM) cation, and the 1-butyl-3-methylimidazolium (BMIM) cation; along with the bis((trifluoromethyl)sulfonyl)amide (TFSA) anion.

The selective deuteration allows us to analyze the fundamental dynamics of the cation through $^1$H ($I = \frac{1}{2}$) and $^2$H ($I = 1$) probe nuclei. The quadrupole $^2$H nucleus is sensitive to rotational dynamics and reflects the interaction between the nuclear quadrupole moment and its electric field gradient. The advantage of determining both $T_1$ and $D$ data comes from the fact that analysis of $T_1$ data and associated correlation times often require an assumption about the relaxation mechanism and its relation to the translational motion of the probe species, while $D$ data provides a direct determination of the translational motion.

Variable pressure has been used in vibrational spectroscopic studies of ILs\textsuperscript{27-31} comprised of various anions and cations including EMIM and TFSA\textsuperscript{18-20} and results show several behaviors, including conformational changes, enhancement of cation-anion hydrogen bonding interactions and shifts of vibrational frequencies to higher values. In this manuscript we present our findings of variable pressure and temperature NMR $T_1$ and $D$ studies for EMIM and BMIM TFSA.
To the author’s knowledge, up to this point, there are no variable pressure NMR studies for these ILs. The objective is to gain insight into the role of the alkyl chain length (i.e. ethyl for EMIM and butyl for BMIM) by studying NMR relaxation times and diffusion. For this purpose, the partial deuteration of the cations is particularly valuable. The results are not entirely new.\textsuperscript{21,22} For reasons elaborated on below, the $T_1$ versus temperature data are assumed to follow a Bloombergen-Purcell-Pound interpretation (i.e. exponential decaying correlation function). However, the $T_1$ pressure dependence for both EMIM and BMIM as presented here in this thesis, is entirely new and presented in the context of the temperature dependence.

3.2 Experimental Section

3.2.1 Sample Preparation

Samples of partially deuterated EMIM and BMIM-TFSA were prepared by reaction of 1-methylimidazole with the appropriately deuterated ethyl bromide or the reaction of 1-ethylimidazole with methyl iodide-$d_3$, followed by metathesis to the TFSA salts using aqueous Li TFSA. Complete details regarding the synthesis can be found at the end of this chapter. The structure and abbreviations for all samples are shown in Fig. 3.1. All samples were handled and stored in a dry argon-filled glove-box to avoid absorption of atmospheric moisture.
Figure 3.1. Structures of the deuterium-labeled (indicated in green) EMIM and BMIM cations and the TFSA anion (cis conformation shown).

3.2.2. Nuclear Magnetic Resonance

The T₁ and D measurements were conducted on a Chemagnetics CMX-300 spectrometer as a function of temperature from 296 to 373 K and pressure (up to 2.5 kbar) with a 7.3T superconducting magnet. For this magnetic field, ¹H, ²H and ¹⁹F resonances occur at frequencies of 309, 47 and 283 MHz respectively. For both the ¹H and ¹⁹F variable temperature T₁ and D measurements, the ILs were inserted into 5 mm NMR tubes. The experiments were performed in a 5mm Nalorac gradient probe and a current amplifier provided by Magnetic Resonance Instruments, Inc.
Multinuclear spin-lattice relaxation measurements ($T_1$) were determined using the inversion recovery ($180^\circ-\tau-90^\circ$-Acq) sequence for about 15 values of $\tau$. At least five $T_1$s were allowed between repetitions of the pulse sequence and uncertainties were ~5%. Self-diffusion coefficients ($D$) can be obtained by using either static or pulsed field gradients with the Hahn spin-echo pulse sequence ($\pi/2 - \tau - \pi$). For the pulsed field gradient technique, $D$ values were obtained using the Hahn spin-echo pulse sequence with square-shaped gradient pulses of equal amplitude $g$, duration $\delta$ and separation $\Delta$ after the rf pulses. The values of $\delta$ and $\Delta$ are chosen to allow sufficient attenuation of the echo amplitude. The resulting attenuation depends on the change in positions and associated frequencies of the spins during the separation interval $\Delta$ and was shown to be represented by the equation (2.21):

$$A(g) = A_0 \exp[-2\tau T_2] \exp[-D(\gamma g)^2(\Delta-\delta)],$$

(2.21)

The value of $D$ was obtained by fitting the echo attenuation data for about 15 values of $g$ ranging from ~0.2 – 3 T/m and uncertainties were ~ 5%. For $D$ values determined by the static field gradient method, the echo attenuation profile is determined:

$$A(\tau) = A_0 \exp[-2\tau T_2] \exp[-2D(\gamma g)^2(\tau)],$$

(3.1)

For all $D$ values calculated, single exponential attenuation profiles were obtained.

For the multi-nuclear variable pressure measurements, the ILs were hermetically sealed in plastic bags, because during the course of measurement within a copper-beryllium pressure vessel the sample is immersed in the pressure transmitting fluid (Fluorinert FC-3283 or vacuum oil). The pressure was generated using a manual pump that is capable of reaching pressures up to
2.5 kbar. The probe used was home built and tunable to 80 MHz (which corresponded to a static field gradient of 35 T/m).

### 3.3. Variable Temperature $T_1$ Results

The $^1$H and $^{19}$F spin-lattice relaxation times ($T_1$s) are shown in Figures 3.2 and 3.3 as functions of inverse temperature. For the samples studied all magnetization recoveries were exponential. The data, residing on the high-temperature side of the $T_1$ minimum and being fairly linear, indicates that the relaxation is governed by a single activation energy (see table 3.2) and is consistent with a BPP magnetic dipolar relaxation mechanism. For EMIM and BMIM $T_1$s associated with protons at positions H4, H5 and H2 of the imidazolium ring are consistently largest than those of the butyl or ethyl group ($\text{CH}_2$) protons at positions 2A, 2B and 2C (see Figs. 3.2 and 3.3). The limited data suggest that methyl protons (designated NH3) have $T_1$ values somewhat less than that of the ring protons but greater than the alkyl group protons. The $^{19}$F $T_1$s for CF$_3$ groups of TFSA were also practically Arrhenius for all the samples. The data presented here are consistent with results previously given in the literature.$^{22,32}$
Figure 3.2. Arrhenius plots of $^1$H and $^{19}$F $T_1$ for the assigned peaks for EMIM TFSA.

Figure 3.3. Arrhenius plots of $^1$H and $^{19}$F $T_1$ for the assigned peaks for BMIM TFSA.
3.4. $^2\text{H} T_1$ vs Temperature EMIM Results

Shown in Figure 3.4 are the linear Arrhenius plots of $^2\text{H} T_1$ data. Unsurprisingly, comparison with Fig. 3.2 shows that the $^{19}\text{F}$ results are independent of the cation deuteration. It is evident the $^2\text{H} T_1$s are dramatically smaller than the associated $^1\text{H} T_1$s in these ILs since $^2\text{H}$ relax via electronic quadrupolar interactions. The $T_1$ results indicate a more efficient relaxation for the CD$_2$ isotopologue, which could be interpreted as meaning the average electric field gradient is strongest in the location of CD$_2$. The data show that generally the $^2\text{H} T_1$s are longest for the terminal ND$_3$ deuterons, followed by CD$_3$ deuterons. The shortest $T_1$s are found for the CD$_2$ deuterons. A somewhat different ordering was observed for the $^1\text{H} T_1$s (see Fig 3.2). The fact that different $T_1$s are observed for the various deuterated groups reflect the differences in the interactions between each group and its surroundings, which is comprised mainly of anions in the first solvation shell. The TFSA and EMIM ions have charge distributions.$^{33-35}$ This asymmetry was demonstrated for the TFSA anion by ab initio calculations from which the natural charge was determined and electrostatic potential based charge calculated for the various points of interactions (N, O and F).$^{33, 34}$ While the values of the charges determined by the two methods differed, the pattern observed was the same, with the unsurprising order, N > O > F for favorable interaction locations.
Figure 3.4. Arrhenius plots of $^2$H and $^{19}$F $T_1$ for the assigned peaks for deuterated EMIM TFSA samples.

3.5. $^2$H Relaxation Times vs Temperature BMIM Results

$^2$H $T_1$s were measured with respect to temperature down to 220 K. Due to the extended temperature range, a more complete $T_1$ behavior (Fig. 3.5) is observed here. For the BMIM ring methyl (ND3), a $T_1$ minimum of 38 ms is observed at 263K. For the butyl side chain, relaxation of the terminal methyl deuterons (CD3) levels-off at temperatures below 263K (i.e. $T_1 = 26$ ms) and the methylene deuterons (CD2) exhibit a minimum at 7.5 ms and 274 K. Again, the general order follows that of the EMIM $^2$H $T_1$s: $T_1$ (ND3) > $T_1$ (CD3) > $T_1$ (Can CD2), thereby illustrating very similar temperature dependences.
Fig. 3.5. Plot of $^2$H spin-lattice relaxation times as a function of inverse temperature for partially deuterated BMIM-TFSA.

It is worth mentioning that for these ILs, a fair possibility exists for supercooling in the liquid state.$^{36-38}$ In order to monitor the phase of the IL linewidths were also measured for BMIM-ND3 between 230 to 340 K (Fig. 3.6). Note the large linewidth increase at temperatures lower than 240 K, where the FWHM values are seen to perhaps exceed 8500 Hz. The FWHM data suggest a liquid-solid transition near 230 K. The differential scanning calorimeter (DSC) studies for BMIM TFSA do not show tendency to crystallize on cooling; however upon heating from the supercooled state, they display spontaneous crystallization. The DSC studies are summarized in table 3.1.
Table 3.1. Literature Values of the Thermal Analysis for BMIM TFSA

In these calorimetric studies the cooling and heating rates and the purity in the ionic liquids are the causes of the different values in the measurements.

![Fig. 3.6. $^2$H NMR line widths vs. T for BMIM-ND3](image)

The general expression relating the spin-lattice relaxation times $T_1$ to the reorientational correlation function for the case of $I = I$ is

$$\frac{1}{T_1} = \frac{3}{10} \pi^2 (Q_{cc})^2 [J(\omega_0) + 4J(2\omega_0)]$$

(3.2)

Where $Q_{cc}$ (kHz) is the quadrupolar coupling constant for the $^2$H nuclei. The rate $1/T_1$ at the resonance frequency yields the spectral density $J(\omega_0)$ which is given by the Fourier transform of $f(t)$. 

<table>
<thead>
<tr>
<th>BMIM TFSA</th>
<th>Tm (K)</th>
<th>Tf (K)</th>
<th>Tcc (K)</th>
<th>Tg (K)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>269</td>
<td>220</td>
<td>184</td>
<td></td>
<td>Gomez 36</td>
</tr>
<tr>
<td></td>
<td>271</td>
<td>229</td>
<td>187</td>
<td></td>
<td>Freedlake 37</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td></td>
<td></td>
<td>184</td>
<td>Blokhin 38</td>
</tr>
</tbody>
</table>
\[ f(\omega_0) = \int_0^\infty dt f(t) e^{-i\omega_0 t} \]  

(3.3)

The particular form for \( f(\omega_0) \) depends on the correlation function for molecular reorientation. The correlation function commonly applied to NMR data is that introduced by Bloembergen-Purcell-Pound (BPP): \( f(t) = \exp[-(t/\tau_c)] \). The correlation time, \( \tau_c \), defines the time scale for changes of the local magnetic field experienced by the resonant nucleus. In this context, the spectral density function, \( f(\omega_0) \), given by the Fourier transform of the correlation function, yields the Lorentzian function:

\[ f(\omega_0) = \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \]  

(3.4)

The \(^2\text{H}\) spin lattice relaxation data were analyzed using the BPP relation at the minimum \( T_1 \): \( \omega_0 \tau_c = 2\pi \nu \tau_c = 0.616 \). In this experiment, \( \nu = 47.47 \text{ MHz} \), therefore: \( \tau_c = 2.065 \times 10^{-9} \text{ s} \).

<table>
<thead>
<tr>
<th>Position</th>
<th>EMIM-MD(_3)</th>
<th>EMIM-TD(_3)</th>
<th>EMIM-D(_2)</th>
<th>EMIM-D(_2)</th>
<th>EMIM-D(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H4, H5</td>
<td>15</td>
<td>10</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>H2</td>
<td>10</td>
<td>10</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>TCH(_3)</td>
<td>12</td>
<td>-</td>
<td>9</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>CH(_2)</td>
<td>17</td>
<td>11</td>
<td>-</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>NCH(_3)</td>
<td>-</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>TFSA ((^{19}\text{F}))</td>
<td>12</td>
<td>12</td>
<td>13</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>(^2\text{H} \ T_1 \ data)</td>
<td>15</td>
<td>16</td>
<td>12</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.2.** Activation energies for reorientational motion determined from \(^1\text{H}\) and \(^{19}\text{F} \ T_1 \ data\) (kJ/mol).
3.6 Self-Diffusion Coefficient vs Temperature

The self-diffusion coefficient $D$ was determined as a function of temperature using the PGSE NMR technique for the cations ($^1$H) and anions ($^{19}$F) and the Arrhenius plots are shown in Figure 3.7. and 3.8. The general behavior is the expected increase in $D$ with increasing temperature. For EMIM, slightly greater diffusion was observed for the cations (relative to the anion $^{19}$F results) over the entire temperature range and results compare well with Hayamizu$^{22}$ and Tokuda$^{10}$ et al. However, in the BMIM case the diffusion coefficients were comparable. There is also a greater mass effect in the EMIM diffusion results, as seen in the spread of the high temperature data. Comparison between data sets shows that the diffusion coefficients were slightly larger for the EMIM cation.

![Arrhenius plots of $^1$H and $^{19}$F self-diffusion coefficient data for EMIM TFSA samples.](image)

**Figure 3.7.** Arrhenius plots of $^1$H and $^{19}$F self-diffusion coefficient data for EMIM TFSA samples.
Figure 3.8. Arrhenius plots of $^1$H and $^{19}$F self-diffusion coefficient data for BMIM TFSA samples.

The hydrodynamic basis for determining the rotational frictional coefficient for a sphere of radius $a$ rotating in a medium of viscosity $\eta$ was introduced by Stokes and then used by Einstein to describe Brownian motion of small particles. The resulting Stokes-Einstein equation reveals a fundamental connection between self-diffusivity and viscosity given by:

$$D = \frac{k_B T}{C \pi \eta R}$$

(3.5)

where $R$ is the effective hydrodynamic radius of a molecule. The coupling factor $4 \leq C \leq 6$ accounts for the different hydrodynamic boundary conditions at the interface between the diffusing sphere and the medium. ILs typically reveal coupling factors between $C = 2$ and 6, with interesting trends in the cation and anion dependence.

In some cases the experimental data show a fractional Stokes–Einstein behavior of the form $D \propto (T/\eta)^m$, with exponents. It has been found\textsuperscript{21} that $m = 0.7$ for CMIM BF$_4$ and $m \sim 0.92$ for
the ionic liquid\textsuperscript{17} BMIM PF\textsubscript{6}. In the field of glassy dynamics such deviations are well-known, and their magnitude seems to be closely coupled to the non-exponential relaxation dynamics described by Kohlrausch exponents, $\beta_{KWW}$, of the dynamical processes. A plot of the $D \text{ vs. } T/\eta$ is shown in Fig. (3.9) the results show that $\beta \sim 1$, which is close to the experimental values reported\textsuperscript{10}. The viscosity data used was taken from Tokuda et.al\textsuperscript{10} These results give further support for a BPP interpretation of the relaxation data.

![Graph](image)

**Figure 3.9.** $^1$H and $^{19}$F Log $D$ vs. Log$T/\eta$ for the BMIM samples.

3.7 Variable Pressure $D$ and $T_1$ data:

3.7.1 EMIM RESULTS

Variable pressure $T_1$ ($^2$H) and $D$ ($^1$H and $^{19}$F) data are shown in Figures 3.10 and 3.11 respectively. The use of pressure allows the changing of the inter- and intra-molecular interactions without affecting the frequency (temperature) or causing compositional changes. While the $D$ data is monotonic, the $T_1$ plots for the two isotopologues that are deuterated adjacent to the imidazolium ring exhibit two distinct linear regions between the pressure ranges

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0.1-100 and 100-250 MPa, which could indicate two different packing arrangements for both the ND₃ and CD₂ deuterated samples. The linearity of the ND₃ group could be due to its distance away from the ring, or the fact that the alkyl chain is less favorable interaction site compared to both CD₃ and CD₂ for hydrogen bonded imidazolium cation-anion interactions.³³-³⁵

**Figure 3.10.** Variable pressure ²H T₁ data for deuterated EMIM TFSA samples.

The Figure 3.11 reveals some fascinating information about the behavior of the diffusion coefficients of the EMIM cation and the TFSA anion with pressure. At ambient pressure the log of their self-diffusion coefficients, measured by ¹H and ¹⁹F respectively, are essentially identical. However, diffusion of the anion decreases faster with increasing pressure than for the cation, resulting in an activation volume that is 60% larger for TFSA compared to EMIM.
Figure 3.11. Variable pressure $^1$H and $^{19}$F self-diffusion coefficient data for EMIM TFSA samples.

In molten ionic liquids, the TFSA anion exists in equilibrium between two conformational states about the C-S-S-C dihedral angles - described as trans or anti ($C_2$ symmetry) and cis or gauche ($C_1$ symmetry). This equilibrium has been studied experimentally by Raman spectroscopy\textsuperscript{20,41} and by electronic structure and molecular dynamics (MD) simulations.\textsuperscript{12,41-46} Under ambient conditions the trans conformer is slightly favored\textsuperscript{20,41} and the enthalpy change from the trans conformer to cis is positive by about 3.5 kJ/mol according to temperature-dependent Raman spectroscopy\textsuperscript{43} and supported by MD simulations.\textsuperscript{12} Pressure-dependent Raman spectroscopy\textsuperscript{20} on $N,N$-diethyl-$N$-methyl-$N$-(2-methoxyethyl)ammonium (DEME) TFSA showed an increasing trans/cis ratio with increasing pressure, finding that the partial molar volume of the trans-TFSA anion conformer is 0.7 cm$^3$/mol smaller than that of the cis one.
The conformation and shape of the cation has also been shown to affect the self-diffusion coefficients of the ions and Tsuzuki et al. demonstrated this for the EMIM cation (with the TFSA anion) using molecular dynamics simulations. D values of both the EMIM cation and TFSA anion were reduced by 35% and 34% respectively when the conformational flexibility of the alkyl chain was restricted along the C₂-N₁-C₇-C₈ torsional angle.

Molecular dynamics (MD) simulations by Borodin et al. showed that artificially increasing the barrier for trans-cis conversion of the anion in EMIM TFSA and N-methyl-N-propylpyrrolidinium TFSA by 12.5 kJ/mol resulted in slowing down of the anion and cation transport by 40-50%. No similar effect was found in the case of the smaller bis(fluorosulfonyl)amide (FSA or FSI) anion. They showed that in the case of TFSA the ionic self-diffusion is coupled to conformational exchange. Although the positive reaction volume for trans-to-cis TFSA conversion (see above) is relatively small, the activation volume for conformational exchange could be much larger, and contribute to the larger activation volume for TFSA anion self-diffusion compared to the EMIM cation.
3.7.2 BMIM High Pressure Data

The variable pressure BMIM $^2$H $T_1$ data (Figure 3.12) exhibit pressure invariance for values over ~ 50 MPa for CD3 and CD2 and after 100 MPa for ND3. This particular result is notable, since results from identical measurements made for EMIM-TFSA samples (Fig. 3.10), do not show this extensive pressure invariance. The differences between data sets must be due to the alkyl side-chain length.

![Figure 3.12. Variable pressure $^2$H $T_1$ data for deuterated BMIM TFSA samples.](image-url)
Figure 3.13. Variable pressure $^1$H and $^{19}$F self-diffusion coefficient data for BMIM TFSA samples.

The BMIM cation in the liquid state has the trans–trans-gauche-trans equilibrium for the NCCC and CCCC angles of the butyl group the rotational isomerism of the BMIM the AA (anti-Gauche) and GA (Gauche) forms and under pressure the GA conformer becomes progressively de-stabilised.\textsuperscript{48}

Russina and coworkers\textsuperscript{48}, using Raman spectroscopy, reported for BMIM PF6 a change in the population of the conformers (AA and GA butyl chain conformers) after 50 Mpa in the liquid state. They compare the behavior with Chang \textit{et al}. for BMIM Br in the crystalline phase\textsuperscript{49},
where it shows a blue shift in frequency (related to the GA conformer) around 300 Mpa. But Chang has limited data in this range and it is not possible to determine in which pressure begins the transition. Russina proposed that these observations in liquid and crystalline samples are related to a structural re-arrangement involving the cation and not to a phase of transition. In other works Chang et al, reported the blue shift in frequency in the same range of pressure 0.-300 MPa without intermediate pressure for BMIM BF$_4$, BMIM TFSI, and EMIM TFSI.

The invariance in relaxation times decreasing temperature or increasing pressure has been studied in molecular liquids and polymers and the dynamics exhibit various transition such as: 1) Arrhenius and non-Debye behavior 2) Dynamic Crossover 3) Vitrification and 4) for anisotropic molecules the development of liquid crystallinity.

The NMR data for BMIM TFSI could be show the structural re-arrangement after 50 Mpa and reveals that relaxation times are independent of pressure. It is important to notice that, in the graph 3.5 for T1 vs. temperature. We can see the invariance with temperature for CD3 and the minimum for CD2 and ND3 in similar T$_1$s values (in comparison with T$_1$ vs P, Fig. 3.12).

These results are remarkable due to the re-structural array in the ILs would be associated with a specific value, of the relaxation time, independent of pressure and temperature in which it could offer an insight between the structure and ionic motions.
3.8 Activation Volumes

The activation volume may be interpreted as the minimum volume required for a physical process to occur. It may also serve as an indicator of the ease of mobility, with higher values oftentimes being attributed to more restricted motion. Since ‘motion’ in this context depends on the properties of the mobile species as well as the surrounding media, the activation volume also reflects the interactions between mobile species and their environment. Activation volumes for relaxation and diffusion as determined by fitting vs. pressure data according to equation (3.6) are given in Table 3.3

\[ \Delta V = -kT \left( \frac{\partial \ln \alpha}{\partial P} \right)_T \]  

(3.6)

Here \( \alpha \) can be \( 1/T \) or \( D \), \( P \) is the pressure, \( T \) is the temperature and \( k \) is the Boltzmann constant.

For EMIM The values obtained for the \( \text{ND}_3 \) and \( \text{CD}_2 \) isotopologues are similar, with that for the 100-250 MPa region being almost half that of the 0.1-100 MPa region. The \( \text{CD}_3 \) isotopologue showed the smallest activation volume and monotonic behavior over the entire pressure range.

<table>
<thead>
<tr>
<th>Deuterated Site</th>
<th>( \Delta V ) (( \text{cm}^3/\text{mol} )) (0.1-100 MPa)</th>
<th>( \Delta V ) (( \text{cm}^3/\text{mol} )) (100-250 MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{ND}_3 )</td>
<td>21 ± 1</td>
<td>11 ± 1</td>
</tr>
<tr>
<td>( \text{CD}_2 )</td>
<td>25 ± 1</td>
<td>12 ± 1</td>
</tr>
<tr>
<td>( \text{CD}_3 )</td>
<td>8 ± 1 (0.1-250 MPa)</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.3:** EMIM activation volumes determined from variable-pressure \(^2\text{H} \ T_1 \) data.
For BMIM the values obtained for the ND₃ and CD₃ are similar. The CD₂ showed the largest activation volume, which could indicate a different effect of pressure on butyl group. A similar trend is observed in the EMIM values (table 3.3 and Fig. 3.11 above).

<table>
<thead>
<tr>
<th>Deuteron Position</th>
<th>Pressure Range (Mpa)</th>
<th>ΔV (cm³/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD₃</td>
<td>0.01-60</td>
<td>13.7 ± 2.8</td>
</tr>
<tr>
<td>CD₂</td>
<td>0.01-65</td>
<td>20.4 ± 2.1</td>
</tr>
<tr>
<td>ND₃</td>
<td>0.01-95</td>
<td>14.9 ± 0.4</td>
</tr>
</tbody>
</table>

**Table 3.4:** BMIM activation volumes determined from variable-pressure ²H T₁ data.

Activation volumes of the BMIM cation and TFSA anion, as derived from ¹H and ¹⁹F diffusion data, are comparable to the EMIM values (Fig. 3.11). The results are also comparable with the lower pressure ²H values. In a relative sense, the magnitudes of the activation volumes are large and are consistent with significant correlated motion associated with ionic transport.

### 3.9 Acknowledgments

This work was with collaboration of Dr. Sophia Suarez, Brooklyn College and Dr. James F. Wishart Chemistry Department, Brookhaven National Laboratory. The work at Brooklyn College was supported by a PSC CUNY grant. The work at Hunter was supported by the Office of Naval Research and the Hunter NIH-supported RISE program. The work at BNL (JLH and JFW) was supported by the US-DOE Office of Science, Division of Chemical Sciences, Geosciences and Biosciences under contract No. DE-AC02-98CH10886 (Brookhaven). Programmatic support via a DOE SISGR grant “An Integrated Basic Research
Program for Advanced Nuclear Energy Separations Systems Based on Ionic Liquids” is gratefully acknowledged.

3.10 References:


3.12. Representative Synthesis

1.1 1-ethyl-3-methylimidazolium bromide (emim Br):

30 ml, 0.394 moles of bromoethane was dissolved in 50 ml of ethyl acetate in an ice bath. 31.2 ml of 1-methylimidazole was added drop wise to the mixture. An additional 25ml of Ethyl acetate was added to the mixture as well. The temperature of the mixture was allowed to slowly reach room temperature. The reaction vessel was then placed in an oil bath and allowed to reflux at 45 °C for 24 hours. The ethyl acetate was decanted off the yellow liquid product. The sample was washed with additional ethyl acetate (4 x 30 ml). The sample was then washed with diethyl ether (3 x 30 ml). The now-solidified sample was dried in a vacuum oven at 60 °C. Since the proton NMR revealed excess 1-methylimidazole, the white crystals were stirred again with 25 ml of ethyl acetate and vacuum filtered under dry nitrogen, which removed the excess reagent. Yield: 35.06g, 46.7%.

δH (400 MHz, DMSO, Me₄Si): 1.40 -1.44 (t) NCH₂C₃H₃, 3.87 (s) -NC₃H₃, 4.19 -4.24 (q) -NC₃H₂CH₃, 7.75 (s) -NCHCHNCH₂CH₃, 7.83 (s) -NCHCHNCH₂CH₃, 9.27 (s) NCHN, δC (101 MHz, DMSO, Me₄Si) 15.11 NCH₂C₃H₃, 35.70 N₃C₃H₃, 44.09 N₃C₃H₂CH₃, 121.94 NCHCHNCH₂CH₃, 123.51 NCHCHNCH₂CH₃, 136.24 NCHN

1.2 1-(ethyl-2,2,2-d₃)-3-methylimidazolium bromide ((e-d₃)mim Br):

5 g, 0.044 moles of bromoethane-2,2,2-d₃ were dissolved in 10 ml of acetonitrile and placed in an ice bath. One equivalent of 1-methylimidazole (3.67 g) was added to the chilled solution, which was then left to stir for 48 hours. The solution was then set to reflux at 50 °C for 12 hours. The sample was then rotary evaporated to remove the acetonitrile. 15 ml of cold ethyl acetate were added to the sample to encourage crystallization. The white crystals were isolated via vacuum filtration under dry nitrogen and washed (10 x 5 ml) with cold ethyl acetate. The crystals were dried in a vacuum oven at 65 °C for 12 hours. Yield: 13.11 g, 92.8%. δH (CD₃CN) 400MHz, Me₄Si) 3.91 (s) NCH₂CD₃, 4.09 (s) -NCH₃, 7.66 (s) NCHCHN, 7.75 (s) -NCHCHN-, 9.66 (s) -NCHN-, δC (101 MHz, CD₃CN, Me₄Si) 12.87-13.65 CH₂CD₃ (m), 35.05 NCH₃, 43.58 NCH₂CD₃, 121.16 NCHCHNCH₂CD₃, 122.33-122.62 NCHCHNCH₂CD₃, 135.74 NCHN

1.3 1-(ethyl-1,1-d₂)-3-methylimidazolium iodide ((e-d₂)mim I):

This compound was synthesized in the same fashion as (e-d₃)mim Br. 4.57 g, 0.0289 mole of iodoethane-1,1-d₂ was combined with 2.37 g of 1-methylimidazole in 10 ml of acetonitrile.
Yield: 5.14 g, 74%. NMR shifts: δH (400 MHz): 1.17 (s) -CD₂CH₃, 3.85 (s) -NCH₂N-CH₃, 7.71 (s) -NCHCHNCD₂-, 7.79 (s) -NCHCHNCD₂-, 9.13 (s) -NCHN-, δC (101 MHz, DMSO, Me₄Si) 14.90 NCH₂CH₃, 35.74 NCH₃, 121.91 NCHCHNCH₂CH₃, 123.53NCHCHNCH₂CH₃, 136.16 NCHN

1.4 1-ethyl-3-(methyl-d₃)-imidazolium iodide (e(m-d₃)im I):
This compound was synthesized in the same fashion as the other samples using 5 g, 0.052 moles of methylimidazole-d₃ and 3.32 g of ethyl imidazole in 15 ml of acetonitrile. Yield: 8.23 g 65.6%. 

δH (400 MHz, DMSO, Me₄Si): 1.41-1.43 (t) NCH₂CH₃, 4.18-4.23 (q) NCH₂CH₃, 7.72 (s) –NCHCHN-, 7.81 (s) –NCHCHN-, 9.17 (s) NCHN- δC (101 MHz, DMSO, Me₄Si) 15.14 NCH₂CH₃, 44.12 NCH₂CH₃, 121.93 NCHCHNCH₂CH₃, 123.47 NCHCHNCH₂CH₃, [114.63, 117.82, 121.02, 124.21] NTf₂, 136.17 NCHN.

1.5 1-(ethyl-2,2,2-d₃)-3-methylimidazolium bis(trifluoromethylsulfonylamide ((e-d₃)mim NTf₂):
11.86 grams, 0.0413 moles of lithium bistrifloromethanesulfonylimide (LiNTf₂) was dissolved in as little water as possible. 13.11 g (inadvertent excess) of (e-d₃)mim Br was also dissolved in as little water as possible and added to the solution, which set to stir at room temperature for 24 hours. The resultant hydrophobic liquid salt was washed with deionized water until no presence of halide was detected (the washings were tested with a drop of 50 mM aqueous silver nitrate). The sample was then dried in a vacuum oven for 48 hours at 65 °C. Yield: 9.22 g, 56.6%. δH (400 MHz, DMSO, Me₄Si) 3.86 (s) –NCH₃, 4.18 (s) NCH₂CD₃, 7.66 (s) –NCHCHN-, 7.74(s) NCHCHN, 9.10 (s) NCHN, δC (101 MHz, DMSO, Me₄Si) 13.96-14.35 (m) NCH₂CD₃, 35.48 NCH₃, 43.91 NCH₂CD₃, 121.81 NCHCHNCH₂CD₃, 123.42 NCHCHNCH₂CD₃, [114.63, 117.03, 121.02, 124.22] NTf₂, 136.15 NCHN.

1.6 1-(ethyl-1,1-d₂)-3-methylimidazolium bis(trifluoromethylsulfonylamide ((e-d₃)mim NTf₂):
(E-d₂)mim NTf₂ was synthesized in the same fashion as (e-d₃)mim NTf₂, using 5.14 g, 0.021 moles of (e-d₃)mim I and 6.15 g of Li NTF₂. Yield: 4.57 g, 55.3%. δH (400 MHz, DMSO, Me₄Si): 1.41 NCD₂CH₃, 3.85 CH₃N, 7.68 NCHCHNCD₂CH₃, 7.76 NCHCHNCD₂CH₃, 9.10 NCHN δC (101 MHz, DMSO, Me₄Si) 14.73 CH₂CH₃, 35.58 NCH₃, 43.33-43.77 (m) NCD₂CH₃, 121.86 NCHCHNCD₂CH₃, 123.49 NCHCHNCD₂CH₃, [114.64, 117.84,121.04,124.24] NTf₂, 136.16 NCHN.

1.7 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylamide (emim NTf₂):
Emim NTf₂ was synthesized in the same fashion as (e-d₃)mim NTf₂ using 13.15 g, 0.069 moles of emim Br and 19.75 g of Li NTF₂. Yield: 14.52 g, 53.8%. δH (400 MHz, DMSO, Me₄Si): 1.43-1.46(t) NCH₂CH₃, 3.91(s) CH₃N-, 4.18-4.23 (q) –NCH₂CH₃, 7.62 (s) -NCHCHN-, 7.70 (s) -NCHCHN-, 9.07 –NCHN- δC (101 MHz, DMSO, Me₄Si) 14.56 NCH₂CH₃, 35.37 NCH₃, 44.09 NCH₂CH₃, 123.34 NCHCHNCH₂CH₃, 123.74 NCHCHNCH₂CH₃, [114.6, 117.81, 121.01, 124.20] NTf₂, 135.81 NCHN.

1.8 1-ethyl-3-(methyl-d₃)-imidazolium bis(trifluoromethylsulfonylamide (e(m-d₃)im NTf₂):
E(m-d₃)im NTf₂ was synthesized in the same fashion as e(d₃)mim NTf₂, using 8.23 g, 0.034 moles of em(d₃)im I and 9.80 g of Li NTf₂. The orange liquid was dissolved in ethyl acetate and stirred with 0.5 g of activated charcoal at room temperature for 24 hours. The charcoal was filtered using slow ashless filter paper. The sample was then stirred with alumina for 24 hours. The alumina was filtered using ashless filter paper and the sample was rotary evaporated to remove the solvent. The clear liquid sample was placed in a vacuum oven at 65 °C for 24 hours. Yield: 4.57 g, yield 33.9%. δH (400 MHz, DMSO, Me₄Si) 1.42-1.46 (t) NCH₂CH₃, 4.18-4.23 (m) NCH₂CH₃, 7.63 NCHCHNCH₂CH₃, 7.72 NCHCHNCH₂CH₃, 9.08 NCHN δC (101 MHz, DMSO, Me₄Si) 14.66 NCH₂CH₃, 34.35-35.22 (m) CD₃, 44.08 NCH₂CH₃, 121.75 NCHCHNCH₂CH₃, 123.35 NCHCHNCH₂CH₃, [114.63, 117.82, 121.02, 124.21] NTf₂, 136.11 NCHN

1.9  Ring-deuterated 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylamide (em(im-d₃) NTf₂):

0.74 g 0.0019 moles of emim NTf₂ were placed in each of two microwave reaction vessels. 5 ml, 0.25 moles of deuterated water was added to each of these vessels along with 0.022 g of potassium carbonate. The vessels were then purged with argon for 20 minutes. Each vessel was placed in a CEM Discover microwave reactor. The power was limited to 300 W, The temperature was set to 125 °C with a ramp time of 5 minutes and the pressure was set to 19.0 bar. The sample was then rinsed 3 x 5 ml with D₂O to remove the potassium carbonate. Yield: 0.93 g, yield 62.4%. δH (400 MHz, DMSO, Me₄Si): 1.41-1.45 (-NCH₂CH₃ (t), 3.85 –NCH₃ (s), 4.17-4.22 –NCH₂CH₃ (q) 7.66 NCHCHN (residual), 7.74 NCHCHN (residual), 9.09 –NCHN- (residual). δC (101 MHz, DMSO, Me₄Si) 14.86 NCH₂CH₃, 35.50 NCH₃, 44.02 NCH₂CH₃, 123.34 NCDCDNCH₂CH₃, 123.74 NCDCDNCH₂CH₃, [114.6, 117.81, 121.01, 124.20] NTf₂, 135.78 NCDN.
Chapter 4: Electrical Properties of BaTiO$_3$ Nanoparticles in Polycarbonate

This work was with collaboration of Dr. Fontanella, U.S. Naval Academy and Dr. Xavier Boggle, Hunter College.

4.1. Introduction

The effort to find improved energy storage devices continues. While there is a great deal of work on new kinds of devices such as super-capacitors, attempts at improving traditional insulator-based capacitors are also being made. In order to try to improve the insulator, nanoparticles are being added to polymers with the goal of improving the electrical properties. This has spawned the field of nano-dielectrics and an overview of the field has been published recently.$^1$ In a recent paper, Lomax et al studied BaTiO$_3$ nanoparticles in poly(ether imide) (PEI).$^2$ PEI was of interest because it has good mechanical properties and a high glass transition temperature, $T_g$, of about 217ºC. Negative aspects of the polymer are that it takes up water and that it has a relatively low real part of the relative permittivity, $\varepsilon'$, (about 3.15) at room temperature and pressure at audio frequencies.$^3,4$ A water-associated electrical relaxation was identified in that material and a low temperature (in the vicinity of 20K) relaxation was found that was associated with the nanoparticles, themselves.$^2,5$ The PEI-BaTiO$_3$ nano-composites were found to be well-behaved in that $\varepsilon'$ vs. nanoparticle content was found to follow a recently proposed Hanai-like equation.$^6$ In the present work BaTiO$_3$ nanoparticles in polycarbonate (PC) are studied. One advantage of PC over PEI is that it has little tendency to take up water. In addition, PC, itself, has been extensively studied$^7$ and the results can be used to determine the effects of the nanoparticles on the material.

The ultimate goal of the work on capacitors is to increase the energy that can be stored in a material. The energy density is given by
\[ u = \frac{1}{2} \varepsilon_o \varepsilon' E^2 \]  

(4.1)

Where \( \varepsilon_o \) is the permittivity of free space and \( E \) is the electric field in the material. Clearly, \( \varepsilon' \) is important because the amount of energy that can be stored in a capacitor is directly proportional to \( \varepsilon' \). The dielectric strength, \( E_o \), representing the maximum electric field that can exist in a material before it breaks down is even more important because the energy density is proportional to the square of the electric field in the material. Two objectives of this work, then, are to increase both \( \varepsilon' \) and \( E_o \). Finally, the imaginary part of the relative permittivity, \( \varepsilon'' \), is proportional to the electrical loss in the material, and consequently, the third goal of this investigation is to minimize \( \varepsilon'' \). Toward this end, \( \varepsilon' \), \( \varepsilon'' \), and dielectric breakdown for nanoparticles in PC have been studied in detail. Solid state nuclear magnetic resonance (NMR) relaxation measurements have been performed in order to assess possible effects of the nanoparticles on molecular motions of the polymer.

4.2 Experimental

4.2.1. Sample Preparation

Polycarbonate was obtained from SABIC Innovative Plastics, Pittsfield, MA. The 99% by metals basis barium titanate (BaTiO\(_3\)) was obtained from Alfa Aesar in the form of 50-70 nm diameter particles. In addition, a series of nanoparticles (50, 100, 200, 300, 400 and 500 nm) was obtained from Research Nanomaterials, Inc (RN50, RN100, etc.).

Some of the 50-70 nm nanoparticles were functionalized (surface treated) as follows. Typically, first, about 1.75 g of the BaTiO\(_3\) nanoparticles was placed in a vacuum oven at 393 K at 0.1 torr for 2 hours. Water (95 g) and aminopropyl-tri-methoy-silane were added to a 125 mL ehrlenmeyer flask along with the dried BaTiO\(_3\). The mixture was stirred at room temperature for
two days. The resulting solid was allowed to settle and most of the supernatant was removed. The samples were washed with a 50/50 mixture of ethanol and water. The mixture was stirred for a few minutes and then centrifuged, and the supernatant decanted. The process was repeated and the wet solid was dried at 353 K for 1 hour. The aminopropylsiloxylated barium titanate (STNP) product was characterized by infrared spectroscopy and TGA. In the IR, absorbances corresponding to C--H and N--H stretches were observed. In combustion TGA, a weight loss event at above 625 K corresponded to burning off the organic from the metal oxide.

Typical nanocomposite samples were made by adding a pre-determined mass of metal oxide solid to 2 g of polycarbonate pellets in a polypropylene mixing jar, adding CH₂Cl₂ (10 g) and closing the lid. The material was allowed to remain in the jar for two hours, when swelling of the polycarbonate was observed, and then sheared in a FlackTec Speed Mixer™ Model DAC 150 SP at 3500 rpm for 10 minutes. Approximately half the sheared sample was cast onto a clean piece of sheet glass. A glass rod (6 mm diameter, approximately 30 cm long, fire polished on both ends) was used to spread and smooth the cast sample. A smooth back and forth motion of the glass rod across the viscous sample thinned it to the depth of the difference of the radius of the glass rod and the glass protruding at the fire polished end. The motion of the glass rod continued as solvent evaporated and the sample thickness decreased until the material became viscous to point of resisting motion. The rod was left in place at one end of the cast film.

Aluminum foil was placed shiny side up on two pieces of glass (20 cm x 20 cm). The foil was flattened, burnished and folded over the edges of the glass with a clean cloth. After the film had dried for one hour, the film edges were released from the glass using a razor, and the sample was lifted using the glass rod and placed onto one of the pieces of foil-covered glass then the glass rod was cut off. The other piece of foil-covered glass was placed over the cast film and
the “sandwich” was placed in a vacuum oven, weighted down with a 400 mL beaker filled with sand. The oven was evacuated to 0.1 torr and heated to 415 K for one hour after which it was turned off and allowed to cool to room temperature.

In order to determine the relative permittivity measurements, aluminum electrodes were vacuum-evaporated onto the flat surfaces of the films to form parallel plate configurations and the complex conductance was measured. For each concentration of BaTiO₃ in PC, at least two circular samples were prepared, one with a diameter of about 15 mm and another with a diameter of about 10 mm. The complex conductance measurements were carried out on the films using a CGA-85 Capacitance Measuring Assembly that operates at 17 frequencies from 10 to 10⁵ Hz. The CGA-85 is a prototype for many of the bridges sold by Andeen Hagerling, Inc. The equivalent parallel capacitance, \( C \), and conductance divided by the angular frequency, \( G/\omega \), were measured. The system is accurate to about 10 aF in both \( C \) and \( G/\omega \).

### 4.2.2 SEM

The internal nanocomposite structure was evaluated using an FEI Dual Beam focused ion beam (FIB) / scanning electron microscope (SEM). A Balzers Union sputter coater was used to apply a thin layer (5 nm) of Au on the surface of the film to prevent charging during imaging. The FIB was used to mill a hole in the film to expose a cross-section that was subsequently imaged with SEM. The initial hole in the film was milled with a Ga⁺ beam current of 6.5 nA at 30kV. After the initial hole was milled, a thin slice (~ 500 nm thick) of the face-on cross section was removed with the Ga⁺ beam set to mild milling conditions (0.46 nA, 30 kV, no SCE). This final cleaning step was done to ensure that the region of the exposed cross section showed no discernable damage for the ion beam. The cross section was imaged via SEM using a high resolution immersion lens (5.0 kV, 0.4 nA).
An SEM micrograph of the surface of one of the nanocomposites (8.0 volume-% made from the 50-70 nm diameter STNP) is shown in Fig. 4.1. The surface of the film is coated with 5 nm of gold.

Significant surface topology is observed (Fig. 1) implying that some nanoparticles are embedded in, but at the surface of, the polymer. A cross section of the 8.0% nanocomposite sample made using STNP is shown in Fig. 4.2. Below that is a region showing particles on or near the surface of the film. In what is clearly the cross section of the film, both isolated individual particles and small aggregates are seen. The aggregates are on the order of 455 nm in diameter, with a standard deviation of 150 nm and the aggregates appear to be clumps of 3 to 5 individual particles. The distribution of the particles and aggregates is relatively uniform.

A cross-section of a 9.9% sample formed using 50-70 nm BaTiO$_3$ UNP is shown in Fig. 3. The cross section shows both small and large aggregates. The small aggregates are similar to those observed for the 8.0% sample described above, while the large aggregates have sizes in the 2.5 to 5 $\mu$m range. In this case the average aggregate size is 370 nm with a standard deviation of 118 nm.
The same trend was also observed for higher concentration samples, nominally 16.5%. Specifically, relatively uniformly distributed individual nanoparticles and small aggregates were observed for the nanocomposites formed using the STNPs while some large aggregates existed in the samples made using the UNPs. The general conclusion is
that STNP give rise to nanocomposites with better internal dispersion of the particles and a lower likelihood of forming large aggregates (> 2μm in diameter).

Micrographs were also prepared for a 2.4% sample made using the STNP and a 2.0% sample made using the UNP. Interestingly, the distribution is the opposite of what might be expected on the basis of the higher concentration samples. The SEM for the 2.4% STNP showed some large aggregates similar to that for the higher concentration materials made using the UNPs, while the distribution for the 2.0% (UNP) sample showed only single nanoparticles and small aggregates. Nonetheless, all of the SEM results are reflected in the physical properties of the nanocomposites reported in the following paragraphs.
4.2.3 Electrical measurements

The first set of dielectric measurements was carried out at room temperature on the as-prepared materials in the laboratory atmosphere. Subsequently, the materials were heated to either 393 K or 423 K in a vacuum furnace that is built into a glove box with a nitrogen atmosphere. After heating, the materials were transferred directly to the measurement assembly inside the glove box, and room temperature measurements were then carried out in the dry nitrogen atmosphere of the glove box.

Two different systems were used to vary the temperature of the samples for the complex impedance measurements. Some measurements were carried out in vacuum from 5.5 K to 350 K in a Precision Cryogenics CT-14 dewar and the temperature was controlled using a LakeShore Cryotronics DR92 temperature controller. Other measurements were carried out at atmospheric pressure in flowing nitrogen gas using a Novocontrol sample holder and Quatro temperature controller. That system operated over the temperature range 150 K to 523 K.

For the film samples, the data were transformed to the complex relative permittivity as follows. First, geometrical measurements were made and the real part of the relative permittivity, $\varepsilon'$, was calculated at room temperature using the usual equation for a parallel plate capacitor

$$C = \frac{\varepsilon_0 \varepsilon' A}{d}.$$  \hspace{1cm} (4.2)

where $A$ is the area of the electrodes and $d$ is their separation.

The real part of the relative permittivity at other temperatures was calculated assuming that the relative permittivity scales with the capacitance (thermal expansion was ignored). Finally, the imaginary part of the relative permittivity and $\tan\delta$ at all temperatures was calculated using
The DC dielectric strength was measured using a Hippotronics model HD140 Auto A, AC/DC hipot tester

The applied voltage at breakdown was converted to an electric field using the measured sample thickness. The cumulative probability for failure was estimated using the median rank approximation.8

4.2.4. Room temperature dielectric permittivity

The approach that was taken in the present work is to add nanoparticles with a large value of $\varepsilon'$ to a polymer with a small value of $\varepsilon'$. In order to obtain large increases in $\varepsilon'$ for a composite the laws of mixing6,9-12 require large concentrations of nanoparticles. (A review of the laws of mixing from an historical perspective is given by Broussau.13) As a consequence, materials were studied over a wide range of concentrations.

The experimental values of the real part of the relative permittivity for the nanocomposites, $\varepsilon' \equiv \varepsilon_C$, at room temperature and 1000 Hz, at various nanoparticle concentrations between 0 and about 24 volume-% are plotted in Fig. 4.4. The results for the as-prepared materials made using UNPs, and for samples after heating to 393 K and 428 K are presented, as well as the results for the as-prepared composites using the STNP. While an equation recently proposed by Calame6 generally provides a better explanation of such data,2 in order to avoid the extra adjustable parameter in the Calame equation, the equation of Hanai9

$$\frac{\varepsilon_1 - \varepsilon_c}{\varepsilon_1 - \varepsilon_b} \left( \frac{\varepsilon_b}{\varepsilon_C} \right)^{1/3} = 1 - p$$  \hspace{1cm} (4.4)
Fig. 4.4. Plot of the real part of the relative permittivity vs. BaTiO$_3$ concentration (volume-%)

was used. In eq. (4) $\varepsilon_b$, $\varepsilon_1$ and $\varepsilon_C$ represent the real part of the relative permittivity of the PC (2.94),$^7$ the BaTiO$_3$ nanoparticles (3300),$^6$ and the nano-composite, respectively, while $p$ is the volume fraction of the particles. Using the given values of $\varepsilon_b$, $\varepsilon_1$ and the densities $\rho_{BaTiO_3} = 6.02$ g/cm$^3$ and $\rho_{PC} = 1.21$ g/cm$^3$, eq. (4) was used to calculate values of $\varepsilon_C$. The resulting predicted values of $\varepsilon_C$ vs. concentration calculated using eq. (4.4) are shown by the curved line in Fig. 4.4.

It is clear from Fig. 4.4 that $\varepsilon_C$ for the materials made using concentrations of UNP greater than about 10 vol-% is significantly larger than the values predicted using the Hanai equation. Some of the difference is due to water, particularly for the as-prepared samples represented by the open squares, which clearly have the largest values of $\varepsilon_C$. A decrease in $\varepsilon_C$ of a few percent was observed after heating to 393 K and a further decrease was observed after heating to 428 K, which is a few degrees above the glass transition temperature. It is inferred that this effect is a result of water being removed from the materials. However, even after heat treatments, the values of $\varepsilon_C$ for the higher concentration UNP-based composites were much larger the predicted values. This difference is probably due to an inhomogeneous distribution of
nanoparticles. In particular, the SEM studies showed that large aggregates exist in higher concentration (9.9% and 16.5%) materials formed using UNPs. At a low concentration (2.0%) of UNPs in PC, the SEM studies showed a relatively uniform distribution of nanoparticles. This is consistent with the agreement between the measured and predicted values of $\varepsilon_C$ at low concentrations.

On the other hand, the values of $\varepsilon_C$ for the materials made using STNPs are in good agreement with those predicted using the Hanai equation. The results at higher concentrations are consistent with the fact that a relatively uniform distribution of nanoparticles is observed and this should give rise to better agreement between the measured and predicted values. In the case of one lower concentration (2.4%) sample, the SEM studies revealed some large aggregates. However, it is apparent from Fig. 4.4 that very little difference in $\varepsilon_C$ is observed between any of these materials. It is suggested that the concentration of large aggregates in the low concentration samples is too low to produce observable effects. This may also apply to some of the materials made using low concentrations of UNPs.

### 4.2.5 Variation of the dielectric properties of the nano-composites with temperature

The values of $\varepsilon'$ and $\tan\delta$ at 1000 Hz for some UNP-nanocomposites are plotted vs. temperature in Figs. 4.5 and 4.6, respectively. The data were collected in vacuum as temperature decreased from high to low.
As is apparent in Fig. 4.5, the real part of the relative permittivity is large for the highest concentration nanocomposites made using UNPs. For the 22.6% material, for example, the UNPs increase the dielectric constant of PC by almost a factor of 4. A second feature, that could also make these materials useful, is that there is little variation of $\varepsilon'$ with temperature. This, of course, is another highly desirable property for practical applications of dielectric materials.

It is clear from Fig. 4.6 that the loss is low for all of the materials, which is crucially important for many device applications. Specifically, $\tan\delta$ is less than 0.01 for all of the materials at room temperature and below. The loss only begins to increase above about 300 K. In addition, Fig. 4.6 shows that the electrical relaxation spectrum consists of two relaxations.
Fig. 4.6. Plot of tanδ vs. T at 1000 Hz for PC and PC containing BaTiO$_3$ 50-70 nm diameter UNPs after heating to 393 K.

The higher temperature relaxation, in the vicinity of 200 K at 1000 Hz, is the well-known $\gamma$ relaxation.\textsuperscript{2,7} It is interesting that the presence of UNPs (up to about 23%) does not affect the $\gamma$ relaxation. Some broadening of the peak is apparent, but this is at least in part due to increased loss from the conductivity on the high temperature side and to increased loss from the low temperature relaxation on the low temperature side. The second relaxation, in the vicinity of 20 K, has been shown to be associated with the nanoparticles, themselves.\textsuperscript{2,5} The 20 K relaxation is particularly useful because its strength can be used as a measure of the nanoparticle content. It is clear that the strength of the 20 K relaxation scales with the nominal concentration.

The effect of nanoparticle size on the loss tangent is shown in Fig. 4.7. It is clear that there is essentially no effect on the $\gamma$ relaxation. The only observable difference is that the loss, as measured by tan$\delta$, begins to rise at the highest temperatures only in the composite materials using the smallest nanoparticles. This is attributable to the
Fig. 4.7. Plot of $\tan \delta$ vs. $T$ at 1000 Hz for PC containing approximately 4.8% BaTiO$_3$ UNP and STNPs of diameters between 100nm and 500nm.

the nanoparticles themselves, because it has been shown that the smaller 100 nm nanoparticles exhibit higher loss than the larger nanoparticles.$^5$

In Fig. 4.8, the loss tangent at 20000 Hz is plotted vs. temperature for both UNP- and STNP-materials with similar and relatively high concentrations. The UNP-based material (concentration of 16.2%) is the same as that for which data at a different frequency are shown in Fig. 9. It is clear that there is very little high temperature loss in the material made using STNPs.
Fig. 4.8. Plot of $\tan \delta$ vs. $T$ at 20000 Hz for PC containing 50-70 nm diameter BaTiO$_3$ nanoparticles: open circles, UNP material (16.2%); filled circles, STNP material (16.7%).

A similar plot is shown in Fig. 4.9 for the 8.0% STNP material compared with the data for the UNP 4.7% and 9.9% material (again, the UNP materials are those for which data are shown in Fig.4.8). As in the previous plots, there is very little conductivity at high temperatures for the STNP-nanocomposites, in contrast to the results for UNP-nanocomposites. The higher conductivity is attributed to large aggregates of nanoparticles and is related to the higher values of $\varepsilon'$ observed for these materials.

The results of these dielectric loss studies are significant as the $\gamma$ relaxation in this type of polymer is generally considered to be associated with local polymer chain motions. The observations that composites with up to about 16 volume-% nanoparticles,
with nanoparticle sizes varying from 100 nm to 500 nm in diameter, for both untreated and surface treated nanoparticles, show no observable differences in the $\gamma$ relaxation are surprising to say the least. This is particularly true because the nanoparticle material has a real part of the relative permittivity that is nearly a factor of a thousand times that of the host polymer, and significant changes in local electric fields might be expected. The results reported here imply that neither physical size effects, nor concentration effects nor modification of the electrochemical reactivity in the particle surface regions have any observable impact on the local environment of chain motions, despite the fact that these chain motions are probed via electric dipole interactions.

4.2.6  NMR Results.

The $^1$H NMR $T_1$ and $T_{1p}$ variable temperature (VT) measurements were performed on a Varian Digital Drive Spectrometer with a 7.1 T magnetic field strength on a static probe with a low proton background signal. The chemical shifts were referenced to tetramethylsilane (TMS) and samples were prepared by cutting the films into strips and then stacking the strips into 4 mm
glass tubes sealed with Teflon stoppers. Dry nitrogen gas was used as both the VT carrier and the probe purge gas in order to minimize complications introduced by subzero temperatures. A saturation recovery sequence was used to determine the T₁ relaxation times with a 5.5µs π/2 pulse and \( n = 30 \). The T₁ₚ measurements were made using a spin-lock pulse (after a 5.5 µs π/2) and 5-100s recycle delay (temperature dependent). All T₁ₚ measurements were carried out at a spinlock power level of 22 kHz.

The \(^1\text{H}\) variable pressure T₁ measurements were performed on a Chemagnetics Spectrometer with a 7.0T magnetic field strength using Fluorinert FC-77 as the hydraulic fluid in the pressure cell. Polymer film samples were sealed in a polyethylene bag (with negligible background signal) prior to being placed in the RF coil inside the copper-beryllium pressure vessel. An inversion recovery pulse sequence was used to determine the T₁ relaxation times with respect to variable pressure with a 10 µs π/2 pulse and 10 s recycle delay.

\(^1\text{H}\) T₁, T₁ₚ, and variable temperature studies were carried out for three polycarbonate (PC) and PC- nanocomposite films. The T₁ studies were performed over a temperature range of 123 - 423 K while the T₁ₚ study was performed across a range of 173 - 423 K. In addition, high pressure ambient temperature NMR T₁ measurements were also obtained for an 8.4% STNP-nanocomposite sample. The static proton NMR spectra of all three samples (PC, PC containing UNP and PC containing STNP) are similar in appearance and show modest narrowing/sharpening with increasing sample temperature, throughout the entire temperature range of 123 – 423K. This narrowing is indicative of considerable molecular motion within the polymeric structures and is consistent with prior results obtained for other polycarbonates, reported in the literature.\(^{19}\)
Figure 4.10. depicts the Arrhenius plots of $T_1$ relaxation times across a 300 K temperature range. All three samples exhibit fairly similar relaxation profiles with the $T_1$ minimum being ~ 0.5s and occurring in a similar temperature range for all three films. Molecular motions with a characteristic correlation time of ~ 1 ns are most likely associated with ring flips connected with the $\gamma$ relaxation,\(^{19}\) and are thus largely unaffected by the nanoparticles. Figure 4.11 displays $T_{1\rho}$ data for all three films, obtained at a spin-lock field of 22 kHz across a 173 K to 423 K temperature range. As depicted, the variable temperature $T_{1\rho}$ profiles of all three films were practically indistinguishable. In each case, there is an abrupt decrease in $T_{1\rho}$ value immediately after attaining its maximum value, at elevated temperature (close examination of the $T_1$ data in Fig. 4.10 reveals a similar phenomenon). This decrease is attributed to the glass transition, and occurs at approximately the same value for all three samples.

![Figure 4.10](image-url)
Figure 4.11. Plot of $T_1$ vs. $1000/T$ for pure PC, and PC containing approximately 8.4% BaTiO$_3$ nanoparticles: filled circles, PC/BaTiO$_3$ (STNP); open circles, PC/BaTiO$_3$ (UNP), open triangles, pure PC.

Variable pressure $T_1$ measurements of PC and the PC/SNTP composite are summarized in Figure 4.12. The $T_1$ values were obtained in 0.01 GPa intervals across a 0.0001 to 0.25 GPa range for the variable pressure analysis. Overall, the two samples exhibit similar responses. The variable pressure plot affords us the ability to compute the activation volume from the corresponding slope (i.e. logarithmic derivative) of the plots. These plots possess at least two distinct slopes, namely the ~0.0001 to 0.04 and ~0.0500 to 0.25 GPa regions. The accuracy of the activation volumes estimated for the lower pressure region is limited by the scatter of the data but one may extract a value of about $20 \pm 5$ cm$^3$-mol$^{-1}$ for both the PC and the SNTP composite. The higher pressure region, 0.05 GPa to 0.15 GPa, gives similar slopes for both samples with a corresponding activation volume of about $6 \pm 1$ cm$^3$-mol$^{-1}$. The activation volume for PC in the lower pressure region is in reasonable agreement with that reported by Walton and coworkers,$^{20}$ calculated from the equivalent temperature shift of the proton NMR line width induced by...
pressure, and by Hansen and coworkers\textsuperscript{21} from the pressure dependence of the $^2$H spin-lattice relaxation time in deuterated PC. Thus the presence of the SNTP does not allow for a significant difference in activation volume.

Thus, in large part the NMR results are consistent with the earlier conclusion that the nanoparticles do not significantly modify the local environment within the nanocomposites.

4.3 Conclusions

Studies of the complex permittivity and dielectric breakdown along with NMR and SEM measurements have revealed several interesting characteristics of PC containing either UNP or STNP BaTiO$_3$ nanoparticles. The SEM studies indicate that there is a tendency for a more uniform nanoparticle distribution in the nanocomposites formed using STNP. For concentrations of UNP greater than about 15\%, $\varepsilon'$ is much larger than expected on the basis of laws of mixing. On the other hand, $\varepsilon'$ for materials made using STNP is “well-behaved” in terms of agreeing quite well with the Hanai equation. Correspondingly, increased conductivity
(as shown by $\varepsilon''$ or $\tan \delta$) in the vicinity of room temperature is observed for the materials made from UNP, compared to data for STNP based composites. The anomalously large values of the complex permittivity are attributed to the presence of large aggregates in the materials made using the UNP. This despite the fact that none of the various nanocomposite materials showed significant changes in the $\gamma$ relaxation, which implies that the nanoparticles do not significantly affect small segment motions of the polymer chains, regardless of size, concentration or surface modification. Finally, variable temperature and pressure NMR relaxation studies demonstrate that the 8.3% particle inclusion has essentially no significant observable effect on the main relaxation mechanism attributed to ring flips. The presence of the STNP also does not appear to have significant effect on the $T_1$ pressure dependence. The NMR measurements were included to ascertain if the enhancement in dielectric properties are attributable only to the electrical properties of the nanoparticles themselves or if there is also an effect on the fundamental polymer structural motions associated with the $\gamma$ relaxation as probed by spin-lattice relaxation. We conclude that there is little if any effect on the latter.

4.4 Acknowledgments

The authors would like to thank Dr. John T. Bendler of BSC, Inc. and Dr. Jeffrey P. Calame of the Naval Research Laboratory for helpful discussions and Amadeo DeLuca-Westrate for assistance in some of the thermal measurements. This work was supported in part by the U. S. Office of Naval Research. JFF and MCW acknowledge support from JJFontanella LLC.
4.5 References


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Chapter 5

Electrophoretic Probe Design

5.1 Introduction

As shown in previous chapters, nuclear magnetic resonance can be adapted for the study of diffusion and transport in matter. One of the advantages of the NMR technique is the ability to provide ion-specific transport information. The importance of this characterization lies in the fact that, e.g. in the case of lithium batteries, low lithium self-diffusion coefficients are associated with high viscosity and low lithium ion conductivity. Furthermore, the formation of a concentration gradient, being characteristic of a low lithium ion transference number, results in an electromotive force that acts in opposition to the desired current. For these reasons, methods like pfg and electrophoretic NMR (eNMR: NMR in the presence of an electric field) provide molecular/atomic/ionic transport information in the direct measure of diffusion coefficients and mobilities respectively. However eNMR measurements are complicated by: non-electrophoretic bulk flow effects from both electro-osmosis and thermal convection. Additionally, there can be substantial electrical noise pickup from the electric leads into the RF coil. Presently no commercial eNMR system is available, and in order to address the experimental difficulties, researchers are designing their own sample cells and pulses sequences. \(^1\text{40}\)

Umecki et al.\(^5\) using eNMR presented for the first time ionic mobilities in a number of ILs: EMI-BF\(_4\), EMI-FSI, EMI-FTI, EMI-TFSI, and BMI-TFSI . The data revealed higher ionic mobilities than those obtained with predictions from diffusion coefficient values. Similar results were obtained from the work of K. Hayamizu and Y. Aihara.\(^3\) Other groups, using eNMR, determined transference numbers in lithium ion-conducting polymer electrolytes\(^30\) and the
electroosmotic drag in Nafion Membranes.\textsuperscript{4} In this project, an electrophoretic cell has been designed and built for the eventual measurement of transference numbers and electrophoretic mobilities.

### 5.2 Theoretical Background of eNMR

#### 5.2.1 Electrophoresis.

Electrophoresis was first observed by Ferdinand Friederich Reuss in 1807. He observed that clay particles dispersed in water migrate under the influence of an applied electric field. Generally, electrophoresis is a technique that involves the separation of charged molecules according to their motion under the influence of an electric field (Fig. 1). It was introduced as an analytical tool by Arne Tiselius in 1937 to separate blood into three constituent parts (alpha, beta and gamma globulin). For his pioneering work in this field, Tiselius was awarded the Nobel Prize in 1948.

![Electrophoresis principle](image)

**Fig. 5.1. Electrophoresis principle**
In the electrophoresis experiment the magnitude of the electric field is defined as
\[ E = \frac{U}{l}, \]
where \( U \) is the potential difference between the electrodes and the distance between them is \( l \). When a charged ion is moving due to an applied electric field in a liquid medium, it experience a force given by \( F = qE \), then

\[ F = qE = \frac{qu}{l} \tag{5.1} \]

According to the Stokes equation for a spherical particle with a hydrodynamic radius \( R_h \) in a medium with viscosity \( \eta \), the frictional force is given by:

\[ f = 6\pi\eta R_h v \tag{5.2} \]

When the electric field is applied each ion will travel toward the electrode of opposite charge. At equilibrium, the frictional force \( f \) is equal to the electric force \( F \), and the charges obtain their equilibrium speed \( v \).

\[ v = \frac{qE}{6\pi\eta R_h} \tag{5.3} \]

### 5.2.2 The eNMR Experiment

The eNMR experiment is similar in design to the pfg diffusion experiment except for the fact that the sample resides within an electrolysis cell. During the application of an electric potential across the cell, an electric field is created and a drift velocity is imparted to the ions. In order to avoid Lorentz forces, the cell is designed such that the electric field is aligned parallel to the magnetic field. The electric field induced mobility of charged entities can now be evaluated in a manner similar to that of diffusion in pfg NMR. The quantity of interest is the mobility \( \mu \)
of the charged species as is defined in terms of $v$ the measured velocity and the electric field strength $E$.

$$\mu = \frac{v}{E}$$

Fig. 5.2 shows the eNMR pulse sequence as a pulse gradient spin echo (PGSE) experiment conducted in the presence of a pulsed electric field. As usual, a pair of linear magnetic field gradient pulses with duration $\delta$ and strength $g$ is used to encode the displacements of molecular ensembles. The electric field is generated by a power supply, and the pulses are conveniently synchronized with the RF and magnetic field gradient pulses. In that the electric field is switched on during the spin echo sequence and then off before acquisition of the second half of the spin echo, the sample magnetization is left to evolve while the ions are drifting. The effect of the drift is explained below.

**Figure 5.2.** The electrophoretic pulse sequence
5.2.3 eNMR Signal Amplitude and Phase

Consider a charged particle experiencing drift velocity, \( v \), in the gradient direction, the position at time \( t \) is:

\[ z(t) = vt, \]

and the resonance frequency at the time \( t \) is

\[ \omega(t) = \gamma B_0 + \gamma gvt \] (5.5)

At \( t = 0 \), we have

\[ \omega_0 = \gamma B_0 \] (5.6)

Then, the frequency difference is just,

\[ \Delta \omega(t) = \gamma gvt \] (5.7)

If we account for the fact that a frequency difference implies a phase angle difference, which increases with \( t \), then the phase difference is simply,

\[ d\phi = \Delta \omega(t) \, dt \] (5.8)

Now the spins are labeled with regard to their position through their phase angle and the angle difference at time \( \tau \) is

\[ \Delta \phi(\tau) = \int_0^\tau \gamma gvt \, dt = \gamma gvt^2/2 \] (5.9)

The \( \pi \)-pulse inverts this difference, \( \Delta \phi(\tau) \rightarrow -\Delta \phi(\tau) \), so for \( t = 2\tau \), eqn. (9) becomes:

\[ \Delta \phi(2\tau) = -\Delta \phi(\tau) + \int_\tau^{2\tau} \gamma gvt \, dt = -\gamma gvt^2/2 + \gamma gvt^2/2 + \gamma gvt^2/2 - \gamma gvt^2/2 = \gamma gvt^2 \] (5.10)
From figure 2, the duration of the field gradient is $\delta$ and the time separation between gradient pulses is $\Delta$. Using these values, the signal phase shift can be written as:

$$\Delta \phi(2\tau) = \gamma g v \delta \Delta$$  \hspace{1cm} (5.11)

Therefore the eNMR signal amplitude $S_f$, resulting from both diffusion and electrophoretic motion of charged species, will exhibit a phase shift given by:

$$S_f = S_0 \exp \left[ -\frac{2\tau}{T_2} - \gamma^2 D g^2 \delta^2 \left( \Delta - \frac{\delta}{2} \right) \right] \cos(\gamma g v \delta \Delta)$$

(5.12)

The subscript $f$ denotes that the signal is recorded in the presence of flow, $S_0$ is the NMR signal amplitude at zero gradients. The exponential term represents the signal attenuation due to the diffusion process, and the cosine term contains the phase shift dependence caused by coherent electrophoretic motion.

Thus with phase sensitive signal detection, the electrophoretic induced phase leads to a cosine modulation of the echo signal. Performing an experiment in which the electric field is absent the effect of flow is discriminated from the effects of transverse relaxation and self-diffusion. Then the intensity ratio at time $2\tau$ with and without the electric field is

$$\frac{S_f(2\tau)}{S_{f=0}(2\tau)} = \cos(\gamma g v \delta \Delta)$$

(5.13)

The most common way of performing an ENMR measurement is by using a constant current instead of a constant voltage as the source for the electric field. The electric field $E$ is then calculated from Ohm’s law as;
and for the drift velocity,

$$v = \mu E = \frac{I_E}{k\sigma}$$  \hspace{1cm} (5.15)\

Where $I_E$ is the electrophoretic current, $k$ is the conductivity of the sample, $\sigma$ is the cross-sectional area perpendicular to the electric field, and $\mu$ is the mobility. The conductivity is measured in a separate step before the experiment or in situ in a specially designed eNMR sample cell. The benefit of this approach is that echo attenuation due to diffusion is constant, at least to first approximation. The application of a current in the sample results in Joule heating effect. This effect attenuates the eNMR signal when the current is changed.

Typically one wants to find the mobility of a particular ion, so the measurements are made by sampling the phase of the NMR signal as a function of electrophoretic current $I_E$ while keeping all other parameters constant, (i.e. $g$, $\Delta$, $\delta$). The mobility, $\mu$, can be obtained from the measured phase with eqns. 5.13 and 5.15.

5.3 eNMR Cell Design

The design of the eNMR sample cell is perhaps the most crucial aspect in planning experiments because, as pointed out previously, the potential presence of non-electrophoretic motional convection (thermal and electro-osmotic) and electrical noise detected by the RF coil adversely affects signal detection. Therefore, eNMR cell design is geared towards minimizing this. Cells have developed basically along two different geometrical forms: U–tube and cylindrical. For the U-tube cells, both electrodes are in the upper part of the cell. This design has
the advantage of venting and ameliorating the effects of bubbles produced during electrical pulsing. This geometry is also effective at reducing the convective motion produced by bubbles. However the disadvantage of the U-tube design is that net ionic drift occurs in opposite directions on either leg of the cell, and as a result, there is a loss of information concerning the sign of the mobility. The cylindrical cell typically can be designed with a higher filling factor than the U-tube and the direction of electrophoretic motion is unambiguous. With this cell design however, bubble production from the lower electrode can induce non-electrophoretic bulk flow. A possible advance in cylindrical cell design might have both electrodes connected to a current source through the upper electrode. A similar sample cell has been successfully utilized in an in-situ design. The idea was to measure Li\(^+\) diffusion through the solid electrolyte interphase (SEI) on the graphite anode. For this experiment, a \(^6\text{Li}\) enriched (95%) graphite coating (LiC\(_6\) + SEI) was fabricated on the cooper electrode of the cell. The cell electrolyte 1M LiPF\(_6\)/EC/DMC was enriched with \(^7\text{Li}\) (98%). A constant potential was applied across the cell while the cell current was recorded (Arbin BT-2000 battery cycler) over a given time period, and the \(^6\text{Li}\) NMR-signal was monitored in order to follow the \(^6\text{Li}\) signal growth within the electrolyte with respect to current. The airtight in-situ cell was designed, along with a doubly tuned NMR probe, for the purpose of monitoring both \(^6\text{Li}\) and \(^7\text{Li}\) NMR signals. This preliminary experiment, where both \(^6\text{Li}\) and \(^7\text{Li}\) NMR signals can be quantified, promises that the unknown lithium content in the SEI can be measured.

In the design presented here, the electrophoretic cell is comprised of a 5\(\text{mm}\) diameter cylindrical pyrex glass tube plugged on the top and bottom by two gold coated electrodes and supported by a fluoroelastomer O-rings to prevent leakage. The distance between the electrodes is 25\(\text{mm}\). The temperature is controlled using air flow around the sample cell. In order to avoid
overheating and evacuate all gases formed during measurement, vent holes were introduced in the Teflon end pieces. The gold plated electrodes may avoid some of the electrolyte degradation reactions encountered with other metals. The RF coil detection region is 15 mm in length in order to minimize electrical noise feedthrough with the metal electrodes eNMR cell designs are shown within the following pages in greater detail.

5.4 References

Figure 5.3. Exploded view and part list of the electrophoresis cell
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