ABSTRACT


Ionic liquids (ILs) are salts with a melting temperature ($T_m$) at or below room temperature. Depending on their structure, they can be nonvolatile, nonflammable, and highly stable, both thermally and electrochemically. These properties make ILs attractive alternatives to the organic solvent-based electrolytes currently in use. However, ILs have a number of drawbacks, including a relatively low ionic conductivity and a $T_m$ greater than that of many solvents which often precludes their use at low (lower than -20 °C) temperature. This work investigates two potential means of addressing these problems: the addition of aprotic solvents to ILs and mixtures containing two ILs. The use of these mixtures in electrochemical double-layer capacitors (EDLCs) is examined and links between properties and capacitor performance quantified.

The physicochemical properties (density, viscosity, ionic conductivity, and thermal phase behavior) of the pure ILs, IL-aprotic solvent mixtures, and IL-IL mixtures containing varying ions were initially investigated. While pure ILs are often highly viscous, with a correspondingly low ionic conductivity, the IL-solvent mixtures containing small amounts (20 mol%) of aprotic solvents are much more conductive and less viscous than the pure ILs. In addition, the presence of solvent molecules inhibits the crystallization of the ILs, thus retaining the liquid phase for these electrolytes to a much lower temperature. The interactions between the ILs and solvent appear to be quite weak, however, allowing the solvent to readily volatilize at higher temperatures. Thus, IL-IL mixtures were also studied as a route to modify the properties of IL-based electrolytes without reintroducing volatility concerns.
Mixing two ILs can result in significant variations in the viscosity, density, and ionic conductivity as compared to that of the pure ILs. Furthermore, the compositions with mixed anions often remain amorphous mixtures, rather than crystallizing, thereby potentially allowing IL-IL mixed electrolytes to be used at low temperatures.

In addition to modifying the properties and phase behavior of electrolytes, the presence of mixed cations and/or anions in an EDLC electrolyte may influence both the energy and power density of a device. The addition of smaller ions to IL-based electrolytes was expected to result in increased specific energy due to the utilization of smaller pores and/or increased specific power due to the higher mobility of smaller ions. However, these effects are not observed for many of the IL-IL electrolytes, suggesting that factors other than ion size influence the performance of IL-based EDLCs. In addition, the noted differences in performance did not correlate with the performance that would be predicted based upon the current understanding of electrolyte optimization for capacitors. Specifically, increases in specific energy may be accompanied by increases in viscosity and decreases in conductivity (counter to what one would expect), while increases in specific power may be observed for mixtures that have no changes in physicochemical properties. In toto, these results suggest that the relationships between electrolyte properties and EDLC performance are complex and require further attention from the research community.
Ionic Liquids and Electrochemical Double-Layer Capacitors: A Study of Electrolyte Structure and Capacitor Performance

by

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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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DEDICATION

To my parents for their constant encouragement.
BIOGRAPHY

Eric was born in Boston, MA in 1984 and grew up on the shoreline in both Massachusetts and Connecticut. In 2002, he headed to Easton, PA to attend Lafayette College where he earned a B.S. in Chemical Engineering. After graduating in 2006, he worked in industry for a year before heading back to school in 2007 to obtain an M.S. in Chemical Engineering from Yale University. In 2010, Eric transferred to North Carolina State University to pursue research opportunities with ionic liquids and obtain his Ph.D. in Chemical Engineering.
ACKNOWLEDGMENTS

Many people contributed greatly to my success here. I would like to thank Dr. Henderson, who has taught me a great deal about conducting research (and how to make a really good looking figure). I would also like to thank the entire ILEET group, in particular Elie Paillard, Joshua Weaver and James Dickmann, for all of their help. Finally, thanks are due to my family and friends for keeping me going during this long process.
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Chapter 1: Introduction

1.1 Motivation

Concerns about energy, such as rising costs and dependence on foreign sources of fuel, necessitate the recovery of energy that previously would be discarded. Energy can be recovered/reused from cyclic applications, such as braking/accelerating a vehicle, moving an elevator down/up, or lowering/lifting cargo via a crane. While the predominant energy storage device, batteries, can easily store the amount of energy that would be recovered from such applications, battery charge/discharge times are typically on the order of hours, which exceed the time scale for energy recovery from processes that take only seconds. Batteries also have limited durability in these applications, as they can only withstand approximately $10^3$ charge/discharge cycles before significant performance degradation occurs. One alternative to batteries is the use of electrochemical double-layer capacitors (EDLCs), also known as supercapacitors or ultracapacitors, for these energy recovery applications. EDLCs can operate for $10^5$ or more cycles without degradation in performance and have charging/discharging times on the order of seconds. The use of EDLCs in many energy recovery applications, however, is hampered by the low specific energy of these devices, as well as their high cost.

A potential solution to both of these problems is to charge EDLCs to a higher potential, which increases the amount of energy stored in the device and thus decreases the number of devices required to store a given amount of energy. Unfortunately, the charging potential for EDLCs is limited by the stability of current electrolytes. Commercial electrolytes are classified as either aqueous or nonaqueous. The former generally consist of $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ or
H$_2$O-KOH mixtures. While these work well (i.e., high charge/discharge rates), the relatively low electrochemical stability of water strongly restricts the upper operating voltage limit of the EDLCs. Nonaqueous electrolytes generally consist of solvent-salt mixtures, often with either acetonitrile (AN) or propylene carbonate (PC) and a tetraalkylammonium salt such as tetraethylammonium tetrafluoroborate (N$_{2222}$BF$_4$). The nonaqueous mixtures are limited, however, by the relatively low salt solubility in aprotic solvents, high volatility of AN and low conductivity of the PC-based electrolytes at low temperature.

One alternative to current electrolytes is the use of ionic liquids (ILs). ILs are salts which are liquid at low temperature and can, depending on choice of ions, have high electrochemical stability and low/negligible volatility. The effect that the ion structure has on the performance of devices using IL-based electrolytes is not well understood. Thus, the goal of this study was to investigate what links exist between ion and solvent structure, measured electrolyte physicochemical properties (e.g., density, viscosity, and ionic conductivity), electrolyte phase behavior, and the performance of EDLCs that use IL-based electrolytes. Towards that end, a number of ILs were prepared and extensively characterized. In addition to pure ILs, IL-aprotic solvent mixtures and IL-IL mixtures were also studied. After characterization, coin cell EDLCs using the studied ILs and mixtures as electrolytes were prepared and their performance evaluated.

1.2 Electrochemical Double-Layer Capacitors (EDLCs)

Electrical energy can typically be stored in two ways. In batteries, energy is stored through chemical (Faradaic) reactions. In Faradaic systems, electrons are transferred across
the electrode interface, resulting in a change in the oxidation state of chemical species. In contrast, in traditional capacitors, which consist of a thin dielectric material which separates two flat Al plates, no electron transfer across the electrode interface occurs as energy is instead stored physically (non-Faradaic). These different means of storing energy explain the significant performance differences between batteries and capacitors. As batteries depend on chemical reactions, they are kinetically limited in their charge/discharge cycles, which results in low power density. In addition, there is always at least a slight irreversibility to chemical reactions. This, coupled with the changes in electrodes due to the intercalation of ions (i.e., Li\(^+\) cations), limits the number of cycles over which a battery can be used to, at best, a few thousand cycles.\(^1\) Unlike batteries, energy in a traditional capacitor is stored on the surface of the electrodes, which limits the energy density of these devices. Energy storage is also limited by the maximum potential the dielectric material can experience without degrading (i.e., the breakdown voltage). However, the lack of chemical reactions removes the kinetic limitations on the power density of a capacitor and eliminates the major source of irreversibility in Faradaic devices, allowing a traditional capacitor to operate, theoretically, indefinitely.\(^1\)

EDLCs are a third means of storing electrical energy. EDLCs have similarities to both batteries and traditional capacitors. At first glance, the structure of an EDLC (Fig. 1.1) looks almost identical to that of a battery. In fact, many of the same components developed for batteries can be used in an EDLC. EDLCs differ from batteries in that energy is stored in the electric double-layer, or Helmholtz layer, rather than through chemical reactions. As no oxidation/reduction of active materials occurs, at least in the ideal case, EDLCs can operate
for $10^5$-$10^6$ cycles.\(^3\) This lack of such reactions also removes many of the kinetic limitations on the specific power of an EDLC. EDLCs differ from traditional capacitors in two significant ways; an electrolyte is present and the electrodes are high surface area materials, commonly activated carbon. An electrolyte is necessary to allow stabilization of the charged electrode-electrolyte interfaces (using the electrolyte ions), while the high surface area electrodes increase the area of the interface and thus the amount of energy an EDLC is capable of storing.
When the performance of electrochemical devices needs to be compared, it is common to discuss specific energy (Wh kg\(^{-1}\)) and specific power (W kg\(^{-1}\)). A plot of these two properties, as first proposed by David Ragone in 1968,\(^4\) is known as a Ragone plot. Such a plot, containing common electrochemical systems, is shown in Fig. 1.2. The values for specific energy and power of EDLCs fall between those of traditional capacitors and batteries.

The energy stored in an EDLC, \(W\), is determined by two factors: the capacitance of the
electrodes, \( C \), and the maximum potential, \( V \), to which the EDLC can be charged without inducing irreversible electrochemical processes. This potential is generally limited by the electrochemical stability of the electrode and electrolyte when in contact. The following equation (Eq. 1) shows the relationship between these three attributes:

\[
W = \frac{1}{2}CV^2 \quad (1)
\]

The power, \( P \), of an EDLC is also a function of the maximum charging potential. In addition, the internal resistance of the EDLC, \( R \), plays an important role in the device power. Internal resistance is the sum of resistance from the electrolyte, electrodes, and all of the other components in the circuit. The resistance from the bulk electrolyte and the electrolyte in the pores of the electrode, however, tends to dominate the internal resistance. The following equation (Eq. 2) shows how the interaction of these two variables affects the power of the device:

\[
P = \frac{V^2}{4R} \quad (2)
\]

Thus, for an EDLC to have both high specific energy and power, it must use electrodes with high capacitance (with a given electrolyte) and an electrolyte that is stable at high potentials, while ensuring that the internal resistance remains low. Of these three criteria, high
electrochemical stability is the most important, as both specific power and energy are proportional to the square of the maximum charging voltage.

1.3 Current Electrolytes

In an EDLC, the most important role of the electrolyte is to facilitate the transport of ions to rapidly stabilize the charge buildup at the electrode interfaces. A frequently used metric for the ability of an electrolyte to do so is ionic conductivity. Combining the Stokes-Einstein model for diffusion of spherical particles and the Nernst-Einstein equation relating conductivity to diffusivity results in a model (Eq. 3) which relates the ionic conductivity, \( \sigma \), of an electrolyte to the concentration of charge carriers, \( c \), the viscosity of the electrolyte, \( \eta \), and the radius of the charge carriers, \( r \). The model also includes the valence charge of the ions, \( z \), the charge of an electron, \( e \), and Faraday’s constant, \( F \).^1

\[
\sigma = \frac{z^2 e F c}{6 \pi \eta r} \quad (3)
\]

The electrolyte also plays a role in determining the capacitance of a system. An electric double-layer (Fig. 4) contains ions (having the same charge as the surface), counterions (having the opposite charge as the surface), and solvent molecules (both free and in the solvation shell around ions). The maximum capacitance occurs in the ideal case of a surface saturated with counterions, but this does not occur in reality. Both ions and solvent molecules are present at or near the surface, resulting in a lower counterion density and further charge-
charge separation between the surface and counterions, both of which result in lower capacitance. The size of the ion solvation shell, which is determined by interactions between the ions and solvent molecules, also affects the counterion density and separation distance. Predicting the counterion density and mean charge-charge separation \textit{a priori} is very difficult. Thus, when selecting electrolytes for use in EDLCs, solvents are often selected principally for low viscosity and the ability to dissolve a specified electrolyte salt to a desired concentration.

As water meets these latter criteria, aqueous electrolytes would seem to be promising materials to use in EDLCs. As noted above, aqueous electrolytes are commonly based on H$_2$SO$_4$ or KOH and have high ionic conductivity.$^{1}$ Using high surface area carbon electrodes, EDLCs based on aqueous electrolytes can obtain gravimetric capacitances of 150-200 F g$^{-1}$.\textsuperscript{6} Unfortunately, aqueous systems have a number of constraints which limit their usefulness in EDLCs. Pure water has a liquidus range between 0 $^\circ$C and 100 $^\circ$C, which limits the temperature range over which an aqueous-based EDLC can be used due to high vapor pressure at elevated temperature and freezing at low temperature. Furthermore, water has a narrow electrochemical window of 1.23 V, which limits both the energy and power of an EDLC. When salt is added, the liquidus and electrochemical stability range may be extended, but not to any significant extent.

One alternative to aqueous systems is to use electrolytes based on organic solvents. A wide variety of aprotic solvents are used in electrochemical devices, with AN and PC being the most prevalent. The most widely used salt is N$_{2222}$BF$_4$.$^{1}$ The salt concentration in these electrolytes is around 1M, as this is where the conductivity maximum of most solvent-salt
mixtures occurs.\textsuperscript{7,8} At lower salt concentrations, the available charge carriers can be depleted thus limiting the conductivity of the system, as well as the capacitance.\textsuperscript{9} At higher concentrations, the salt ions may begin to associate forming ion pairs and aggregates which contribute less to the conductivity and/or capacitance. Further, electrolytes based on organic solvent are often more viscous than their aqueous counterparts and have a correspondingly lower conductivity.\textsuperscript{10} These electrolytes also generally result in a lower specific capacitance than aqueous electrolytes with carbon electrodes, with values near 100 F g\textsuperscript{-1} being common.\textsuperscript{11,12} Aprotic solvents have one significant advantage, however, as compared to aqueous systems in that their electrochemical stability windows can be two to three times greater than water (2-4 V).\textsuperscript{10} As the performance of an EDLC is proportional to the square of the maximum charging voltage, this high stability more than offsets the lower capacitance of these systems. However, the use of organic solvents comes with a number of drawbacks, including high volatility and flammability. Rather than using a binary or tertiary electrolyte containing water or organic solvents and salts, it may be possible to instead use an IL that serves to provide both a high concentration of charge carriers and the medium through which ions are transported.  

1.4 Ionic Liquids

ILs are salts, generally composed of large, asymmetric organic cations and inorganic anions. Some of the common anions and cations found in ILs are shown in Fig. 1.3. These salts melt at low temperature (often below room temperature), due to the structure of the bulky, often weakly interacting, ions which destabilizes the ordered packing of the ions at
ILs were first discovered in the early 1900s, with ethylammonium nitrate being one of the first to be reported in 1914.\textsuperscript{13} ILs were not well studied, however, until the 1980s when chloroaluminate (AlCl\textsubscript{4}\textsuperscript{-}) salts were investigated as solvents.\textsuperscript{14-18} These ILs were of limited use, as the AlCl\textsubscript{4}\textsuperscript{-} anion violently decomposes in the presence of water and thus cannot be used in ambient air. The synthesis of water-stable BF\textsubscript{4}\textsuperscript{-}-based ILs, coupled with the rise of the Green Chemistry movement, in the 1990s led to a significant increase in the amount of research conducted on ILs.\textsuperscript{19,20} As appropriately designed ILs can be non-volatile, non-flammable, and able to dissolve a wide variety of substances, they may be able to replace the volatile organic solvents used in many applications, including non-aqueous electrolytes. In addition, ILs can be highly stable, both thermally and electrochemically. ILs can also have an electrochemical stability window in excess of 5.0 V with Pt or glassy carbon electrodes, but certain anions, such as halides, undergo anodic oxidation at low potentials, while some cations, such as 1-alkyl-3-methylimidazolium (IM\textsubscript{10R}\textsuperscript{+}), undergo cathodic
ILs are also composed entirely of ions, which provides a high concentration of charge carriers. All of these properties are useful attributes in an electrolyte. Select physicochemical properties of some ILs are shown in Table 1.1. In this table, a methoxyethyl group is represented by the subscripted “1O2.”

ILs have a number of unattractive properties, however, relative to organic solvent-based electrolytes. ILs are generally quite viscous (10-100 times the viscosity of water),\(^{21}\) in contrast with many aprotic solvents which are less viscous than water. High viscosity may be indicative of low ion mobility, which could lead to a low ionic conductivity and high internal resistance in an electrochemical device. Further, high viscosity can result in poor wetting of the porous separator (which separates the electrodes) and porous electrode materials, which will further limit the performance of an EDLC. Although the high thermal stability and low volatility allow IL-based electrolytes to be used at high temperatures, they generally have a melting point \((T_m)\) close to 0 °C, which is problematic as electrolytes need to remain liquid to

<table>
<thead>
<tr>
<th>Salts</th>
<th>(T_g ) [°C]</th>
<th>(T_m ) [°C]</th>
<th>(\eta) [cP]</th>
<th>(\sigma) [mS cm(^{-1})]</th>
</tr>
</thead>
<tbody>
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<td>PY(_{14})BF(_4)</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>PY(_{1(1O2)})BF(_4)</td>
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<td>213</td>
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<tr>
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Viscosity and conductivity measured at 25 °C

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11
-40 °C or below to be suitable for many electrochemical applications. ILs are also generally quite costly as compared to current electrolyte materials. Despite these limitations, the potential advantages of IL electrolytes have led to a number of studies investigating the use of ILs in Li-ion batteries and EDLCs.

Although studies have been performed on a number of different ILs containing different cations and anions, the most commonly studied ILs have IM_{10R}^+ or PY_{1R}^+ cations and BF_4^- or TFSI^- anions. With the use of high surface area activated carbons, gravimetric capacitance values of 100-200 F g^{-1} have been obtained, which is comparable to the values of many organic solvent-based electrolytes. The specific power of IL-based EDLCs is usually on the order of 10^2-10^3 W kg^{-1}, while the specific energy falls between 1-10 Wh kg^{-1}. These values place EDLCs in the intermediate region between traditional capacitors and batteries. Temperature plays an important role in these attributes, with both specific energy and specific power decreasing with decreasing temperature. This is likely due to decreased ion mobility, which is observed through an increase in viscosity and decrease in the conductivity. The nature of the ions present can also play a large role in the performance of EDLCs. As seen in Table 1, varying the ion structure can greatly affect the salt's physicochemical properties, which in turn affects electrolyte performance in an EDLC. Furthermore, the size of the ions relative to the size of the pores in the electrode material will affect the ion accessibility to the electrode surface and thus both the specific energy and power.
1.5 Ionic Liquids and Electrodes

The interaction between the electrolyte and electrode plays an important role in determining the performance of an EDLC. As the specific energy of an EDLC is proportional to the surface area, high surface area activated carbons are most commonly used. Depending on the fabrication process, these materials can have a surface area up to $2000 \text{ m}^2 \text{ g}^{-1}$ with pore sizes ranging between 2 nm (micropores) to 50 nm (macropores). Initial work focused on maximizing the surface area of the electrodes by decreasing pore size, but increasing surface area was found to increase the capacitance of a system only to a certain point (approximately 5 nm). Once the average pore size is less than 5 nm, the capacitance of the electrode starts to decrease slightly. This decrease is likely due to a fraction of the electrode’s surface being inaccessible to the electrolyte, as the solvated ions are too large to fit into the smaller pores.

A breakthrough in electrode designed occurred when an anomalous increase in capacitance was observed with electrodes containing pores smaller than 2 nm. It is believed that ions in confined geometry are stripped of their solvation shell. In pure ILs, no solvent molecules are present, but computational works suggests that the coordination number of ions is reduced in confined geometry, allowing the ions to more closely approach the surface. Fig. 1.4 shows the traditional understanding of how ions in solution interact with a charged planar surface (i.e., a tradition electric double-layer) and how ions interact in small and large pores. The capacitance of a system is inversely proportional to the mean charge-charge separation and the absence of a solvent shell allows charges to be located adjacent to the electrode surface, which leads to increased capacitance. Some work suggests that the
Figure 1.4 Ion interactions with charged surfaces. On the right is the traditional understanding of the electric double-layer, where oppositely charged ions preferentially position near the surface to achieve charge neutrality. In the middle is the double-layer as it forms in porous materials. Both similarly charged ions and solvent molecules enter the pore decreasing overall capacitance. On the left, ions entering micropores are desolvated, decreasing charge separation and increasing the area accessible to ions. Reproduced with permission from reference 43.

permittivity of the distorted solvate shell in pores should decrease, which would decrease the capacitance of the system, but the change in charge-charge separation appears to dominate.

One class of materials that is being used extensively to investigate the role of pore size and pore size distribution is carbide-derived carbons (CDC). The pore size distribution in these carbons is remarkably narrow and the pore size can be tuned with sub-Ångström accuracy. In an initial study using $\text{N}_2\text{BF}_4$, a large increase in specific capacitance was observed around pore sizes of 0.7 nm (Fig. 1.5). This corresponds closely to the size of the $\text{N}_2\text{BF}_4^+$ cation (0.68 nm), but is significantly larger than the size of the $\text{BF}_4^-$ anion (0.33 nm). Similar results were obtained when IM$_{102}$TFSI was used, with the maximum occurring
around 0.7 nm, which corresponds well to the size of the imidazolium cation (0.43 to 0.76 nm depending on orientation), as well as the size of the TFSI$^-$ anion (0.79 nm).\textsuperscript{53}

Other materials that are of interest for EDLCs are onion-like carbons (OLC) and carbon nanotube (CNT) arrays. The exterior surface of these materials is completely accessible to ions, which should overcome the ion transfer limitations imposed by tortuous microporous paths.\textsuperscript{54} Experiments using electrodes made from these materials and an electrolyte composed of an equimolar mixture of PI$_{13}$FSI and PY$_{14}$FSI have shown that the high accessibility of these carbons allows an ELDC to be cycled quickly (from 20 V s$^{-1}$ at 100 $^\circ$C

\textbf{Figure 1.5} Capacitance of N$_{2222}$BF$_4$ with a porous carbon material. Reproduced with permission from reference 5.
to 5 mV s\(^{-1}\) at -50 °C.\(^{54}\) CNT-based electrodes showed no loss in normalized capacitance at temperatures as low as -50 °C. Clearly, the accessibility of the electrode material is as significant of a factor as the surface area of an electrode in determining the performance characteristics of an EDLC.

In addition to the geometry of the electrodes, another factor that can limit the performance of an EDLC is the ability of an IL to wet the electrode or separator materials. When the double-layer capacitance of IM\(_{102}\)TFSI was measured using a planar electrode made of glassy carbon, a capacitance of 12 μF cm\(^{-2}\) was observed.\(^{55}\) When this measurement was repeated using activated carbon electrodes, the measured capacitance was 4 μF cm\(^{-2}\). These values remain roughly constant even with a variety of cations and anions (IM\(_{102}\)\(^{+}\), IM\(_{104}\)\(^{+}\), PY\(_{13}\)\(^{+}\), BF\(_{4}\)\(^{-}\), PF\(_{6}\)\(^{-}\), TFSI\(^{-}\)).\(^{36}\) This lower value per unit area of electrode surface may be due to the variable manner in which ILs wet different electrodes, meaning that less than the full surface area is used for charge storage.\(^{55}\)

The wetting behavior of ILs, as roughly quantified by the contact angle, has been studied for many electrode or separator materials. A smaller contact angle corresponds to a higher degree of wetting. As with the physical properties of an IL, the wettability of an IL is a

![Figure 1.6](image_url) Drop shape analysis of water and two ILs on a GC surface.\(^{56}\)
function of the cation and anion structure. Fig. 1.6 shows the wetting behavior of water and two IM$_{11}$RTFSI ILs on a glassy carbon (GC) surface. Surface tension is believed to be one of the best indicators of wettability, with high surface tension corresponding to poor wetting behavior.$^{57-60}$ The surface tension of an IL is largely a function of the interaction between the cation and anion. The length of the alkyl chain on the cation plays a role, with surface tension decreasing with increasing chain length.$^{61}$ The role the anions plays is unclear with some studies showing smaller anions lead to higher surface tension$^{61}$ and other showing no trend in surface tension with anion size.$^{57}$

The nature of the electrode material, be it hydrophilic or hydrophobic, also plays a large role in whether or not an IL will wet the electrode. The wetting behavior of two ILs, PY$_{14}$TFSI and IM$_{102}$TFSI, on an activated carbon surface changed after the surface was treated at 1050 $^\circ$C under argon.$^{21}$ This treatment removed oxygen functional groups from the surface of the carbon, resulting in a more hydrophobic surface, which lead to better wettability from the ILs, both of which are considered hydrophobic. The same behavior was observed with some hydrophilic ILs, which wet glass surfaces (hydrophilic due to hydroxyl groups) to a much higher degree than PTFE (hydrophobic) surfaces.$^{62}$

Unfavorable interactions between ILs, electrodes, and/or separator materials may be a significant barrier to achieving high specific energy and power. Careful design and selection of ILs, electrodes, and separators may offer a method to overcome these challenges. In addition, chemical or electrochemical pretreatment of electrode and/or separator materials may allow the use of materials that would otherwise be unacceptable.
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Chapter 2: Experimental Procedures

2.1 Synthesis and Purification

2.1.1 Materials

*Solvents* Solvents (Fig. 2.1) used in this work were acetonitrile (AN) (99.8%, anhydrous), diethyl carbonate (DEC) (≥ 99%, anhydrous), dimethyl carbonate (DMC) (≥ 99%, anhydrous), ethyl acetate (EA) (99.8%, anhydrous), ethyl butyrate (EB) (99%), ethylene carbonate (EC) (99%, anhydrous), ethyl propionate (EP) (99%), γ-butyrolactone (GBL) (≥ 99%), γ-valerolactone (GVL) (≥ 99%), methyl acetate (MA) (99%), methyl butyrate (MB) (99%), methyl isobutyrate (MI) (99%), methyl propionate (MP) (99%) and propylene carbonate (PC) (99.7%, anhydrous); all of which were purchased from Sigma-Aldrich. The water content of each solvent was checked with a Mettler-Toledo DL39 Karl-Fischer coulometer. The solvents were used as-received, except for GBL, GVL, EB, EP, MA, MB, MI, and MP, which were dried using 3 Å molecular sieves until a water content of less than

![Figure 2.1 Structures of solvents used in this study.](image-url)
100 ppm was measured. The solvents were stored in hermetically sealed bottles in either a Vacuum Atmospheres N₂ or Ar glovebox (< 10 ppm O₂ and < 5 ppm H₂O).

Reagents

1-Iodomethane (99%), 1-iodoethane (98%), 1-iodopropane (99%), 1-iodobutane (98%), 1-iodopentane (97%), 1-iodohexane (≥ 98%), 1-bromopropane (99%), 1-bromobutane (99%), N-methylpyrrolididine (98%), N-methylpiperidine (99%), N-methylmorpholine (99%), 1-methylimidazole (99%), 1,2-dimethylimidazole (98%), NaBF₄ (98%), and N₂₂₂BF₄ (98%) were purchased from Acros Organics. LiTFSI (battery grade) was purchased from 3M. KFSI (> 99.9%) was donated by Suzhou Fluolyte Company. The salts were stored in sealed containers in the glovebox.

2.1.2 Synthesis

A general reaction scheme for the synthesis of a variety of ILs is shown in Scheme 2.1. Preparation of FSI, TFSI and BETI ILs

The appropriate base (i.e., amine) was reacted with the appropriate 1-haloalkane (X-R) in EA at a molar ratio of 1.00:0.95 to ensure complete reaction of the haloalkane. The resulting solids were washed and filtered with EA until the halide salts were white. The purified PY₁RX salts were then reacted with LiTFSI, KFSI, or LiBETI in water at a molar ratio of 1.00:1.05 to ensure complete reaction (metathesis) of the halide salts. If the resulting ILs were a liquid at room temperature, they were allowed to separate from the aqueous layer and the aqueous layer was decanted. If the ILs were instead solids (i.e., low melting salts which
melt above ambient temperature), they were recovered from the reaction medium via filtration. The solid and liquid ILs were washed with deionized water to remove the excess lithium or potassium salts until the addition of AgNO₃ to the wash solution did not form a precipitate. The ILs were carbon treated at 200°C until colorless and dried under vacuum at 100 °C for 24-48 h. ILs that are colorless to the human eye have been shown to have, at most, a ppm level of impurities.³

The salts that were solid at room temperature were dissolved in EA to facilitate carbon treatment. The water content was checked using Karl Fischer coulometry and found to be less than 50 ppm for all of the ILs. The purity of the ILs was verified by ¹H NMR spectroscopy. Table 2.1 shows the TFSI− ILs that were prepared. In addition, PY₁₃FSI, PY₁₄FSI, and PY₁₄BETI were synthesized for study.

**Preparation of BF₄⁻ Salts**

Two BF₄⁻ salts, PY₁₃BF₄ and PY₁₄BF₄, were also prepared for use in this study. Both salts have a $T_m$ in excess of 100 °C. To synthesize the salts, the desired base was reacted with the appropriate 1-bromoalkane in EA at a molar ratio of 1.00:0.95 to ensure complete reaction of
the haloalkane. The resulting solids were washed and filtered with EA until the bromide salts were white. The salts were then dried in a vacuum oven at 100 °C for 24 h. The bromide salts were then dissolved in the glovebox in anhydrous AN and equimolar amounts of dried NaBF₄ were added to the solutions. A precipitate of insoluble NaBr formed in each case and was removed through filtration. The BF₄⁻ salts remained dissolved in the AN and the solutions were purified through treatment with activated carbon until colorless. The majority of the solvent was then removed (by rotoevaporation) and the salts were dried under vacuum at 100 °C for 24-48 h. The water content of the salts was checked with Karl Fischer coulometry and the purity was verified with elemental analysis. The water content for both of the salts was less than 50 ppm. The salts were stored in sealed containers in the glovebox.

2.2 Characterization

Phase Behavior

DSC measurements were performed with a TA Instruments Q2000 DSC equipped with a liquid N₂ cooling system. The instrument was calibrated with cyclohexane (solid-solid phase transition at -87.06 °C, T_m at 6.54 °C) and indium (T_m at 156.60 °C). The samples were prepared in the glovebox and hermetically sealed in Al pans. To ensure complete
crystallization, the samples were cycled/annealed repeatedly below their $T_m$ until no glass transition ($T_g$) was observed upon heating.

**Density and Viscosity**

Density and viscosity measurements were performed using an Anton-Paar SVM 3000 Stabinger viscometer. The instrument was calibrated using Cannon viscosity (density) standard fluids as follows: 3.689 mPa s$^{-1}$ (0.8150 g cm$^{-3}$), 50.02 mPa s$^{-1}$ (0.8209 g cm$^{-3}$) and 1105 mPa s$^{-1}$ (0.8456 g cm$^{-3}$) at 20 °C. The samples were removed from the glovebox and transferred to the instrument in a syringe sealed by plunging it into a silicon stopper. The instrument was sealed during use to prevent water contamination. Water content was checked through Karl Fischer coulometry after the measurements were completed and was found to be < 200 ppm for all samples (and generally < 50 ppm). Density and viscosity values were generally recorded from 100 °C to 0 °C in 10 °C increments, although in some cases the temperature was instead increased for the measurements and then rechecked at low temperature to verify that the sample composition (for the samples containing solvents) remained unchanged.

**Ionic Conductivity**

The conductivity of the ILs was measured with electrochemical impedance spectroscopy using a Solartron 1287A potentiostat and 1260A impedance analyzer or a BioLogic VMP3 potentiostat/galvanostat with electrochemical impedance spectroscopy modules installed. Spectra were collected from $10^6$ to 20 Hz with a 10 mV AC perturbation and no DC bias. The conductivity cells were prepared in the glovebox and then sealed. These cells consisted of two parallel Pt electrodes and had cell constants of approximately one, as determined
using aqueous KCl standard solutions. Samples were equilibrated in a Binder environmental chamber at temperatures between 100 °C to 0 °C. Temperature steps were 10 °C with at least 45 min allowed for equilibration after each temperature change before the measurements were taken.

2.3 Capacitor Assembly and Testing

Materials

Size 2032 coin cell cases, springs, and spacers fabricated from 316 stainless steel were purchased from MTI Corporation. PTFE separators were supplied by Gore. Carbon-coated Al current collectors were donated by ExoPack Inc. Carbon electrodes were purchased from Y-Carbon.

Assembly

The coin cells were assembled with one 1.1 mm thick Belleville Washer style spring and three 0.5 mm thick spacers, following methods described in the literature.5-7 The electrodes were separated with two layers of PTFE separator to ensure that the capacitor did not form a short circuit. Electrolyte was added between the current collectors and electrodes, the electrodes and separators, and between the two separators to ensure complete wetting of all components. All assembly steps took place under a N₂ or Ar atmosphere before the cells were hermetically sealed. After assembly, the coin cells were allowed to sit for at least 24 h to facilitate complete wetting of the components.
Methods

Electrochemical measurements for the coin cell capacitors were performed using a BioLogic VMP3 potentiostat/galvanostat with electrochemical impedance spectroscopy modules installed. The capacitance of the assembled coin cells was determined using cyclic voltammetry or galvanostatic cycling methods, which are discussed in detail in Chapter 6. The capacitor temperature was controlled using a Binder environmental chamber. The coin cells were allowed to equilibrate for at least 2 h after each temperature change before the measurements were taken.
References


Chapter 3: Properties of Neat Ionic Liquids

3.1 Introduction

The first step of this study was to synthesize a number of ILs, which are enumerated in Chapter 2. The physicochemical properties and thermal phase behavior of these ILs were then characterized. As discussed in Chapter 1, changes in the structure of the IL ions can cause dramatic changes in the salt properties and it is therefore crucial to have a detailed understanding of the pure IL properties and phase behavior before attempting to modify these IL characteristics.

3.2 Properties of Pure ILs

The values for the density at 20 °C of the ILs used in this work are shown in Fig. 3.1. The most significant structural component of the prepared ILs that affects density is the length of the alkyl chain on the cation head group. As the alkyl chain length increases, the density decreases, due to a lower abundance of heavy atoms (e.g., S or F). The type of head group chosen also affects the density. In general, increasing the head group size leads to decreasing density. The planar, aromatic imidazolium groups have the highest density values. These groups are some of the smallest studied, allowing for more efficient packing. The salts with the morpholinium head group are anomalous, as their size (comparable to that of those with the piperidinium head group) and the presence of an ether group containing two electron lone-pairs should result in ILs with lower values of density than the aromatic head groups. The repulsive nature of the electron lone-pairs with other lone-pairs on neighboring cations and with anions should decrease the rotational freedom of the cation, and lead to less
Figure 3.1 Density, viscosity, and conductivity at 20 °C of several pure ILs as a function of alkyl chain length R.
efficient packing and lower density. However, these morpholinium-based ILs have density values that are comparable to the IM$_{10R}$TFSI ILs.

Fig. 3.1 shows the viscosity values for the prepared ILs at 20 °C. As with density, the length of the alkyl chain on the cation head group plays a significant role in determining the viscosity of an IL. Increasing the chain length from two carbons to six results in an almost doubling of the viscosity for the studied ILs. The behavior of the IM$_{11R}$TFSI salts shows that increasing the number of carbons in the alkyl chains present on the cation leads to higher viscosity. A priori, an increase in alkyl chain length would be expected to lead to a decreased viscosity, as the alkyl chain serves to shield the charge center on the cation and thus reduced electrostatic interactions in the IL. Such reduced interactions would lead to a lower energy barrier for ion motion and lower observed viscosity. Several explanations have been advanced to explain why increasing alkyl chain length does not correspond to decreased viscosity. The presence of longer, non-polar alkyl chains may lead to increased van der Waals interactions between the cations and increased drag/friction experienced by ions in motion.\textsuperscript{2} It has also been suggested that van der Waals interactions lead to high ion association, with the larger size of aggregated ions leading to increased viscosity.\textsuperscript{3} A competing explanation is that changes in transport properties are driven by microstructuring in the IL. At longer chain lengths, the cation head group and anions form polar regions in the IL (driven by Coulombic interactions), and exclude the non-polar alkyl chains.\textsuperscript{1,4} This ordering increases the energy required to move ions, as disrupting this ordering is energetically unfavorable. The size of the head groups and structure of the moieties present play a role in the viscosity as well. Smaller head groups, such as the planar IM$_{10R}^+$ cations,
appear to be more mobile, leading to lower viscosity. Once again, the morpholinium head group is anomalous, having values for viscosity that are much greater than any of the other ILs prepared for this work. The repulsive nature of the electron lone-pairs may serve to increase the energy barrier to ion motion in the IL, and thus increases viscosity.

Values of ionic conductivity for the prepared ILs at 20 °C are shown in Fig. 3.1. Larger cation head groups and longer alkyl chains correspond with lower values of conductivity. This decrease in the conductivity is indicative of decreasing ion mobility, which is discussed in the section on viscosity. Increasing from a propyl chain to a hexyl chain results in a substantial decrease in the conductivity. IM$_{10}$TFSI conductivity values stand out from the reported values for the other four classes of IL, as they have exceptionally high conductivity values. The conductivity of the PY$_{1}$TFSI, PI$_{1}$TFSI, and IM$_{11}$TFSI salts display a behavior that corresponds well with their viscosity, as the more viscous ILs are less conductive. MO$_{1}$TFSI ILs are once again anomalous, as their conductivity is close to that of the PI$_{1}$TFSI ILs, despite having a very high viscosity.

As with other physicochemical properties of ILs, the structures of the ions present significantly affect the thermal phase behavior. DSC heating traces for several pure ILs are shown in Fig. 3.2. The driving force for crystallization is the optimization of the electrostatic and other interactions between the cations and anions. Small and/or symmetric ions are able to easily orient to minimize a crystal’s free energy, and thus ILs containing these type of ions often have a high $T_m$ (e.g., PY$_{14}$BF$_4$ ($T_m = 152$ °C) or PY$_{11}$TFSI ($T_m = 133$ °C)). As ion sizes get larger or asymmetry greater, there are, in some cases, multiple stable crystal structures that can form. If these structures are too energetically similar, crystallization is often
frustrated as both phases are equally likely to form (e.g., PY$_{14}$TFSI which is slow to crystallize or PI$_{14}$TFSI which does not crystallize). Once the alkyl chains on the anion surpass a certain length (butyl to octyl depending on the IL), new crystal structures form, with layers alternating between polar regions and non-polar regions. This structuring is driven both by electrostatic attraction between the cation head groups and anions, as well as van der Waals interactions between the non-polar alkyl chains.
MO$_{1R}$TFSI ILs are anomalous, having a much higher $T_m$ than the corresponding PI$_{1R}$TFSI ILs. The presence of two repulsive electron lone-pairs on the cation ring structure should serve to limit the conformational freedom of the cation and thus inhibit the close approach of the cations and anions. Such inhibition should lead to a lower $T_m$, as a greater driving force would be needed to induce crystallization.

3.3 Conclusions

The relationship between the chemical structure of an IL's ions and its physicochemical properties and thermal phase behavior is complex. While it is possible to tune a specific property by adjusting the structure of the ions present in an IL, this change is always accompanied by changes in other properties, some of which may be undesirable. Specifically, increases in the IL ionic conductivity are often accompanied by an increase in the $T_m$ of the salt. Thus, other means of modifying the properties of ILs are worthy of consideration to overcome the limitations to the widespread adoption of IL-based electrolytes in EDLCs imposed by the relatively low conductivity and somewhat limited liquidus range of pure ILs.
References


Chapter 4: Ionic Liquid – Aprotic Solvent Mixtures

4.1 Introduction

One method that can be used to modify the properties of ILs is the addition of aprotic solvents. Such solvents have a long history of being used in many applications, including battery and EDLC electrolytes, which means that the solvent properties and behavior are well understood. The viscosity of aprotic solvents is orders of magnitude lower than that of pure ILs, so IL-solvent mixtures should be significantly less viscous than pure ILs. Furthermore, the aprotic solvents used for electrolytes generally solvate cations; thus the presence of solvent molecules decreases the Coulombic interactions between the ions. A lower interaction strength should increase the mobility of the ions, thereby increasing the conductivity. The presence of solvent molecules will also decrease the temperature at which some or all of the electrolyte will crystallize. Finally, aprotic solvents are generally relatively inexpensive, so the cost of IL-solvent mixtures may be lower than that of pure ILs.

Currently, the dielectric constant/permittivity of a solvent is widely utilized as a predictor of the solvation behavior of a solvent. A higher permittivity solvent should result in more solvated ions, which should lead to a lower viscosity and higher conductivity. Several studies have examined the effect that the addition of solvents has on the physicochemical properties of IL-solvent mixtures.¹⁻¹⁰ Common solvents used in these studies include water, chloroform, EA, dichloromethane, acetone, and AN. While the use of small amounts of solvent (20 mol%) has been shown to decrease the viscosity significantly (up to 50% reduction), this reduction is almost independent of the solvent chosen which has thus far suggested that the permittivity does not significantly influence the behavior of IL-solvent mixtures.¹⁻⁵ The
addition of solvents to ILs has been reported to significantly increase the conductivity.\textsuperscript{1,5-10} The highest measured conductivity for IL-solvent mixtures is consistently found for those containing AN ($\varepsilon_r = 38$), which has much lower permittivity when compared to other solvents such as propylene carbonate ($\varepsilon_r = 65$) or water ($\varepsilon_r = 80$). This discrepancy could be explained by the increasing association of the ions present in the ILs when solvent is added. Both PC and dichloroethane ($\varepsilon_r = 11$) appear to increase the association of $N_{122(201)}BF_4$ and $N_{122(201)}TFSI$,\textsuperscript{11} while the addition of water to IM$_{104}$PF$_6$ does not appear to promote or discourage ion association.\textsuperscript{12} Clearly, the interaction between an IL and a molecular solvent is complex.

An interesting discovery from the reported work with ILs and solvents suggests that the large, bulky ions comprising an IL behave in some ways very similarly to the lithium salts commonly used in electrolytes for batteries. Independent of the solvent or salt chosen, ionic conductivity maximums are observed in the 1-2 M concentration range.\textsuperscript{13,14} Conductivity below this concentration drops due to a scarcity of charge carriers. Above this concentration, ions are believed to begin to associate into neutral ion pairs, which reduces the effective concentration of ions available to conduct charge.

Given the limited ability to predict which solvents will serve as the optimal diluents/additives for ILs, it is important to better understand the links between IL-solvent properties and solvent/ion structure. Towards this end, solutions of common aprotic solvents and ILs were prepared and their physicochemical properties and thermal phase behavior studied.
4.2 Properties of PY$_{15}$TFSI -Solvent Mixtures

A single IL (i.e., PY$_{15}$TFSI) was selected for study with a large number of different solvents. The properties of the aprotic solvents used are noted in Table 4.1 with solvent structures being depicted in Fig. 4.1. The donor numbers (DNs) are very similar. This is likely due to the fact that all of the solvents (except AN) have a coordinating carbonyl group available. The density of the liquid solvents tends to be higher if the solvents are carbonates instead of esters, and if they are cyclic rather than acyclic. The permittivity of the solvents is uniformly low if the solvents are acyclic (whether esters or carbonates), intermediate for the

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<td>5.9$^b$</td>
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</tbody>
</table>
cyclic esters (GBL and GVL), and much higher for the cyclic carbonates (EC and PC). It is interesting to note that there is a significant difference in the permittivity of EC and PC which differ in structure only by the methyl group, whereas the difference between GBL and GVL is minor. The same general trends noted for permittivity are also found for viscosity, with higher permittivity solvents tending to have a higher viscosity (AN is the exception). Solvents with longer alkyl groups generally have a higher viscosity than those with shorter alkyl groups.

Figs. 4.2 and 4.3 show the thermal phase behavior of the IL mixtures with EC and EB, respectively. The IL-EC mixtures have simple eutectic solid-liquid phase behavior with a eutectic composition of about $x = 0.45$ (mol fraction of the solvent EC). A significant $T_m$ depression of approximately 25 °C is thus possible with the addition of a relatively small amount of solvent (an $x = 0.50$ composition corresponds to a 1/1 mole ratio of IL/solvent). The phase behavior of the IL with EB is somewhat different. Unlike EC which has a $T_m$ (37
°C) higher than that of the IL (11 °C), the \( T_m \) of EB is quite low (-97 °C). As EB is added to the IL, the IL melting peak decreases and shifts to lower temperature. A new peak is evident just below -50 °C, but this peak shifted depending upon how the samples were crystallized.
This is tentatively assigned to a solvate phase consisting of the IL and EB. It is possible that the shift in the $T_m$ for this phase actually corresponds to two different phases which may crystallize (a thermodynamically favored IL-solvent phase and an alternative kinetically formed phase with different solvent and ion packing, but perhaps the same composition). The addition of solvent to the IL substantially extends the temperature range over which the mixtures remain liquid. Other IL–solvent mixtures studied also have similar increases in liquid temperature range.

Fig. 4.4 shows the TGA results for the IL–solvent mixtures with either EC or AN. All of the EC and AN readily volatilize from the mixtures well before their normal boiling point ($T_b$)
leaving the pure IL which begins to decompose above 300 °C. The solvents in the mixtures are volatilized at a higher temperature, however, than for the pure solvents. This is likely due to a colligative effect as the surface of the liquids consists principally of non-volatile ions rather than solvent molecules. The data suggest that the ion-solvent interactions are relatively weak. An IL–solvent electrolyte may thus be constrained by similar volatility limitations as current organic salt-solvent electrolytes (i.e., 1 M AN-N\textsubscript{2222}BF\textsubscript{4}). These results
were obtained, however, with an open TGA sample pan with N₂ flow in the furnace. The DSC thermograms (Figs. 4.2 and 4.3), obtained with hermetically-sealed DSC pans, did not show any solvent evaporation up to 100 °C, which should also be the case in a sealed device.

The density variation of the mixtures is shown in Fig. 4.5. If the data is instead plotted vs. weight fraction (not shown), then linear variations are found between the pure IL and solvents, as expected. The excess molar volume (Vᵢ) determined from the density data is also shown in Fig. 4.5. The IL mixtures with the four cyclic solvents (i.e., EC, PC, GBL, and GVL) all have relatively small negative Vᵢ over the entire concentration range. This suggests that solvent molecules with little conformational flexibility do not impact the excess molar volume significantly. In contrast, the mixtures with acyclic solvents result in a much larger negative Vᵢ. A solvent's molecular volume has been correlated with the molecular polarizability. The polarizability values (Å³) for the acyclic solvents are: AN: 4.4, MA: 7.0, DMC: 7.6, MP: 8.8, EP: 8.8, EA: 8.9, MB: 10.7, DEC: 11.3 (and EC: 6.6, GBL: 7.9). This suggests that there may be a link between the molecular volume and Vᵢ for the flexible solvent molecules (although AN is not flexible).

Fig. 4.6 shows the viscosity data for the mixtures. A comparison of the data for x = 1 (neat solvents at 20 °C) indicates that there is reasonable agreement with the literature values given in Table 1 at 25 °C and these experimentally measured values. Even the addition of 5 mol% (x = 0.05) solvent results in a substantial decrease in the IL viscosity, especially at low temperature. Note that although EC is a solid at ambient temperature, the mixtures with EC remain liquid indefinitely at 20 °C up to 90 mol% (x = 0.90) EC. Over the entire concentration range, the tendency of the solvents to affect the viscosity remains relatively
constant. Some differences are noted, however, in the ordering for the acetates (i.e., MA and EA) and AN. The difference between the linear carbonates and linear esters decreases as \( x \) increases and the viscosity approaches that of the pure solvents.

**Figure 4.5** Density and excess molar volume of \((1-x)\) PY\(_{15}\)TFSI–\(x\) solvent mixtures at 20 °C (data for pure EC at 40 °C). The solvent to IL (S/IL) mole ratio is indicated at the top of the figure.
It has previously been noted that when considering the entire composition range between an IL and molecular solvent mixture, several different regimes may be distinguished.\textsuperscript{26,27} For the neat IL, only ions are present. If the cation has a relatively long (butyl or longer) linear alkyl chain, then the charged portions of the cations and anions tend to cluster leaving the uncharged alkyl chains aggregated together. In the present study, the IL cations have a pentyl alkyl chain. This length is approximately the point at which some interdigitation is first noted.\textsuperscript{28} But as solvent is added to an IL, the localized structuring of the ions is impacted. How a solvent molecule interacts with the ions depends upon both the structure of the solvent and its concentration. Nonpolar solvents interact principally with the alkyl chains of the cations, whereas polar solvents interact to a greater extent with the charged portions of the ions.\textsuperscript{27,29} For dilute salt concentrations, the solvent molecules far outnumber the ions; the ions thus become dispersed as the solvent molecules shield the ions from one another. The extent to which this shielding occurs is dependent upon the strength of the solvent-ion interactions. More polar solvents will therefore disperse the ions (reduce ion aggregation and correlated motion) to a greater extent than less polar solvents.

The variations in the viscosity may be linked with the solvent's structure. Upon the addition of solvent, the solvent both occupies space and interacts with the ions. As noted previously, the solvents utilized have comparable DN values (Table 4.1), but, due to steric hindrance about the positively charged nitrogen atoms of the cations, strong coordination between the solvent molecules and cations is not expected. Rather, the solvent molecules will direct the carbonyl oxygen atom's (or AN nitrogen atom's) electron lone-pair(s) toward these charge centers without the formation of coordination bonds (as occurs for the solvation of
alkali metal cations). The permittivity of the solvent may thus be more relevant than the DN for understanding property variations. Addition of the acyclic carbonates (i.e., DMC and DEC), which have the lowest permittivity values (Table 4.1), results in a lower viscosity

![Figure 4.6 Viscosity of (1-x) PY$_{15}$TFSI–(x) solvent mixtures at 20 °C. Bottom plots are expanded sections from the top plot.](image-url)
reduction than the acyclic esters. Surprisingly, however, the cyclic carbonate (i.e., EC and PC), followed by the cyclic ester (i.e., GBL and GVL), solvents have the highest permittivity values, but also the lowest reduction in the viscosity. Other factors than permittivity which are likely critical are the size/shape of the solvent, its conformational flexibility and the number of electron lone-pairs. The latter will have repulsive interactions with anions (and other solvent molecule electron lone-pairs) and may, in addition, result in increased (attractive) interactions between a given solvent molecule and multiple neighboring cations (if multiple electron lone-pairs are available). Both of these effects will increase the energy barriers for the ions to rearrange themselves (rotational and translational motion) when subjected to shear stress. Notably, AN has a comparable permittivity to that of the cyclic esters, but results in a much lower viscosity. This is perhaps surprising as the small size would be expected to disrupt (shield) the ion-ion interactions to a lesser extent than for the larger solvent molecules. But AN also has only a single electron lone-pair which may therefore result in lower barriers to ion mobility in its vicinity than for the cyclic esters. Multiple factors evidently influence the role that the solvent plays in the viscosity variations of the mixtures.

Fig. 4.7 shows the ionic conductivity of the mixtures with AN, DMC, GVL, PC, EA, and EP. Several points are notable. For low $x$ values (IL-rich compositions), despite the relatively large differences in viscosity found based upon solvent structure, only minor differences in the conductivity are noted for the different solvents. For higher $x$ values (solvent-rich compositions), variability in the conductivity is found for the different solvents, but this does not correlate well with the viscosity differences noted in Fig. 4.6. A maximum is found for
Figure 4.7 Conductivity of (1-x) PY$_{15}$TFSI–(x) solvent mixtures vs. mole fraction of solvent at 20 °C and 70 °C - data for the pure IL are on the left.

the mixtures between 1.2 and 2.0 M IL concentration (Fig. 4.7 and Appendix B), which is similar to the behavior of traditional organic salt-solvent electrolytes. The peak is generally attributed to an increased conductivity due to an increase in the number of charge carriers (upon salt addition to the pure solvent). A further increase in the salt concentration (reduction in x), however, results in a decrease in the conductivity due to increased ion-ion interactions (i.e., ionic association). The peak shifts to more dilute solutions (higher x values) for the most conductive mixtures. The variation may be linked to both the solvent's permittivity and viscosity, with the latter seemingly being more of a factor, as the addition of DMC (low $\varepsilon$ and
η) results in a somewhat higher conductivity than for GVL (high ε and η), whereas the addition of AN (high ε and low η) results in a dramatic improvement in the conductivity.

The molar conductivity, Λ (S cm² mol⁻¹), is defined as the conductivity, σ (S cm⁻¹), divided by the salt concentration, C (mol dm⁻³): Λ = σ/C. This is a form of normalization of the conductivity in terms of the number of charge carriers. A plot of the molar conductivity (Fig. 4.8) shows very interesting variations for the mixtures. It is worth recalling that the mixtures consist of the same salt (i.e., charge carriers), but different solvents. In particular, in the dilute concentration region (high x), the molar conductivity of the AN mixtures rapidly increases, even though the conductivity itself decreases (Fig. 4.7). This is because the salt
(i.e., charge carrier) concentration decreases more rapidly than the conductivity for the AN mixtures. The same trend, although to a lesser extent, is noted for the cyclic solvents GVL and PC. This is not the case, however, for the mixtures with the acyclic carbonate and ester solvents (i.e., DMC, EA, and EP). For the latter mixtures, the molar conductivity peaks as the mixtures become more dilute and then decreases upon further dilution (increasing $\chi$).

Explanations for the noted behavior are not immediately evident from the available experimental data, but a computational MD simulation analysis is underway with a collaborator to aid in discerning the origin of the results. Preliminary work indicates excellent agreement for the calculated viscosity and conductivity data with the experimental results (Fig 4.9). In particular, for the dilute (high $\chi$) concentrations, the viscosity of IL-AN and -DMC mixtures is similar, whereas that of PC mixtures is much higher (as found experimentally in Fig. 4.6). The simulations also indicate that the conductivity of the

![Figure 4.9 Comparison of MD simulation and experimental results for (1-$\chi$) PY$_{15}$TFSI-$\chi$ solvent mixtures at 60 °C.](image)
mixtures is similar for low $x$ compositions. The DMC mixtures have a slightly higher calculated conductivity than the PC mixtures near the peak at $x = 0.7$ and 0.8, but this is reversed with the PC mixtures being more conductive than the DMC mixtures for the $x = 0.9$ composition (as found experimentally in Fig. 4.7). The AN mixtures are found to be much more conductive than the PC and DMC mixtures (also as found experimentally in Fig. 4.7). The simulations further indicate that the degree of ion correlated motion (i.e., tendency for ionic aggregation/clustering)\(^{26,27}\) is an important factor for the property variations as, for the high $x$ compositions, the DMC mixtures have significant correlated motion which is not the case for the AN and PC mixtures (Fig. 4.10). Thus, the AN mixtures display a remarkable conductivity (Fig. 4.8) because both the ion-ion interactions are reduced/weakened and the mobility of the constituent species is high (as exemplified by the low viscosity). In contrast,
although the PC mixtures also have reduced ion-ion interactions, the mobility of the species is much lower than for the AN mixtures (i.e., a much higher viscosity), whereas for the DMC mixtures, the mobility is relatively high, but the solvent does not effectively break up the ion clusters (i.e., there is significant ion correlated motion).

4.3 Properties of Other IL-Solvent Mixtures

To study the effect IL structure has on the interaction between solvents and ILs, mixtures of solvent and either PI$_{15}$TFSI or MO$_{15}$TFSI were prepared. The density of these mixtures (Fig. 4.11) exhibits similar behavior to that of the PY$_{15}$TFSI mixtures, with only small decreases in density observed at low mole fractions of solvents and large decreases observed in the solvent-rich region. MO$_{15}$TFSI is more dense than PI$_{15}$TFSI, which results in mixtures that are more dense than corresponding PI$_{15}$TFSI mixtures, even in solvent-rich regions. When excess molar volume is examined for each mixture (Fig. 4.11), the general behavior of these mixtures (i.e., magnitude of deviation from ideality, composition at which maximum deviation occurs) is very similar to that of the PY$_{15}$TFSI mixtures. One difference is the presence of a small composition region around 5 mol% solvent in PI$_{15}$TFSI where positive values are measured for $V^E$. The magnitude of these deviations is small, suggesting that this may perhaps be explained by a small amount of the solvent (already at a low concentration) evaporating from the mixture during sample preparation or testing.

Values for the viscosity of the PI$_{15}$TFSI- and MO$_{15}$TFSI-solvent mixtures at 20 °C are shown in Fig. 4.12. Even small amounts of solvent result in large reductions in the viscosity, with the relative magnitude of the variations corresponding well to those found for the
Figure 4.11 Density and excess molar volume of (1-x) IL–(x) solvent mixtures at 20 °C. The solvent to IL (S/IL) mole ratio is indicated at the top of the figure.

PY$_{15}$TFSI-solvent mixtures. Once again, AN results in the greatest reduction in the IL-poor region. MO$_{15}$TFSI is substantially more viscous than PI$_{15}$TFSI, but the solvent-rich mixtures with these two ILs have very similar viscosity values. A priori, the presence of an ether group (and repulsive electron lone-pairs) on the MO$_{15}^+$ ring structure should affect how solvent
molecules solvate the cation. Substantial differences are found for the PI\textsubscript{15}TFSI- and MO\textsubscript{15}TFSI-DMC mixtures up until the solvent-rich (i.e., $x > 0.8$) compositions.

The ionic conductivity of the PI\textsubscript{15}TFSI- and MO\textsubscript{15}TFSI-solvent mixtures is reported in Fig. 4.13. Consistent with the PY\textsubscript{15}TFSI work, mixtures containing AN had, by far, the

**Figure 4.12** Viscosity of (1-$x$) IL–($x$) solvent mixtures at 20 °C. Bottom plots are expanded sections from the top plots.
highest conductivity. Mixtures containing DMC had very similar values for conductivity, with the mixtures with PI\textsubscript{15}TFSI having a slightly higher conductivity than those containing MO\textsubscript{15}TFSI (Fig. 4.13), but lower than those with PY\textsubscript{15}TFSI (Fig. 4.7). Once again, maximum values for conductivity are observed in the 1-2 M region. When the molar conductivity of these mixtures is examined (Fig. 4.14), the PI\textsubscript{15}TFSI-AN mixtures have maximum values that are slightly lower than those for the PY\textsubscript{15}TFSI-AN mixtures (Fig. 4.8), perhaps due to the larger size of the PI\textsuperscript{15}\textsuperscript{+} cation resulting in lower ion mobility. The data suggest that the trends in conductivity noted for the pure ILs (i.e., PY\textsubscript{15}TFSI > PI\textsubscript{15}TFSI > MO\textsubscript{15}TFSI) persist for the mixtures, even for the solvent-rich compositions.

Figure 4.13 Conductivity of (1-x) IL–(x) solvent mixtures vs. mole fraction of solvent at 20 °C and 70 °C - data for the pure ILs are on the left.
4.4 Conclusions

The addition of aprotic solvents to ILs greatly decreases the viscosity of a given IL and, up to a certain mole fraction of solvent, increases the conductivity. Furthermore, the addition of solvent can greatly increase the temperature range over which the mixtures remain liquids. The solvent and IL do not appear to interact strongly, however, so that the volatile solvent readily evaporates at elevated temperature. These changes in properties appear to be largely independent of the structure and nature of the ILs used (with TFSI anions). Thus, the properties of the IL-solvent mixtures can be tuned significantly with a judicious choice of both the solvent and the composition (as well as the IL).
References


Chapter 5: Ionic Liquid – Ionic Liquid Mixtures

5.1 Introduction

Mixing two or more ILs together offers an alternative means of modifying the properties of an electrolyte other than changing the structure of the IL or adding a volatile organic solvent. The presence of smaller, potentially more mobile, ions in an IL generally corresponds to an increased ionic conductivity and lower viscosity (Chapter 1). ILs containing smaller ions, however, often also crystallize at higher temperatures (Chapter 3). In contrast, ILs with large, asymmetric ions generally have a low $T_m$, as the presence of such ions results in unfavorable packing of the ions in the crystal lattice.\(^1\) An IL\(_1\)-IL\(_2\) mixture consisting of both small and large ions could thus potentially have the most favorable properties (high ionic conductivity and a wide liquidus range) of the constituent ILs.

There have been a number of studies that investigated the dissolution of salts into various ILs. One study, using changes in equilibrium redox potentials, examined deviations from ideal solution behavior when high melting silver salts (AgX) with three anions (Cl\(^-\), thiocyanate, or acetate) were dissolved into an IL composed of IM\(_{102}^+\) cations and the same anion present in the silver salt.\(^2\) Given the high $T_m$ for each silver salt, and the abundance of anions present, it might be assumed that the Ag\(^+\) cations would be strongly associated with anions. Instead, these mixtures were found to behave similarly to dilute (ideal) mixtures of salts in molecular solvents, as the Ag\(^+\) cations were largely unassociated. Similar results have been shown for mixtures containing two IM\(_{10R}BF_4\) salts.\(^3\) IR spectroscopy studies of iodide salts dissolved in IM\(_{104}BF_4\) or IM\(_{104}TFSI\) suggest that the ions do not form ion pairs\(^4\) and remain well-mixed even on the nanoscale level.\(^5\) This differs from the idea proposed in
several papers which suggest that, even in a pure IL, ion pairs are formed.\textsuperscript{6-8} One potential limiting factor for mixtures composed of two or more different ILs is immiscibility or phase separation. Several studies examined immiscible IL\textsubscript{1}-IL\textsubscript{2} combinations and found that significant structural differences (e.g., tetraalkylphosphonium cations with long (> 10 carbon) alkyl chains and IM\textsubscript{10R}\textsuperscript{+} with short alkyl chains) are required for ILs to phase separate.\textsuperscript{9-11} The ability of ILs to dissolve a variety of high melting salts and the significant structural differences required for two ILs to be mutually immiscible suggest that it should be possible to prepare a variety of homogenous mixtures containing common ILs for characterization as potential electrolytes.

Several studies have investigated the properties of mixtures composed of two different ILs. Most work has focused on mixed anions, with mixtures of FSI/TFSI\textsuperscript{12-14} and TFSI/(trifluoromethanesulfonyl)(nonafluorobutanesulfonyl)imide (IM\textsubscript{14}),\textsuperscript{1,15} although the effect of mixed alkyl chain lengths on the cation\textsuperscript{13} and mixed cations\textsuperscript{12} has also been investigated. The anion structure is believed to be the most significant factor in determining the thermal phase behavior of a pure IL and it seems likely that this would carry over into a mixed system.\textsuperscript{13,16} Mixtures containing two slightly different anions (e.g., FSI\textsuperscript{−} and TFSI\textsuperscript{−}) with the PY\textsubscript{13}\textsuperscript{+} cation experience a $T\textsubscript{m}$ depression of up to 30 °C.\textsuperscript{13,14} When an asymmetric anion, like IM\textsubscript{14}\textsuperscript{−}, is added to a TFSI\textsuperscript{−} salt, a large amorphous composition range is observed, as mixtures with more than 20 mol\% of the IM\textsubscript{14}\textsuperscript{−} salt have no observable $T\textsubscript{m}$.\textsuperscript{1} In addition to mixing anions, the presence of multiple types of cations increases the liquidus range of an IL. The length of the alkyl chain on the cation has a large effect on the crystal structure for an IL,\textsuperscript{17} and thus the presence of different alkyl chain lengths can serve to frustrate crystallization. The
liquidus range of equimolar mixtures containing the PY$_{13}^+$ and PY$_{14}^+$ cations with either FSI$^-$ or TFSI$^-$ is over 20 °C greater compared to the neat ILs.$^{13}$ Some work has been done studying the effects of mixing different cation head groups, but the groups (PI$_R^+$ and PY$_R^+$) often have different alkyl chain lengths, making it difficult to separate the effect of mixed alkyl chain lengths from mixed cation head groups.$^{12}$ Overall, the addition of a second IL to another induces defects into the crystal structure resulting in lower $T_m$ for the mixtures if the mixture crystallizes or may inhibit crystallization altogether.

Phase behavior is not the only property that can be modified through the mixing of two ILs. Increasing the mobility of the charge carriers (ions) in an IL could enhance the performance of electrochemical devices.$^{18}$ Thus, knowing what effect mixing ILs will have on two potential indicators of ion mobility (viscosity and ionic conductivity) would greatly aid in the ability to tailor binary IL$_1$-IL$_2$ mixtures. In general, the viscosity$^{3,19}$ and conductivity$^{14}$ of mixtures of ILs appear to have little deviation from the values that would be predicted using an ideal log mean mixing rule (Eq. 1), where $\eta$ is the property of interest and $x_i$ is the mole fraction of each component.

$$\ln(\eta_{mix}) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) \quad (1)$$

While knowing that ideal mixing rules work well for mixtures of two ILs that are each liquid at the temperature of interest is useful, many salts that are desirable for use in electrochemical applications are solid in their pure state (e.g., BF$_4^-$ salts). As the viscosity of a solid cannot be measured and the ionic conductivity of a solid is orders of magnitude lower
than that of liquids, log mean mixing rules are no longer applicable. A survey of the literature does not reveal any proposed means of predicting the properties of these IL-salt mixtures.

The limited work that has been performed on mixtures containing multiple ILs indicates that such mixtures may be promising candidates for use as electrolytes. The lack of a general understanding of how the properties of the constituent ILs affect the properties of the mixtures, however, is a significant obstacle to tailoring such mixtures for a specific application. To quantify the mixing behavior of ILs, three types of mixtures (PY$_{1r}^+$ cations with mixed alkyl chain lengths, mixed cation head groups, and mixed anions) have been prepared and studied.

5.2 Properties of Mixed ILs Containing Different Cation Alkyl Chain Lengths

A logical place to start when examining IL$_1$-IL$_2$ mixtures would be to study mixtures sharing both the same anion and cation head group, but differing in the length of the alkyl chains on the cation head group. The length of this alkyl chain has a significant effect on the properties of a given IL, allowing ILs with very different physicochemical properties and phase behavior to be chosen, while still retaining single phase solutions. Mixtures of PY$_{11}$TFSI-PY$_{14}$TFSI, PY$_{11}$TFSI-PY$_{15}$TFSI, PY$_{12}$TFSI-PY$_{13}$TFSI, PY$_{12}$TFSI-PY$_{14}$TFSI, PY$_{12}$TFSI-PY$_{15}$TFSI, and PY$_{13}$TFSI-PY$_{15}$TFSI were therefore chosen to be studied.

The addition of a salt with a smaller cation with shorter alkyl chains, such as PY$_{11}^+$, PY$_{12}^+$, or PY$_{13}^+$, to an IL with a longer alkyl chain on the cation, such as PY$_{13}$TFSI, PY$_{14}$TFSI, PY$_{15}$TFSI, results in mixtures with a density higher than that of the pure IL (Fig. 5.1). The density values of such mixtures agree well with those predicted by an ideal mixing
Figure 5.1 Density, viscosity, and ionic conductivity for (1-x) IL₁-(x) IL₂ mixtures containing different cation alkyl chain lengths at 60 °C.
model with additive behavior observed in all cases. Higher density, coupled with a lower average molecular weight, means that the IL$_1$-IL$_2$ mixtures have a higher concentration of charge carriers relative to the original neat IL (with the longer alkyl chain)—this increase may, however, be modest if the ions are similar in size (i.e., PY$_{12}$TFSI-PY$_{13}$TFSI mixtures).

The viscosity data for the IL$_1$-IL$_2$ mixtures at 60 °C are shown in Fig. 5.1. In mixtures containing PY$_{11}$TFSI and either PY$_{14}$TFSI or PY$_{15}$TFSI, as well as mixtures of PY$_{12}$TFSI and PY$_{13}$TFSI, the viscosity increases with the concentration of the smaller IL. However, when PY$_{12}$TFSI is added to PY$_{14}$TFSI or PY$_{15}$TFSI, the viscosity remains constant or slightly decreases with increasing PY$_{12}$TFSI. Both PY$_{11}$TFSI ($T_m = 133$ °C) and PY$_{12}$TFSI ($T_m = 90$ °C) are solid at 60 °C, which prevents the measurement of their viscosity at this temperature. However, the behavior of the mixtures can be well modeled over the studied concentrations by assigning 'effective' viscosity values to PY$_{11}$TFSI or PY$_{12}$TFSI, respectively, and incorporating these values into an ideal mixing model. The effective viscosity value at 60 °C for PY$_{11}$TFSI is then about 27 mPa s, while PY$_{12}$TFSI has a value close to that of pure PY$_{14}$TFSI, or 21 mPa s. When PY$_{13}$TFSI is added to PY$_{15}$TFSI, the viscosity of the resulting mixtures again displays ideal mixing behavior. Given the structural similarity and weakly interacting nature of the ions in the ILs used, such ideal behavior is not surprising.

The conductivity for the IL$_1$-IL$_2$ mixtures at 60 °C is shown in Fig. 5.1. Given that the addition of smaller cations to the salt mixtures modifies both the density (charge carrier concentration) and the viscosity (charge mobility since the mixtures are composed solely of ions), changes to the conductivity of such mixtures are expected, but whether the conductivity will be higher or lower is not clear \textit{a priori}. When PY$_{11}$TFSI is added to
PY$_{14}$TFSI, the conductivity of the mixtures is roughly constant. However, when the same salt is added to PY$_{15}$TFSI, a significant increase in conductivity is observed. As with the viscosity behavior, the changes in conductivity to these two systems can be modeled with an ideal mixing model and an effective conductivity value for the PY$_{11}$TFSI of approximately 11 mS cm$^{-1}$. The behavior of mixtures containing PY$_{12}$TFSI can be modeled by assigning an effective conductivity value of approximately that of pure PY$_{13}$TFSI, or 12 mS cm$^{-1}$, to PY$_{12}$TFSI. Thus, the addition of PY$_{12}$TFSI to PY$_{13}$TFSI does not result in mixtures with increased conductivity, but when PY$_{12}$TFSI is added to PY$_{14}$TFSI or PY$_{15}$TFSI, a significant increase in conductivity occurs. Mixtures of PY$_{13}$TFSI and PY$_{15}$TFSI, both liquid at 60 °C, exhibit a conductivity that is consistent with an ideal mixing model. The addition of a smaller cation to an IL electrolyte will therefore generally increase the conductivity of the system, but it is unclear why the PY$_{11}$TFSI salt has a lower effective conductivity than PY$_{12}$TFSI.

DSC heating traces for each combination of ILs are shown in Fig. 5.2. When PY$_{11}$TFSI is added to PY$_{14}$TFSI, a new phase appears to form with a $T_m$ of 33 °C. The $T_m$ for the PY$_{14}$TFSI salt is also slightly depressed. This may correspond to the formation of a eutectic between the PY$_{14}$TFSI salt and mixed salt phase. The peak at 68 °C noted for the $x = 0.50$ sample is likely due to the crystallization of a small amount of the neat PY$_{11}$TFSI phase. Note that the presence of the peaks at -11, 33, and 68 °C suggests that this sample was not in thermodynamic equilibrium. Despite extensive efforts to homogenize the sample during the crystallization procedure by fully melting the mixture, quenching to low temperature and crystallizing using a variety of thermal protocols, similar thermal heating traces were obtained for the $x = 0.50$ sample for the PY$_{11}$TFSI-PY$_{14}$TFSI mixtures. For the PY$_{15}$TFSI
Figure 5.2 DSC heating traces of (1-\(x\)) IL\(_1\)-(\(x\)) IL\(_2\) mixtures.
mixtures with PY\textsubscript{11}TFSI, three new peaks are observed at about 18, 49, and 70 °C. As with the PY\textsubscript{11}TFSI-PY\textsubscript{14}TFSI, the presence of these peaks suggests that this sample was not in thermodynamic equilibrium. The 49 °C peak may correspond to a new mixed salt phase (with the small peak evident at about 6 °C for the $x = 0.30$-$0.50$ samples perhaps attributed to a solid-solid phase transition for the mixed-salt phase), whereas the peak at 18 °C may again be due to a eutectic between this phase and the PY\textsubscript{15}TFSI salt (or instead due to a new mixed salt phase). Note that a single crystal was extracted from the $x = 0.40$ mixture at room temperature and confirmed to be the PY\textsubscript{11}TFSI phase via unit cell determination from x-ray diffraction.

Notably, none of the PY\textsubscript{11}TFSI-PY\textsubscript{14}TFSI or PY\textsubscript{11}TFSI-PY\textsubscript{15}TFSI compositions has a $T_m$ that is significantly lower than that of the pure PY\textsubscript{14}TFSI or PY\textsubscript{15}TFSI salts, nor do the mixtures of PY\textsubscript{12}TFSI-PY\textsubscript{13}TFSI have a $T_m$ lower than that of the neat PY\textsubscript{13}TFSI. For the latter mixtures, the ions are similar in size, so it may be that the PY\textsubscript{12}\textsuperscript{+} cations can be incorporated into the lattice of the crystalline PY\textsubscript{13}TFSI salt, but such cationic defects would likely decrease the $T_m$ for the crystalline phase rather than increase it. For the $x = 0.40$ and 0.50 samples, a new peak is evident which likely corresponds to the formation of some crystalline PY\textsubscript{12}TFSI.

The addition of PY\textsubscript{12}TFSI to PY\textsubscript{14}TFSI differs from other reported mixtures containing PY\textsubscript{11}TFSI or PY\textsubscript{12}TFSI, as a 10 mol% PY\textsubscript{12}TFSI mixture ($x = 0.10$) has a $T_m$ that is 9 °C lower than that of pure PY\textsubscript{14}TFSI. This is a significant increase in the liquidus range. However, at concentrations above 10 mol% PY\textsubscript{12}TFSI, a higher melting phase is evident. The significant variance in the $T_m$ between the $x = 0$ (neat PY\textsubscript{14}TFSI) and $x = 0.10$ samples is
attributed to the ‘kinetic’ phase which has been reported for the PY\textsubscript{14}TFSI salt (a competing polymorphic phase which can form instead of the higher melting phase, depending upon the thermal history of the salt).\textsuperscript{20} Thus, the inclusion of some PY\textsubscript{12}TFSI appears to stabilize this kinetic phase, whereas the inclusion of PY\textsubscript{11}TFSI does not. The formation of a polymorphic phase for PY\textsubscript{13}TFSI may also account for the slight increase in the \(T_m\) for the mixtures with some PY\textsubscript{12}TFSI, as it was also noted that the PY\textsubscript{13}TFSI salt may also form a kinetic phase.\textsuperscript{20}

The behavior of mixtures of PY\textsubscript{12}TFSI and PY\textsubscript{15}TFSI has some similarities with that of the PY\textsubscript{11}TFSI analogues, as the \(T_m\) of the mixtures is only slightly lower than that of the pure PY\textsubscript{15}TFSI. However, only a single phase is observed crystallizing over a much wider range of concentrations, with a higher melting phase not being observed until 40 mol\% PY\textsubscript{12}TFSI. This extended window of single phase behavior could be due to frustrated crystallization from the presence of ILs with very different crystal structures.

The final mixture studied, PY\textsubscript{13}TFSI and PY\textsubscript{15}TFSI, shows different behavior from that of the five previously discussed mixtures. At 70 mol\% PY\textsubscript{13}TFSI, the \(T_m\) is 20 °C less than either pure IL. The minimum occurs at a higher concentration of the shorter chain containing IL than for the other studied systems. This is likely due to the similar \(T_m\) of each IL. There is also a significant region (30 to 50 mol\% PY\textsubscript{13}TFSI) where only a single melting peak is observed. An increase in the liquid temperature range of an IL-based electrolyte can therefore be obtained via the addition of a second cation. The salt that is added, however, must have a \(T_m\) that is not too much greater than that of the first IL. Furthermore, the two cations need to have enough structural variation to frustrate crystallization.
5.3 Properties of Mixed ILs Containing Different Cation Head Groups

Given that small structural changes to the cation head group often result in significant changes in the physicochemical properties of an IL, it seems likely that IL$_1$-IL$_2$ mixtures with cations with different head groups could have properties that vary greatly from those of the pure constituent ILs. To study the effect that the different cations have on mixture properties, mixtures of PY$_{13}$TFSI-PI$_{13}$TFSI and PY$_{13}$TFSI-MO$_{13}$TFSI were prepared. In addition, mixtures of N$_{2222}$TFSI and PY$_{14}$TFSI were studied to examine the effect of mixing acyclic cations with cyclic cations has on the mixture properties.

The density of mixtures of PY$_{13}$TFSI and PI$_{13}$TFSI (Fig. 5.3) is almost identical to what would be predicted by an additive model, with deviations being less than 1%. As the less dense PI$_{13}$TFSI is added, the density of the mixture decreases linearly with increasing mole fraction of the salt. Given the strong similarity between the two ILs in structure and the lack of any exotic moieties, such ideality is not surprising. Furthermore, given the close molecular weights of the two ILs and the small difference in the density of the salts, the concentration of ions is roughly constant between all compositions.

Mixtures of PY$_{13}$TFSI and MO$_{13}$TFSI (Fig. 5.3) exhibit the same ideality as the PI$_{13}$TFSI mixtures, with deviations from ideality being much less than 1%. The presence of the ether group on the cation might be expected to cause mixtures containing MO$_{13}$TFSI to behave differently than those containing PI$_{13}$TFSI. As the denser MO$_{13}$TFSI is added, the density of the mixture increases linearly with mole fraction. MO$_{13}$TFSI is much denser than PI$_{13}$TFSI, so the change in density of MO$_{13}$TFSI containing mixtures is much larger than the corresponding mixtures containing PI$_{13}$TFSI.
Figure 5.3 Density, viscosity, and ionic conductivity for (1-x) IL$_1$-(x) IL$_2$ mixtures with ILs containing different cations at 20 °C and 60 °C.
When N$_{2222}$TFSI is added to PY$_{14}$TFSI, no change in density is observed (Fig. 5.3). N$_{2222}$TFSI is a solid at the studied temperatures, making the prediction of liquid mixture density with an ideal model impossible. However, the slight increase in density at 20 °C and 50 mol% N$_{2222}$TFSI is likely due to partial crystallization of N$_{2222}$TFSI (Fig. 4), which suggests that the IL is more dense than PY$_{14}$TFSI. Thus, the unchanging density of the mixtures is surprising. N$_{2222}$TFSI is a slightly smaller (by a methylene group) cation with lower molecular weight and greater conformation freedom. This suggests that this cation should be able to pack more efficiently, which should lead to higher density. Why this is not observed is both surprising and unclear. Finally, the very similar molecular weight of the two ILs and constant density means that the concentration of ions is roughly the same at all compositions.

The viscosity values for the mixtures of PY$_{13}$TFSI and PI$_{13}$TFSI (Fig. 5.3) correspond well with those predicted by ideal mixing. Maximum deviation is less than 1% from the predicted values. The addition of the more viscous PI$_{13}$TFSI results in mixtures with a viscosity greater than that of pure PY$_{13}$TFSI. Mixtures of PY$_{13}$TFSI and MO$_{13}$TFSI also exhibit near ideal behavior, with similarly low deviations from the predicted values. As MO$_{13}$TFSI is much more viscous than PI$_{13}$TFSI, these mixtures exhibit a much larger increases in viscosity.

As with the density, the addition of N$_{2222}$TFSI to PY$_{14}$TFSI (Fig. 5.3) does not noticeably change the viscosity from that of pure PY$_{14}$TFSI. This is surprising, as the addition of high melting salts (e.g., PY$_{11}$TFSI or PY$_{14}$BF$_4$) to other ILs results in large increases in the viscosity. The viscosity of an IL is significantly affected by the Coulombic interactions.
between the cations and anions, which suggests that the degree to which the alkyl chains on the N\textsubscript{2222}\textsuperscript{+} and PY\textsubscript{14}\textsuperscript{+} cation shield the charged nitrogen atoms are similar. At 20 °C and a 1:1 molar ratio, an increase in viscosity is observed, which is due to the partial crystallization of the sample.

The conductivity of the studied mixtures at 20 °C and 60 °C is shown in Fig. 5.3. Pure PY\textsubscript{13}TFSI is more conductive than PI\textsubscript{13}TFSI, which is, in turn, more conductive that MO\textsubscript{13}TFSI. The mixtures of PY\textsubscript{13}TFSI-PI\textsubscript{13}TFSI show values for conductivity that are near those predicted using an ideal log mixing model, with mixture conductivity decreasing as the concentration of PI\textsubscript{13}TFSI is increased. Given the near ideal mixing behavior noted for the density and viscosity, having the conductivity also exhibit ideal behavior is not surprising.

Mixtures of PY\textsubscript{13}TFSI and MO\textsubscript{13}TFSI deviate slightly from ideal behavior, having real conductivity values that are greater than would be predicted, with maximum deviation occurring at a 1:1 molar ratio. The magnitude of the difference from the predicted values decreases with increasing temperature. The addition of the PY\textsubscript{13}\textsuperscript{+} cation may serve to increase the separation of the ether electron lone-pairs on the MO\textsubscript{13}\textsuperscript{+} cation, and thus decrease the repulsions that the lone-pairs exert on each other. This serves to decrease the energy barrier to ion movement, and thus decrease the viscosity. At higher temperature, the greater kinetic energy of the ions would obviate some of the hindrance to ion motion from energy barriers induced by such repulsive interactions, which means that the addition of the PY\textsubscript{13}\textsuperscript{+} cation does not have as significant of an effect on the conductivity of the mixture as at lower temperature. The conductivity decreases rapidly with increasing concentration of the much
less conductive MO$_{13}$TFSI. For the mixtures with higher concentrations of MO$_{13}$TFSI, partial or complete crystallization leads to large decreases in the conductivity at low temperatures.

As with the density and viscosity, the values of conductivity for the mixtures of N$_{2222}$TFSI and PY$_{14}$TFSI (Fig. 5.3) are nearly identical to the conductivity of pure PY$_{14}$TFSI, with the exception of the partially crystallized 50 mol% sample at 20 °C. As ionic conductivity is determined largely by the movement of ions in response to an applied potential, this once again suggests that the degree of shielding of the charged nitrogen atoms (and thus the ion-ion interactions) in both N$_{2222}^+$ and PY$_{14}^+$ is similar.

DSC heating traces for the three sets of mixtures are shown in Fig. 5.4. When PY$_{13}$TFSI is added to PI$_{13}$TFSI, a moderate depression in the $T_m$ of the mixtures occurs, with a maximum decrease occurring at a 1:1 molar ratio. The magnitude of this decrease is not large though, as the $T_m$ of a 50 mol% mixture is only 15 °C less than that of the pure ILs. While the smaller size of the PY$_{13}^+$ cation and the shared anion between the two ILs suggest that the PY$_{13}^+$ cation should easily fit into the crystal lattice of PI$_{13}$TFSI, the presence of any impurity in a material will increase the size of the driving force needed for crystallization to occur. No higher melting phase is observed, suggesting that these two ILs remain well-mixed for a variety of concentrations and temperatures. The broader melting peaks observed in binary mixtures is also indicative of the melting phase containing impurities/defects.

In contrast to PY$_{13}$TFSI or PI$_{13}$TFSI, MO$_{13}$TFSI has a much higher $T_m$ (42 °C), due to the presence of an ether group on the cation head group resulting in a different mode of ion packing. Similarly to the PY$_{13}$TFSI-PI$_{13}$TFSI mixtures, the maximum $T_m$ depression occurs for the PY$_{13}$TFSI-rich mixtures, at approximately 80 mol%. The high $T_m$ of the pure
Figure 5.4 DSC heating traces (5 °C min⁻¹) for (1-x) IL₁-(x) IL₂ mixtures with ILs containing different cations.
MO$_{13}$TFSI leads to the minimum $T_m$ of the mixtures being only approximately 10 °C less than that of pure PY$_{13}$TFSI, but this is 40 °C less than pure MO$_{13}$TFSI. Unlike what is found for the PY$_{13}$TFSI-PI$_{13}$TFSI mixtures, classic eutectic behavior is observed for the MO$_{13}$TFSI-containing mixtures, with a eutectic phase with a $T_m$ of approximately 7 °C forming. The presence of the ether group in the ring of the MO$_{13}^+$ cation apparently provides enough structural variation that the two cations are not readily incorporated into the crystal lattices of the pure ILs. This suggests that larger changes in cation structure can have an effect comparable to that of the anion on the phase behavior of mixtures.

The addition of N$_{2222}$TFSI to PY$_{14}$TFSI results in a maximum $T_m$ depression of about 10 °C. The -17 °C peak is likely composed of nearly pure PY$_{14}$TFSI, as the $T_m$ is constant regardless of the composition. The size of the peaks does decrease, indicating that the abundance of this phase is decreasing. Unlike PY$_{13}$TFSI, PY$_{14}$TFSI is polymorphic and slow to crystallize. Thus, a 10 °C depression for PY$_{14}$TFSI is much less significant than a 15 °C depression for the PY$_{13}$TFSI containing mixtures. The relatively high $T_m$ of pure N$_{2222}$TFSI suggests that the formation of crystalline N$_{2222}$TFSI is energetically favorable, and thus a strong driving force exists for a higher melting phase to form. This higher melting phase is observed in the 40 and 50 mol% samples.

5.4 Properties of Mixed ILs Containing Different Anions

The viscosity of a liquid is strongly dependent upon the interactions between the molecules/ions present (Fig. 5.5). The BF$_4^-$ anion is smaller than either the FSI$^-$ or TFSI$^-$ anions, which results in less shielding of the negative charge.$^{21}$ Furthermore, the smaller size
Figure 5.5 Density, viscosity, ionic conductivity, and molar conductivity for (1-\(x\)) IL\(_1\)-(\(x\)) IL\(_2\) mixtures with ILs containing different anions at 20 °C and 60 °C.
allows for the BF$_4^-$ anion to more closely approach the cations. Both of these attributes result in increased electrostatic interactions between the anions and cations, which increases the energy barriers to ion mobility, as evidenced by increased viscosity. The larger size of the TFSI$^-$ anion may result in increased steric hindrance, which leads to a higher viscosity for pure PY$_{14}$TFSI as compared to PY$_{14}$FSI, but also limits how closely the PY$_{14}^+$ cations pack together. Greater separation of the cations reduces the electrostatic interactions, thus reducing the resistance to ion motion and viscosity.

The addition of BF$_4^-$ anions to PY$_{14}$FSI results in large changes in the value of the molar conductivity as compared to pure PY$_{14}$FSI (Fig. 5.5). At 20 °C, the conductivity of a 50 mol% PY$_{14}$BF$_4$ mixture is half that of the pure PY$_{14}$FSI. At 60 °C, the conductivity is two thirds that of the pure IL. The rate of decrease also increases as the concentration of BF$_4^-$ increases. Mixtures of PY$_{14}$BF$_4$ and PY$_{14}$TFSI also have decreasing conductivity with increasing BF$_4^-$ concentration, but the size of this decrease is much smaller (Fig. 5.5). At both 20 and 60 °C, only a 20% decrease in conductivity occurs at a 40 mol% concentration of PY$_{14}$BF$_4$. Despite larger decreases in the conductivity, all of the PY$_{14}$FSI mixtures have a higher molar conductivity than the corresponding PY$_{14}$TFSI mixtures.

The decrease in conductivity for both systems is a function of two factors. The first is decreasing ion mobility, as discussed previously in the viscosity section. The second factor is the increasing concentration of ions due to the smaller size and lower molecular weight of the BF$_4^-$ anion. The difference in molecular weight between BF$_4^-$ (86.8 g mol$^{-1}$) and FSI$^-$ (180.1 g mol$^{-1}$) is smaller than that between BF$_4^-$ and TFSI$^-$ (280.1 g mol$^{-1}$), which leads to the PY$_{14}$TFSI mixtures having a larger increase in the ion concentration than the PY$_{14}$FSI
mixtures. However, the PY$_{14}$TFSI mixtures experience smaller decreases in conductivity, suggesting that the electrostatic interactions in the PY$_{14}$FSI mixtures are stronger than those in the PY$_{14}$TFSI mixtures. This corresponds well with the viscosity behavior.

The addition of PY$_{14}$BF$_4$ to either PY$_{14}$FSI or PY$_{14}$TFSI results in mixtures with phase behavior that differs substantially from that of the pure ILs (Fig. 5.6). For PY$_{14}$FSI, the addition of 10 mol% PY$_{14}$BF$_4$ depresses the $T_m$ until the melting peak is almost concurrent with a solid-solid phase transition of the pure PY$_{14}$FSI salt at $-29 \, ^\circ$C. Then, for concentrations of 20 and 30 mol% PY$_{14}$BF$_4$, an amorphous region is observed. Such behavior is surprising, as both of the PY$_{14}$FSI and PY$_{14}$BF$_4$ salts have rapid crystallization kinetics in when unmixed. Also, given the high $T_m$ of pure PY$_{14}$BF$_4$, a separate higher melting phase might be expected to form from the mixtures. For concentrations of 40 mol% and above, this expected behavior does occur, with a new high melting peak being observed.

Pure PY$_{14}$TFSI is polymorphic, with two competing phase that can form with different melting points ($T_m = -7$ or $-18 \, ^\circ$C, respectively). These competing phases lead to an IL that is slow to crystallize, even in its pure form. Thus, when compared to PY$_{14}$FSI, it might be expected that a larger amorphous composition range would be observed. This, however, is not found as an amorphous concentration range only occurs between 20 and 23 mol% PY$_{14}$BF$_4$ (Fig. 5). However, the 17 mol% composition has only a small melting peak, suggesting that much of this sample is, in fact, amorphous. In fact, the addition of PY$_{14}$BF$_4$ appears to promote the formation of the lower melting phase, as exemplified by the 25 mol% composition. Despite careful thermal cycling, the higher melting phase seen in most of the samples ($T_m = -11 \, ^\circ$C) could not be formed at this composition. Even at those compositions
Figure 5.6 DSC heating traces (5 °C min⁻¹) for (1-x) IL₁-(x) IL₂ mixtures with ILs containing different anions.
where the -11 °C phase formed, the thermal history of the sample was crucial in isolating this phase. The higher melting phase observed after 40 mol% PY$_{14}$BF$_4$ in the PY$_{14}$FSI samples appears to form at lower concentrations in the PY$_{14}$TFSI mixtures (greater than 30 mol%). This separation at lower concentration may be due to the larger differences between the size and shape of the TFSI$^-$ and the BF$_4^-$ anions when compared to the FSI$^-$ anion. For both mixtures, the amorphous regions bear further investigation for use as electrolytes.

Unlike the PY$_{14}$BF$_4$-containing mixtures, the mixtures of PY$_{14}$FSI and PY$_{14}$TFSI are amorphous for better than half of the studied compositions. The low $T_m$ of the PY$_{14}$FSI or PY$_{14}$TFSI salts, as compared to PY$_{14}$BF$_4$, indicates that the ion packing in the former ILs is more readily thermally disrupted than that for PY$_{14}$BF$_4$. This makes crystallization less favorable, which results in amorphous mixtures. The polymorphic nature of PY$_{14}$TFSI also leads to this amorphous behavior, as crystallization is already slow due to competing phases. The addition of small amounts of PY$_{14}$FSI appears to result in additional solid-solid phase changes being observed. This extra degree of freedom is enough to preclude crystallization of mixtures between 30 and 90 mol% PY$_{14}$FSI.

### 5.5 Conclusions

IL$_1$-IL$_2$ mixtures are found to have physicochemical properties and a thermal phase behavior that deviate significantly from that of the pure ILs that make up the mixtures. This behavior can generally be well modeled by the use of ideal mixing models. The addition of smaller cations (e.g., PY$_{11}^+$ or PY$_{12}^+$) to an IL with the same anion and larger cations can result in an increase in the conductivity as compared to the pure IL, but generally results in a
more limited temperature range over which the mixtures are liquid. The presence of smaller cations also leads to higher packing efficiency and thus greater density. The addition of ILs that are solid at room temperature (PY$_{11}$TFSI or PY$_{12}$TFSI) generally leads to increased viscosity, but not always, as shown by mixtures of N$_{2222}$TFSI and PY$_{14}$TFSI. This difference may be the result of differences in the interactions between cyclic cations and anions relative to those for non-cyclic cations and anions. The addition of ILs containing smaller cations that are liquid at room temperature, however, results in decreases in the viscosity. This difference is likely explained by differences in how strongly the cations of the different ILs associate with the anions present. Variations in the structure of the head group of the cations appear to result in ideal mixing behavior of the physicochemical properties, while only having a small effect on the phase behavior. Overall, mixing salts with cations having different head groups offers only a limited ability to tune the properties of an IL electrolyte.

Mixtures containing different anions exhibit dissimilar behavior to those mixtures containing mixed cations. The addition of the smaller, highly associating BF$_4^-$ anion leads to decreases in the density and conductivity and increases in the viscosity. The magnitude of these changes may be a function of how the two different anions interact. Anions appear to play a dominant role in determining the phase behavior of mixtures of ILs, with every studied anion pairing resulting in mixtures with significant crystallinity gaps. Despite the strong associative nature of BF$_4^-$, studied mixtures containing that anion have crystallinity gaps, resulting in mixtures that are amorphous at all temperatures. At concentrations above these gaps, the BF$_4^-$ salt generally readily separates from the bulk IL and forms a higher melting phase. In sum, the nature of the anions present in a mixture appears to play a much larger role
in determining the properties and phase behavior of a mixture. As such, mixed anions are probably the most promising route to use when attempting to tune the properties of an IL electrolyte.
References


Chapter 6: Ionic Liquids and Electrochemical Double-Layer Capacitors

6.1 Introduction

Ultimately, the previously reported physical properties need to be linked to the performance of the studied materials in actual capacitors. Capacitance measurements were performed in coin cells, which offer a number of advantages including small size (low material requirements) and hermetic-sealing, which allows sample analysis to be performed outside the N₂ or Ar atmosphere of a glovebox.

Values for the capacitance of an IL-electrode system can be obtained using a variety of techniques. For this study, two methods, galvanostatic cycling (GS) or cyclic voltammetry (CV) cycling, were used. During GS cycling, the potential is varied so that a constant current is applied to the capacitor. When the applied potential is plotted versus time for a charge/discharge cycle, a plot similar to that in Fig. 6.1a is obtained. The capacitance of a system can be determined from GS data using the slope of the linear portion of the discharge step, $dV/dt$, and the fixed value of the current applied to the capacitor, $I$, coupled with Eq. 1.¹

\[ C = \frac{I}{dV/dt} \quad (1) \]

During CV cycling, a constant potential sweep rate is applied to the coin cell and the resulting current is measured. When the current is plotted against the potential, a plot similar to Fig. 6.1b is obtained. If the area between the discharge curve and $I = 0$ A is integrated over
Figure 6.1 Typical results of (a) GS testing and (b) CV testing for an EDLC containing carbon electrodes and PY_{14}FSI electrolyte. (1 mV s\(^{-1}\), 60 °C).

a potential range, \(\Delta V\), the total charge discharged by the capacitor, \(Q\), during that potential step can be found. Using this information along with the sweep rate, \(s\), the capacitance of a device can be calculated using Eq. 2.\(^1\)

\[
C = \frac{Q}{\Delta V \times s} \quad (2)
\]
The capacitance given by Eqs. 1 or 2 is the total capacitance of the studied EDLC. However, EDLCs contain two capacitors in series, consisting of the cathode/electrolyte (i.e., anions) and anode/electrolyte (i.e., cations). Eq. 3 shows how the total capacitance for a series of capacitors depends upon the capacitance of the component capacitors.

\[
\frac{1}{C_{\text{total}}} = \frac{1}{C_1} + \frac{1}{C_2} \quad (3)
\]

Given that the charge stored by each electrode must be equal for the charge in the system to be balanced, the capacitance of each must be equal (when a charging potential is applied, electrons are driven from one electrode to the other where they are stored when the electric circuit is isolated). If \(C_1\) and \(C_2\) are equal, the capacitance of each individual electrode is twice that of the entire cell. This capacitance can then be normalized by the mass of the electrode, to obtain the gravimetric capacitance.

The time constant, \(\tau\), and equivalent series resistance (ESR), \(R\), are both indicators of how rapidly an EDLC can be charged or discharged, with higher values for either characteristic corresponding to lower power for the device. If an EDLC is allowed to discharge for a time equal to one time constant, the discharge current will be approximately one third of the initial discharge current. Both the time constant and ESR can be determined using a potentiostatic pulse where the potential applied to the EDLC, \(\Delta E\), is changed and the resulting current, \(i(t)\), is measured over a period of time, \(t\). Eq. 4 shows the relationship between these properties.
The gathered data can be fitted to a polynomial curve using software (for this work, EC-Lab was used) to give values for the time constant. At time zero, Eq. 4 reduces to Eq. 5.

\[ i(t) = \frac{\Delta E}{R} e^{-t/\tau} \quad (4) \]

\[ i(0) = \frac{\Delta E}{R} \quad (5) \]

Given the initial current and the size of the potential step applied, the ESR for an EDLC can be easily calculated.

### 6.2 Electrode Selection

Commercially available electrodes were used for all capacitance measurements in this study as a means of ensuring consistency and reproducibility between all of the coin cells. The two carbon CDC (Carbide-Derived Carbon) electrode materials purchase from Y-Carbon (part numbers EX-SC-1-S-003 and EX-SC-1-S-004, referred to as 003 and 004, respectively) were characterized with BET N\textsubscript{2} and CO\textsubscript{2} adsorption through a collaboration with Drexel University. The adsorption curves are shown in Fig. 6.2. The mean pore size for the 003 material is approximately 0.6 nm, while that for the 004 material is approximately 0.8 nm.

The manufacturer of the electrodes reports that the electrodes offer specific capacitance values of 150 F g\textsuperscript{-1} (003) or 100 F g\textsuperscript{-1} (004) with an IM\textsubscript{102}TFSI electrolyte at room
Figure 6.2 $\text{N}_2$ and $\text{CO}_2$ BET adsorption for the two electrode materials used.

temperature. However, initial GS testing with this IL and a current of 1 mA gave a capacitance of 40 F g$^{-1}$ for the 003 electrode, which is approximately 25% of the theoretical value. Further testing with lower current (0.3 mA) gave higher values for capacitance, with approximately 70% of theoretical value being achieved. This large change shows that the capacitance of the EDLCs with the selected commercial electrodes is strongly dependent on the rate of charge or discharge. A CV with a sweep rate of 1 mV s$^{-1}$ gave capacitance values that were 80% of the theoretical value for the 003 material and 95% of theoretical value for the 004 material for the same electrolyte. As the 004 electrode material could be cycled more
quickly and gave more reproducible results than the 003 material, the 004 material was used in all capacitors prepared for this study.

6.3 Performance of Pure IL-Electrolytes in EDLCs

In order to understand the effects that the IL-solvent or IL₁-IL₂ mixtures have on the performance of capacitors using such mixtures as electrolytes, it is first necessary to quantify the performance of these devices using the respective pure ILs as electrolytes. As the performance of these devices is a function of many factors, especially the nature of the electrode material, it is impractical to rely on the literature when establishing a pure IL baseline for performance. Thus, the first step in linking capacitor performance to the physicochemical properties of the electrolytes was to measure the performance of capacitors with several neat ILs (PY₁₃FSI, PY₁₄FSI, PY₁₄BETI, PY₁₅TFSI, PY₁₄TFSI, and PY₁₅TFSI). While other salts were used in this study, their high $T_m$ precluded their being used as an electrolyte when not mixed with solvents or other ILs.

ILs are touted for their high electrochemical stability. As part of designing experiments for this work, EDLCs using IL electrolyte and CDC electrodes were prepared and subjected to CV testing at increasing potentials until irreversible electrochemistry was observed. A typical result is shown in Fig. 6.3. As the potential increases, the magnitude of the charging and discharging current increases, which is expected given that capacitance is a weak function of potential. At a potential difference ($\Delta E$) of approximately 3.4 V, a small spike in current is observed, indicating that an irreversible process is occurring. The 2.5 and 3.0 V scans have current profiles that are roughly superimposed, suggesting that the same
capacitance values can be obtained from either measurement. As 2.5 V testing takes less time, all CV testing in this work was over a potential difference of 2.5 V.

While an ideal capacitor has a specific capacitance that is independent of the potential sweep rate, real capacitors can have substantial variation in performance as sweep rate changes, especially for those with viscous electrolytes. For this work, it was important to quantify the effect sweep rate has on the measured capacitance. Thus, EDLCs using pure ILs as electrolyte and CDC electrodes were prepared and testing with several sweep rates (Fig. 6.4a) An ideal capacitor has a rectangular shape, and the degree to which a real capacitor approaches ideality can be approximated by how rectangular its cyclic voltammogram is. For
Figure 6.4 Results of CV testing of an EDLC using PY$_{14}$FSI as the electrolyte at 60 °C: (a) effect of varying sweep rates (mV s$^{-1}$, labeled on graph) and (b) results after the current was normalized by the sweep rate.
the selected IL, a 1 mV s\(^{-1}\) sweep rate results in a very rectangular shape. As the sweep rate increases, the plots become more pointed and the charging/discharging currents are no longer parallel with the abscissa. The degree of ideality can also be determined by normalizing the current by the sweep rate used (Fig. 6.4b). In an ideal case, the normalized current for all sweep rates should be superimposed. For the cells with IL electrolytes, this is not the case and a significant decrease in current and capacitance occurs with increasing sweep rate. This departure from ideality is largely kinetic in origin, as the faster cycling prevents the ions in the viscous electrolyte from fully intercalating into the porous electrode materials.

It is also important to analyze the stability and repeatability of the measurements performed with these materials. Fig. 6.5 show several superimposed cycles from the CV testing. Each cycle corresponds well with every other cycle, indicating that the EDLC electrodes are fully wetted and no degradation of the materials occurs. In the first cycles of this testing, a small irreversible current is observed around 2.5 V, suggesting the presence of an impurity. This may be due to functional groups on the carbon electrode surface which react with the electrolyte. The small peak rapidly disappears upon cycling, suggesting that the concentration of the impurity is low and that the impurity is fully consumed and thus no longer affects the magnitude of the current.

Finally, the specific capacitance of EDLCs using several pure ILs as electrolyte was measured. The results of this testing are shown in Fig. 6.6. For alkyl chain lengths between three and five carbons, the length of the alkyl chain present on the cation does not seem to have a significant effect on the maximum capacitance of the EDLCs with CDC electrodes. Thus, the cations for potential electrolytes can be chosen based on other criteria, such as their
thermal phase behavior. In contrast, the anion plays a large role in determining the capacitance of the EDLC electrodes (Fig. 6.6). The salts with the smallest imide anion, FSI-, have the highest capacitance of those studied. The small size of this anion may allow it to more fully penetrate the tortuous pores of the carbon electrodes, and thus utilize more of the electrode surface area. Higher utilization leads to higher energy storage. The slightly larger TFSI- anion has a slightly reduced capacitance than the FSI- anion, while the capacitance of a BETI- anion containing electrolyte is roughly half that of an FSI- containing electrolyte. As the decrease in capacitance corresponds inversely to anion size, this supports the idea that large anions are unable to fully utilize the surface of the electrodes. While increasing anion

Figure 6.5 First 10 cycles of the CV testing of an EDLC containing a PY14TFSI electrolyte (1 mV s\(^{-1}\) sweep rate, 60 °C).
size does correspond to increasing salt viscosity, the slow scan rate used (1 mV s\(^{-1}\)) means that the observed differences should not be due to any kinetic effects.

### 6.4 Effect of Mixed Anions on EDLC Performance

Studies have shown that electrolytes containing aprotic solvents and BF\(_4^-\)-based ILs (salts) have a performance that is superior to electrolytes with other anions.\(^2\) Furthermore,
This performance difference is unexpected based upon the physicochemical properties of the BF$_4^-$ ILs, as compared to the other ILs. Unfortunately, the presence of solvent reintroduces temperature limitations to EDLCs (due to volatility). However, the same superior EDLC performance may occur when BF$_4^-$ salts are dissolved into a low melting IL. To investigate this, EDLCs were prepared using two mixtures, PY$_{14}$BF$_4$-PY$_{14}$FSI and PY$_{14}$BF$_4$-PY$_{14}$TFSI, as electrolytes. The concentration of PY$_{14}$BF$_4$ varied from 5-30 mol% in 5 mol% increments. Concentrations above 30 mol% were not studied due to the phase behavior of the more concentrated mixtures. The performance was characterized by examining the specific capacitance of the electrodes with the salt mixtures and comparing this to the values for the neat FSI$^-$ or TFSI$^-$ ILs. In addition, the effect of increasing cycling rate was examined by varying the sweep rate used in the CV testing. The results of this work are shown in Fig. 6.7.

The maximum capacitance values for the two pure ILs, as measured with a slow sweep rate of 1 mV s$^{-1}$, are 73 F g$^{-1}$ for PY$_{14}$TFSI and 90 F g$^{-1}$ for PY$_{14}$FSI at 20 °C (Fig. 6.7). Simulations suggest that the presence of FSI$^-$ or TFSI$^-$ anions causes the PY$_{14}^{+}$ cations to orient differently at a positively charged electrode surface.$^3$ In the presence of TFSI$^-$ anions, the cations lay flat on the surface, which means fewer cations can closely approach. In contrast, in FSI$^-$-containing ILs, the cations orient perpendicularly to the surface, allowing for a higher density of cations. Although the electrodes used in this study are porous, and thus the flat plate model used in the simulations is not directly applicable, ion orientation likely does play a role in the differences in the specific capacity. At 60 °C, these values increase by approximately 10% for each IL, with measured values of 80 F g$^{-1}$ for PY$_{14}$TFSI and 100 F g$^{-1}$ for PY$_{14}$FSI (Fig. 6.7). The higher temperature leads to higher ion mobility, which
Figure 6.7 Specific capacitance as a function of electrolyte composition and sweep rate for (1-x) IL$_1$-(x) IL$_2$ mixtures. Filled symbols are at 20 °C and open symbols are at 60 °C.
overcomes some of the ion transport limitations that may occur at lower temperature, allowing a higher fraction of the electrode material to be utilized.

Given the differences in ion size, properties and phase behavior between PY$_{14}$FSI and PY$_{14}$BF$_4$, the addition of BF$_4^-$ anions to the FSI salt would be expected to modify the capacitance of the system. However, when the BF$_4^-$ anion is introduced, the capacitance remains constant with increasing PY$_{14}$BF$_4$ concentration (Fig. 6.7), despite the presence of the BF$_4^-$ anion resulting in significantly increased viscosity and decreased conductivity. The current understanding of electrolytes suggests that these changes in physicochemical properties should lead to worse performance (i.e., lower capacitance, especially at higher scan rates). It is possible that at very slow scan rates, the decreasing ion mobility, as indicated by viscosity and conductivity, is not a limiting factor. However, at higher scan rates, even up to 100 mV s$^{-1}$, the same independence from BF$_4^-$ anion concentration is observed. This suggests, at least for these specific ILs, that viscosity and conductivity may not be good predictors of a material’s usefulness as an electrolyte. With increasing scan rate does come reduced capacitance, however, as transport limitations result in a lesser fraction of the electrode surface being used.

Unlike the mixtures with PY$_{14}$FSI, the addition of PY$_{14}$BF$_4$ to PY$_{14}$TFSI results in a 25% increase in the specific capacitance, with a maximum being observed around 10 mol% PY$_{14}$BF$_4$. At concentrations greater than this, the capacitance variation is flat or slightly decreasing with increasing concentration of PY$_{14}$BF$_4$. The addition of a small amount of the BF$_4^-$ anion may allow the electrolyte to access previously inaccessible pores, as the BF$_4^-$ anion (0.33 nm) is significantly smaller than the TFSI$^-$ anion (0.76 nm).$^4$ This effect was not
observed with the PY\textsubscript{14}FSI mixtures, as the size of the FSI\textsuperscript{-} anion is much closer to that of the BF\textsubscript{4} anion. This behavior is observed for all of the scan rates used, although the magnitude of the capacitance decreases with increasing scan rate. As with the PY\textsubscript{14}FSI mixtures, higher scan rates result in lower utilization of electrode material. Furthermore, once again the decrease that would be expected based upon the viscosity and molar conductivity variations is not observed at any scan rate. It is interesting to note that the relative change in the magnitude of the capacitance between each scan rate is roughly the same for both the FSI\textsuperscript{-} and TFSI\textsuperscript{-} mixtures, despite the corresponding compositions having quite divergent viscosity and conductivity values. In addition to increasing the capacitance, the presence of the BF\textsubscript{4} anion leads to a smaller decrease in capacitance with increasing sweep rate (Fig. 6.8) At high temperatures, mixtures containing as little as 5 mol\% PY\textsubscript{14}BF\textsubscript{4} have 15\% greater specific capacitance during faster charging/discharging. This effect is most pronounced at 60 °C, with little or no increase in capacitor power being observed at 20 °C.

6.5 Effect of Multiple Cations on EDLC Performance

In an effort to better understand the results obtained from EDLCs using IL electrolytes with mixed anions, electrolytes containing mixed cations were prepared and their performance in EDLCs quantified (Fig. 6.7). For this work, salts with the N\textsubscript{2222}\textsuperscript{+} and PY\textsubscript{14}\textsuperscript{+} cations were chosen along with the TFSI\textsuperscript{-} anion. Like the PY\textsubscript{14}BF\textsubscript{4} salt used for the mixed anion work, N\textsubscript{2222}TFSI has a much higher $T_m$ that PY\textsubscript{14}TFSI (105 °C vs. -7 °C). The lack of a ring structure also gives this cation a substantially higher degree of conformational freedom, which seems likely to affect how the N\textsubscript{2222}\textsuperscript{+} cations interact with the anode surface. The
Figure 6.8 Normalized specific capacitance as a function of electrolyte composition and sweep rate for (1-x) IL\textsubscript{1}-(x) IL\textsubscript{2} mixtures. Filled symbols are at 20 °C and open symbols are at 60 °C.
mixed anion work suggests that such differences in ion-surface interactions should lead to a noticeable change in the specific capacitance. The lack of the ring structure may also allow the cation to better intercalate into small pores, which would also lead to an increase in capacitance. The results of these experiments are shown in Fig. 6.7.

For slow scan rates (1 mV s⁻¹), the addition of N₂₂₂₂TFSI does not appear to have an effect on the specific capacitance of the prepared EDLCs (Fig. 6.7). The same lack of change is observed at higher scan rates at 20 °C. At 60 °C, mixtures containing N₂₂₂₂TFSI vary significantly from the performance of pure PY₁₄TFSI. At the higher scan rates (10, 20, 100 mV s⁻¹), the capacitance of electrolytes with N₂₂₂₂TFSI at concentrations of 5, 10 and 15 mol% is much higher than for the electrolyte with pure PY₁₄TFSI. For the 15 mol% mixtures, the capacitance is nearly twice that of the pure PY₁₄TFSI. The N₂₂₂₂⁺ cation has a high degree of conformation freedom, which results in a lower energy barrier for ion movement, allowing improved performance at high scan rates.⁵ When the capacitance is normalized by the maximum capacitance (Fig. 6.8), the increase in capacitance values becomes even more clear. This conformational freedom does not, however, result in improved utilization of the electrode surface area, as shown by the independence of the specific capacitance with N₂₂₂₂⁺ concentration. Improved performance at high scan rates is not observed at 20 °C.

6.6 Conclusions

Electrolytes containing mixed salts with variable anions or cations can have significantly different performance in EDLCs relative to those with pure ILs electrolytes. Different anions interact differently with charged surfaces and this can be used to improve the specific
capacitance of an EDLC, such as when the BF$_4^-$ anion is introduced to PY$_{14}$TFSI. Different anions also affect the way that cations interact with electrodes, which can also improve the specific energy. Furthermore, the small size of the BF$_4^-$ anion likely allows the electrolyte to better wet porous activated carbons and thus utilize smaller pore sizes, boosting the amount of energy stored by an EDLC using these materials. For some systems, the presence of smaller anions leads to decreases in the magnitude of lost capacitance at higher cycling rates.

Unlike with mixed anions, the presence of mixed cations does not appear to affect the maximum specific capacitance of EDLCs using the CDC carbon electrodes. What the presence of mixed cations does affect is the magnitude of the loss of specific energy at higher cycling rates, with the presence of even small amounts of the N$_{2222}^+$ cation leading to a near doubling of the specific capacitance when compared to the pure PY$_{14}$TFSI, in which the N$_{2222}$TFSI was mixed. Note that this effect appears to be highly temperature dependent, with the improvement in cycling only observed at 60 °C and not observed at 20 °C.

Finally, there appears to be no direct link between the physicochemical properties discussed in Chapter 5 and the performance of EDLCs using mixed ILs as electrolytes. While decreases in ionic conductivity and increases in viscosity would be expected to result in greater losses in energy storage at high cycling rates, this was not observed in any of the studied systems. In fact, the systems containing the N$_{2222}^+$ cations experience an increase in performance, despite the traditional understanding of electrolytes suggesting that no change should have been measured as the viscosity and conductivity of these mixtures remains constant (Chapter 5).
References


Conclusions

The suitability of several IL-based electrolytes for use in EDLCs with carbon electrodes has been investigated. Multiple pure ILs, mixtures of ILs and aprotic solvents, and mixtures of ILs containing mixed anions or cations were prepared and their physicochemical properties and thermal phase behavior quantified. EDLCs containing these materials as electrolytes were assembled and tested to determine what influence the ion structure and electrolyte properties have on EDLC performance.

Initial work focused on the addition of aprotic solvents to ILs in an effort to overcome some of the less attractive properties of IL electrolytes (low ionic conductivity, relatively high $T_m$). The addition of even a small amount of solvent (20 mol%) was found to decrease the viscosity of an IL by almost 50%, independent of the IL or solvent combination selected. In addition, solvent addition results in an ionic conductivity maximum at IL concentrations of 1-2 M, which corresponds to a mole fraction of 0.80 to 0.95 depending upon the IL and solvent used. Such behavior is consistent with organic solvent-based electrolytes with high melting salts (i.e., N$_{2222}$BF$_4$). An examination of the molar conductivity shows that the nature of the solvent chosen appears to strongly influence the ion aggregation behavior in solution. Solvents such as AN and cyclic esters or cyclic carbonates promote ion dissociation, while linear carbonates promote aggregation. The crystallization of ILs is inhibited by the addition of solvent, which can result in mixtures that remain liquid at much lower temperatures. Solvents do not appear to interact strongly with the IL ions, so the presence of solvents results in a volatile mixture and may reintroduce flammability limitations. Thus, despite the
many favorable adjustments to properties induced by solvent addition, these limitations
motivated the study of alternative methods of modifying the IL properties.

The second step of this work looked into the feasibility of tuning the properties of IL-
based electrolytes by the combination of two ILs. Depending upon the ions chosen, the
combination of ILs results in property changes that range from small to large. The addition of
smaller cations to an IL based on larger cations can result in an increase in the conductivity
over that of the pure IL. However, the salts containing the smaller cation (when in high
concentration) generally crystallize out of the mixtures at low temperatures, which is
undesirable in an electrolyte. Electrolytes with mixed cations generally do not display
properties that are greatly different from those of the pure ILs that compose the mixture. In
contrast, the addition of smaller anions to an IL can result in large decreases in conductivity
and increases in viscosity. Anions appear have a significant role in determining the phase
behavior of an IL, and this holds true for the mixtures studied. The presence of ILs with
differing anions generally results in large composition ranges that are amorphous, even when
high melting salts are used ($T_m > 100 \, ^\circ C$). These amorphous regions are also found in
mixtures that contain anions that are structurally similar (e.g., $\text{FSI}^-$ and $\text{TFSI}^-$). Overall, the
best route for modifying the physicochemical properties of an IL appears to be adjusting the
size and nature of the cations present, while anions are the key to creating ILs that remain
liquid at low temperatures.

Finally, EDLCs using pure ILs or mixed IL electrolytes were assembled and their
performance, as quantified by the maximum specific capacitance and specific capacitance as
a function of charge/discharge rate, was measured. EDLCs using mixtures of $\text{PY}_{14}\text{BF}_4$ and
PY$_{14}$TFSI did not exhibit any change in maximum capacitance as the concentration of PY$_{14}$BF$_4$ increased. Furthermore, at all compositions, these devices experience the same magnitude of decrease with increasing charging/discharging rate, despite large increases in the viscosity and decreases in the conductivity with increasing PY$_{14}$BF$_4$ concentration. In contrast to the PY$_{14}$FSI-based electrolytes, mixtures of 10 mol% PY$_{14}$BF$_4$ in PY$_{14}$TFSI have a specific capacitance that is 10% larger than that of pure PY$_{14}$TFSI, but this increase in capacitance decreases with further increasing PY$_{14}$BF$_4$ concentration. For both the PY$_{14}$FSI- and PY$_{14}$TFSI-based mixtures, the size of the decrease in capacitance with increasing scan rate is constant, despite large changes in the electrolyte physicochemical properties. In contrast, EDLCs using mixed cation electrolytes (N$_{2222}^+$ and PY$_{14}^+$) do not have an increase in maximum capacitance. These devices do, however, experience a much lower decrease in capacitance with increasing scan rate at high temperatures. The viscosity and conductivity of these mixtures is independent of the N$_{2222}$TFSI concentration, which, given the traditional understanding of the links between conductivity/viscosity and capacitor performance (i.e., higher conductivity and lower viscosity are optimal electrolyte criterion), is quite surprising.

Overall, this study has shown that there are a number of facile methods for tuning the physicochemical properties and phase behavior of IL electrolytes, as well as methods to modify the performance of EDLCs based upon IL electrolytes. The results of this research offer valuable insights into the role that the solvent structure and properties play in tuning IL-solvent mixture properties. The roles that the cations and anions play in affecting the characteristics of mixed ILs have also been better elucidated. Although these mixtures are complicated, a foundation has been established for future work with these intriguing
mixtures. Finally, a number of interesting phenomena with mixed IL electrolytes and EDLCs have been identified and offer guidance into how to intelligently design IL-based capacitor electrolytes.
Figure A.1 $^1$H NMR for synthesized ILs (in CD$_3$CN referenced to TMS (0 ppm)).
Appendix B – Chapter 4

Figure B.1 Conductivity of (1-x) PY$_{15}$TFSI-(x) solvent mixtures as a function of temperature and mole fraction of the solvent.
Figure B.2 Conductivity of (1-x) PY$_{15}$TFSI-(x) solvent mixtures as a function of temperature and IL concentration.
Figure B.3 Molar conductivity of (1-x) PY$_{15}$TFSI-(x) solvent mixtures as a function of temperature and mole fraction of the solvent.
Figure B.4 Molar conductivity of \((1-x) \text{PY}_{15}\text{TFSI}_{x}\) solvent mixtures as a function of temperature and IL concentration.
Figure B.5 Conductivity of (1-x) IL-(x) solvent mixtures as a function of temperature and mole fraction of the solvent or concentration of the IL.
Figure B.6 Molar conductivity of (1-x) IL-(x) solvent mixtures as a function of temperature and mole fraction of the solvent or concentration of the IL.
Figure C.1 Temperature dependence of the density of \((1-x)\) IL\(_1\)-(\(x\)) IL\(_2\) mixtures containing varying alkyl chain lengths.
Figure C.2 Temperature dependence of the viscosity of $(1-x)$ IL$_1$-$(x)$ IL$_2$ mixtures containing varying alkyl chain lengths.
Figure C.3 Temperature dependence of the conductivity of $(1-x)\text{IL}_1-(x)\text{IL}_2$ mixtures containing varying alkyl chain lengths.
Figure C.4 Temperature dependence of the density of (1-x) IL1-(x) IL2 mixtures containing mixed anions or mixed cations.
Figure C.5 Temperature dependence of the viscosity of (1-x) IL₁₋ₓ(1-x) IL₂ mixtures containing mixed anions or mixed cations.
Figure C.6 Temperature dependence of the conductivity of (1-x) IL₁-(x) IL₂ mixtures containing mixed anions or mixed cations.
Appendix D – Diffusion Coefficients from $^{13}\text{C}$ PGSE NMR Measurements
— Fluorine-Free Ionic Liquids with the DCTA$^-$ Anion
Diffusion Coefficients from $^{13}$C PGSE NMR Measurements—Fluorine-Free Ionic Liquids with the DCTA$^-$ Anion

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Supporting Information

ABSTRACT: Pulsed-field gradient spin–echo (PGSE) NMR is a widely used method for the determination of molecular and ionic self-diffusion coefficients. The analysis has thus far been limited largely to $^1$H, $^2$H, $^{19}$F, and $^{31}$P nuclei. This limitation handicaps the analysis of materials without these nuclei or for which these nuclei are insufficient for complete characterization. This is demonstrated with a class of ionic liquids (or ILs) based on the nonfluorinated anion 4,5-dicarbonitrile-1,2,3-triazole (DCTA$^-$). It is demonstrated here that $^{13}$C-PGSE NMR can be used to both verify the diffusion coefficients obtained from other nuclei, as well as characterize materials that lack commonly scrutinized nuclei — all without the need for specialized NMR methods.

SECTION: Kinetics, Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy, especially the pulsed-field gradient spin–echo (PGSE) technique, has been used extensively to measure diffusion coefficients of molecules and ions,1–5 including the ions in ionic liquids (ILs), salts that melt at low temperature.6–11 For the ILs reported here, however, the anion, 4,5-dicarbonitrile-1,2,3-triazole (DCTA$^-$) (Figure 1), is dessicated of both fluorine and hydrogen, which typically serve as convenient probes. Attempts to follow $^1$H-enriched DCTA$^-$ have proven unsuccessful due to the poor NMR properties (low $T_1$, long relaxation times) of this nucleus. $^{13}$C nuclei were therefore utilized instead (at natural abundance, Figure 2) as the probe — an approach that has never been attempted before with conventional PGSE-NMR (although there are a few reports of the use of the $^{13}$C nuclei for specialized NMR diffusion measurement techniques19–21). Reported here are the results for the diffusion coefficient measurements of the IL anions and cations from $^{13}$C- and $^1$H-NMR, as well as the thermal phase behavior and transport properties of the ILs.

Potential and practical applications of ILs are growing exponentially due to their favorable properties such as high thermal stability, low to negligible vapor pressure, tunable polarity as solvents, high conductivity, and so forth.22–24 The basic principles for designing ILs are to combine charge delocalization and low surface energy for both the cation and anion with shape factors, such as low symmetry and five-membered rings, which make close packing in a crystal more improbable, thus reducing the melting point ($T_m$) of the salt. The classical example is the 1-butyl-3-methylimidazolium (BMIM$^+$) cation (Figure 1), which readily forms low melting salts with a wide variety of anions.11 The most widely used anion is bis(trifluoromethanesulfonyl)imide or N(SO$_3$CF$_3$)$_2^-$ (TFST$^-$), which, though very bulky, possesses extensive charge delocalization and conformational flexibility due to the facile rotation around the S—N=S bond.25–27 The use of nonfluorinated anions such as DCTA$^-$, instead of TFST$^-$, is of

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Table 1. Properties of the ILs (20°C)

<table>
<thead>
<tr>
<th>IL</th>
<th>Tm [°C]</th>
<th>η [mPa s]</th>
<th>ρ [g cm⁻³]</th>
<th>σ [mS cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM₄DCTA</td>
<td>40</td>
<td>3.05</td>
<td>1.11</td>
<td>2.9</td>
</tr>
<tr>
<td>IM₄DCTA</td>
<td>36</td>
<td>1.11</td>
<td>1.10</td>
<td>2.8</td>
</tr>
<tr>
<td>PY₄DCTA</td>
<td>101</td>
<td>1.07</td>
<td>1.07</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 2. Cation and Anion Self-Diffusion Coefficients for the ILs

<table>
<thead>
<tr>
<th>IL</th>
<th>$D_{\text{cat}}$ [×10⁻¹² m² s⁻¹]</th>
<th>$D_{\text{anion}}$ [×10⁻¹² m² s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM₄DCTA</td>
<td>1.41 (±0.15)</td>
<td>1.68 (±0.15)</td>
</tr>
<tr>
<td>IM₄DCTA</td>
<td>1.36 (±0.05)</td>
<td>1.47 (±0.15)</td>
</tr>
<tr>
<td>IM₄DCTA</td>
<td>2.07 (±0.05)</td>
<td>1.81 (±0.15)</td>
</tr>
<tr>
<td>IM₄DCTA</td>
<td>2.50 (±0.15)</td>
<td>2.76 (±0.15)</td>
</tr>
<tr>
<td>IM₄DCTA</td>
<td>1.01 (±0.08)</td>
<td>1.80 (±0.15)</td>
</tr>
<tr>
<td>IM₄DCTA</td>
<td>12.32 (±0.10)</td>
<td>12.06 (±0.10)</td>
</tr>
<tr>
<td>IM₄DCTA</td>
<td>7.42 (±0.20)</td>
<td>7.22 (±0.20)</td>
</tr>
<tr>
<td>IM₄DCTA</td>
<td>8.63 (±0.10)</td>
<td>7.80 (±0.05)</td>
</tr>
<tr>
<td>IM₄DCTA</td>
<td>8.60 (±0.05)</td>
<td>8.70 (±0.10)</td>
</tr>
<tr>
<td>IM₄DCTA</td>
<td>7.71 (±0.05)</td>
<td>6.38 (±0.20)</td>
</tr>
</tbody>
</table>

Charge is therefore delocalized on seven centers. This anion, with its shape and charge delocalization, can be considered as the counter equivalent of imidazolium cations.

The $T_m$'s of the ILs are reported in Table 1 (and the Supporting Information). Both IM₄DCTA and PY₄DCTA are solid at room temperature, although they can remain supercooled liquids for extended periods once melted. Most of the ILs have simple phase behavior with a single low-temperature crystalline phase prior to the $T_m$ (see Supporting Information). IM₄DCTA gave evidence for a solid-solid phase transitions near –31 °C, albeit this was of low energy, indicating that only a minor structural change occurred during the transition. Note that a previous investigation reported that the $T_m$ is –26 °C for IM₄DCTA and that no $T_m$ could be determined for IM₂DCTA and PY₂DCTA. The reported $T_m$ for IM₄DCTA seems to be an error in which the solid–solid phase transition was mistaken for the melt transition as the DSC heating trace is only reported to 0 °C. Depending on the thermal history for the salt, IM₄DCTA had a $T_m$ of either ~5 or 22 °C (Supporting Information). This can be explained by the salt crystallizing into one of two different polymorphic phases, as occurs for halide salts with the IM₄⁺ cation.\(^{24,25}\)

Self-diffusion coefficient measurements were performed with a Varian Direct Digital Drive 300 NMR spectrometer ($B_0 = 7.1$ T) with a Doty dual frequency (6 and 8 mm for X and H, respectively) z-gradient water-cooled diffusion probe. Diffusion coefficients were measured for the \(^1\)H and \(^13\)C nuclei, respectively, at 800.1 and 75.5 MHz, π/2 pulses were determined to be 23 μs for \(^1\)H and 18 μs for \(^13\)C nuclei. Tetramethylsilane (TMS) was used as a reference for both nuclei. The sample temperature was calibrated with the standard ethylene glycol method and controlled with ±0.5 K accuracy. A PGSE sequence was used to obtain the self-diffusion coefficients for both the \(^1\)H and \(^13\)C nuclei, according to the very long relaxation times of these nuclei in these media (typically, values were $T_2(\text{H}) \approx 500$ ms and $T_2(\text{C}) > 5$ s).

The values of the self-diffusion coefficients were extracted from the classical Stejskal and Tanner equation\(^1\):

$$A(g) = A(0) \exp \left[ -D \gamma^2 T^2 \delta^2 \left( \Delta - \frac{\delta}{2} \right) \right]$$

where $A(0)$ and $A(g)$ are the integrated intensities of the signals obtained, respectively, without and with gradient pulses, $D$ is the self-diffusion coefficient, $\gamma$ is the gyromagnetic ratio, $\delta$ is the
gradient field strength, is the duration of gradient pulses, and \( \Delta \) is the time between the two gradient pulses. The gradient pulse duration \( d \) was fixed to 1.5 ms for \( ^1H \) and 4 ms for \( ^13C \); its strength was varied from 50 to 600 G cm\(^{-1}\) in 16 steps, and \( \Delta \) was fixed to 100 ms for both nuclei. \( ^13C \) spectra were recorded without \( ^1H \) decoupling and 52 free induction decays (FIDs) were needed to get a reasonable S/N ratio; the recovery delay was 30 s, which enabled the full set of measurements necessary to determine a diffusion coefficient in 4.5 h. Spectra were recorded with 4000 data points and zero-filled to 16 000 to improve the digital resolution. An exponential filter of 7 Hz was applied to the FID. For the \( ^1H \) nuclei, eight FIDs were added, and a recovery delay of 15 s was used.

The self-diffusion coefficients of the ILs (Table 2) exhibit the behavior that is expected from the traditional Stokes–Einstein understanding of diffusion. Larger cation or anion size correlates with lower diffusion coefficients. For the different cations, it is possible to determine \( D_{\text{app}} \) from both the \( ^1H \) and \( ^13C \) data with good accuracy, which provides a strong measure of confidence for the \( ^13C \) results. Discrepancies between the cation diffusion coefficient determined from both nuclei (Table 2 and Figure 3) are around \( \pm 10\% \) (this may include a small systematic variation introduced by the larger gradient duration required for the \( ^13C \) nuclei). This work therefore clearly demonstrates the validity and utility of using standard PGSE NMR methods to obtain diffusion coefficients with the \( ^13C \) nuclei, a readily available probe for a diverse range of molecules and ions.

**ASSOCIATED CONTENT**

**Supporting Information**

Sample preparation procedure, experimental details and data (DSI, ionic conductivity and viscosity). This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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(7) Hayamizu, K.; Tanaka, S.; Seki, S. Molecular Motions and Ion Differences of the Room-Temperature Ionic Liquid \( \text{1,3,5-triazole-4-ethyl-4,4',5,5'-biphenylenediazolium \( \text{bis}(\text{trifluoromethylsulfonyl})\) imidazolium (DMPIImTFSA)} \) Studied by \(^1H\), \(^13C\), and \(^35Cl\) NMR. J. Phys. Chem. A 2008, 112, 12027–12030.


Supporting Information:
Diffusion Coefficients from $^{13}$C PGSE NMR Measurements—Fluorine-Free Ionic Liquids with the DCTA Anion

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Sample Preparation & Experimental Details:
Materials and Preparation of ILs: 1-ethyl-3-methylimidazolium chloride (EMIMCl) and 1-butyl-3-methylimidazolium chloride (BMIMCl) were purchased from Fluka. N-Methylpyrrolidone (98%), 1-bromopropane (99%) and 1-bromobutane (99%) were purchased from Sigma-Aldrich. To prepare PY$_3$Br and PY$_4$Br, respectively, equimolar amounts of N-methylpyrrolidone and 1-bromopropane or 1-bromobutane were combined with a small amount of acetonitrile and stirred. The reactions were allowed to proceed for 24 h at 40°C under a N$_2$ blanket of gas. The resulting salts were recrystallized by the addition of ethyl acetate and then dried under vacuum at 110°C.

The acid form of 4,5-dicarboxyimide-1,2,3-triazole (DCTA) was synthesized by reacting diaminomethylene-nitride and tert-butyl nitrite (10 mol% excess) in diethyl ether at 0°C. The solution was centrifuged to remove impurities. The diethyl ether was then removed through evaporation, leaving a brown powder. The crude DCTA was sublimated at 80°C at least twice to obtain pure white crystals. NH$_4$DCTA was prepared by reacting equimolar amounts of NH$_3$ (7M solution in MeOH) and DCTA. The resulting precipitated salt was dried under vacuum at 80°C for two days.

DCTA-based ILs were prepared by reacting the appropriate dried halide salt (IM$_3$Cl, IM$_4$Cl, PY$_3$Br, or PY$_4$Br) with an equimolar quantity of NH$_4$DCTA in anhydrous acetonitrile in a Vacuum Atmospheres N$_2$ glove box (< 0.5 ppm O$_2$ and H$_2$O). Preempted NH$_4$Cl and NH$_4$Br were filtered off and the acetonitrile was removed through rotary evaporation. The resulting ILs were dried under vacuum at 100°C for two or more days. Samples of the ILs were submitted to Atlantic Microlab for elemental analysis (see Table S1).

Thermal Characterization. Differential scanning calorimetry (DSC) measurements were performed with a TA Instruments Q2000 DSC equippd with a liquid N$_2$ cooling system. The instrument was calibrated with cyclohexane (solid-solid phase transition at -87.06°C, melt transition at 6.54°C) and indium (melt transition at 156.60°C). Samples were hermetically sealed in Al pans in the glove box. To ensure complete crystallization, samples were cycled from below the $T_g$ to below the $T_m$ repeatedly. The final heating traces reported (Fig. S2) were performed from -150°C to 150°C at a heating rate of 3°C min$^{-1}$. Fig. S3 shows different heating traces for the same IM$_3$Cl DCTA sample in which the thermal history (cycling and annealing conditions) was varied confirming that different polymorphic crystalline phases form for this salt.

**Table S1.** Elemental analysis results for the ILs studied.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Element</th>
<th>Theory</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM$_3$Cl</td>
<td>C</td>
<td>52.39</td>
<td>52.22</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>4.84</td>
<td>4.81</td>
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<tr>
<td></td>
<td>N</td>
<td>42.77</td>
<td>42.76</td>
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<tr>
<td>IM$_4$Cl</td>
<td>C</td>
<td>56.02</td>
<td>55.92</td>
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<tr>
<td></td>
<td>H</td>
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<td>6.07</td>
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<tr>
<td>PY$_3$Br</td>
<td>C</td>
<td>58.51</td>
<td>57.64</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>7.37</td>
<td>7.61</td>
</tr>
<tr>
<td></td>
<td>N</td>
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<td>C</td>
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<td>7.74</td>
<td>7.93</td>
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<tr>
<td></td>
<td>N</td>
<td>32.28</td>
<td>31.93</td>
</tr>
</tbody>
</table>

**Figure S2.** DSC heating traces (5°C min$^{-1}$) for the ILs studied.
Ionic Conductivity. The conductivity of the ILs was measured with electrochemical impedance spectroscopy using a Solartron 1260A potentiostat and a 1260A impedance analyzer. Two-electrode platinum Pt electrode conductivity cells (Materials Motas Italy) were prepared in the glove box and then hermetically sealed. The cell constants were determined using KCl aqueous standards. Measurements were performed in a Binder MK 53 environmental chamber from 100°C to 0°C. Temperature steps were 10°C and the samples were allowed to equilibrate for at least 45 min after each temperature change before the measurements. The conductivity of the four ILs is shown in Fig. S4. Although there are no clear trends, longer alkyl chains on the cation appear to lead to lower conductivity.

Density and Viscosity. Measurements were performed using an Anton-Paar SVM 3000 Stabinger viscometer (with an internal density meter). Calibration of the instrument was performed with CANNON certified viscosity standards. Ethyl acetate and N₂ gas (> 99.999%, H₂O concentration 2.5 ppm) were used to clean the instrument before and after the measurements. The instrument was sealed during use to prevent water contamination. The H₂O content determined with Karl Fischer coulometry, checked before and after the measurements, was found to be less (for most of the samples significantly less) than 125 ppm for all the ILs. Density and viscosity values were recorded from 20°C to 100°C in 10°C increments with a 1°C min⁻¹ heating rate. There was not enough of the IMIm(DCTA) salt available (several mL) for the density and viscosity measurements. While the phase behavior varies between the ILs, the viscosity and density (Figs. S4 and S5) of the ILs are quite similar. It is notable that the reported conductivity and viscosity values are amongst the highest and lowest, respectively, known for aprotic ILs.

Ionicity: An excellent discussion regarding how the transport properties of ILs are frequently correlated with ionic interactions has been reported. Variable-temperature conductivity, viscosity and diffusion coefficient values are presented above and in the manuscript. Fig. S6 shows a Walden plot for comparison with previously reported data on ILs. When diffusion coefficients are available for ILs, molar conductivity values are sometimes calculated from these data (\(\Lambda_{\text{m}}\)):

\[
\Lambda_{\text{m}} = \frac{N_{\text{A}}D_e^2}{\kappa}
\]

where \(N_{\text{A}} = 6.0221415 \times 10^{23}\) (\text{mol}⁻¹), \(e = 1.60217646 \times 10^{-19}\) (C) and \(\kappa = 1.3806503 \times 10^{-23}\) m² kg s⁻¹ K (multiple by 10,000 for unit conversion to S cm⁻¹ mol⁻¹ if the \(D_e\) values have units of m² s⁻¹). Such values are then usually compared with the values obtained from the measured conductivity and density of the ILs (\(\Lambda_{\text{m}}\)):

\[
\Lambda_{\text{m}} = (1 - \Lambda_{\text{m}})\Lambda_{\text{m}}
\]

Figure S3. DSC heating traces (5°C min⁻¹) for IMIm(DCTA).

Figure S4. Variable-temperature ionic conductivity and viscosity of the ILs (viscosity data was not determined for IMIm(DCTA)).

Figure S5. Variable-temperature density of the ILs (density data was not determined for IMIm(DCTA)).
to obtain a deviation ($\Delta_1$ is used rather than $\Delta$ to differentiate it from the delta values used in the Tanner equation). A value of zero for $\Delta_1$ is interpreted to mean that the salt is fully dissociated, whereas values which deviate significantly from this are generally attributed to ionic association interactions. The values of $\Delta_1$ for ILs are frequently quite small (on the order of ± 0.1), but can also be as large as 0.2-0.5. Calculated values for $\Delta_1$ are shown in Table S2. Given the relatively high $\Delta_1$ values obtained (Table S2), it is difficult to assign any particular significance to this in a meaningful manner when this information is compared with the other data presented for the salts (i.e., high conductivity and low viscosity relative to many other ILs). Therefore, the values are reported here simply for the reader’s consideration.

**Figure S6.** Walden plot for the ILs.

**Table S2.** $A_{\text{sc}}$, $A_{\text{se}}$ and $\Delta_1$ values for select ILs at 60°C.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ILs</th>
<th>$^{13}$C $D_{\text{axis}}$ (m² s⁻¹)</th>
<th>$^{13}$C $D_{\text{perp}}$ (m² s⁻¹)</th>
<th>$A_{\text{sc}}$ (S cm² mol⁻¹)</th>
<th>$A_{\text{se}}$ (S cm² mol⁻¹)</th>
<th>$\Delta_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>333.15</td>
<td>IM$_{1}^{+}$DCTA</td>
<td>$7.22 \times 10^{10}$</td>
<td>$7.42 \times 10^{10}$</td>
<td>4.92</td>
<td>3.13</td>
<td>0.360</td>
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<tr>
<td></td>
<td>PY$_{1}^{+}$DCTA</td>
<td>$7.80 \times 10^{10}$</td>
<td>$8.60 \times 10^{10}$</td>
<td>5.51</td>
<td>3.42</td>
<td>0.370</td>
</tr>
<tr>
<td></td>
<td>PY$_{2}^{+}$DCTA</td>
<td>$6.39 \times 10^{10}$</td>
<td>$7.71 \times 10^{10}$</td>
<td>4.74</td>
<td>2.85</td>
<td>0.397</td>
</tr>
</tbody>
</table>

**REFERENCES**
