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SUMMARY

The IL’s used in this study were either synthesized or commercially available. Preparation of the IL’s involved 2 step processes: firstly the heating of distilled 1-methylimidazole with distilled 1-chlorobutane under reflux to obtain 1-butyl-3-methylimidazolium chloride; secondly, the metathesis reaction of sodium tetrafluoroborate with 1-butyl-3-methylimidazolium chloride to obtain 1-butyl-3-methylimidazolium tetrafluoroborate. The addition of sodium tetrafluoroborate, sodium hexafluorophosphate and lithium trifluoromethane sulfonamide with 1-butyl-3-methylimidazolium chloride produced good yields of 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide respectively. The IL’s are hygroscopic and must be stored under a nitrogen atmosphere. The IL’s were analyzed using $^1$H and $^{13}$C NMR analysis with CDCl$_3$ as solvent.

The physical and chemical properties of these IL’s were compared to commercial products. The physical and chemical properties compared well to reference values from the literature. The physical properties measured include the density, conductivity and electrochemical window. The electrochemical window is dependant primarily on the resistance of the cation to reduction and the resistance of the anion to oxidation. The electrochemical windows of the IL’s were very similar to the reference windows obtained from literature and it can be seen that some IL’s have a slightly lower window which can be due to water present. Water content in the IL’s was determined with the use of a Karl Fischer titrator, with Hydral 5 Composite as titrant and HPLC grade methanol as the base. The concentration of halide in the IL’s was determined with a Perkin-Elmer ICP-MS.

The anodic coupling of 2,6-di-$t$-butylphenol was studied, leading first to the 3,3′,5,5′-tetra-$t$-butyl-4,4′-dihydroxybiphenyl and then to the 3,3′,5,5′-tetra-$t$-butyldiphenoquinone. The para C-O coupling would be less likely to occur than para C-C coupling because of the increased steric affect that would come into play in such a situation,
due to the proximity of the \( t \)-butyl groups to the hydroxyl group. This reaction was studied in 3 different ways:

a) using traditional organic solvent (CH\(_2\)Cl\(_2/\) CH\(_3\)OH) together with an supporting electrolyte (LiClO\(_4\));

b) using the pure IL's that was synthesized as well as the commercial products;

c) using the IL's, that was suitably diluted with acetonitrile to obtain its maximum conductivity.

It was shown that the main limitation in the performance of the neat IL was their conductivity. This is due to ion association, leading to the formation of ion pairs, which do not contribute to the overall conductance of the medium. Four solvents were selected, acetonitrile, acetone, methanol and dichloromethane, to investigate whether the addition of the solvent in small quantities to the IL caused an increase in conductivity. It was found that upon adding each of the solvents to each of the IL's, there was at first a sharp increase in conductivity, followed by a maximum and gradual decrease due to further dilution. Acetonitrile produced the best results, giving maximum conductivity upon addition of the smallest volume in each case. The sequence of performance of these solvents in decreasing order of effectiveness was:

\[\text{Acetonitrile} > \text{Methanol} > \text{Acetone} > \text{Dichloromethane}\]

This trend was explained in terms of the dielectric constant of the solvent, as well as the dipole moment of the solvent.
CHAPTER 1

INTRODUCTION

1.1 General aspects of ionic liquids

1.1.1 History of ionic liquids

Ionic liquids (IL) have been known for many years; for example, ethylammonium nitrate (EtNH$_3$[NO$_3$]) was first described in 1914. Ethylammonium nitrate is a liquid at room temperature with a melting point of 12°C but usually contains concentrations of 200-600 ppm water. In the late 1940s, Hurley and Weir at Rice University studied N-alkylpyridinium chloroaluminites as electrolytes for electroplating aluminium with more extensive research by Hussey, Osteryoung and Wilkes in the late 1970s.

One of the first 1,3-dialkyylimidazolium room temperature ionic liquids (RTIL’s) was reported in the early 1980s by Wilkes and co-workers. This was obtained through the mixing of 1-ethyl-3-methylimidazolium chloride ([emim]Cl) with aluminum trichloride. Organo-aluminate IL has a limited range of applications due to the high reactivity of the chloroaluminate anion towards water.

In the early 1990s, Wilkes reported two new IL such as 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF$_4$) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF$_6$). In the middle of the 1990’s, a renaissance of the rich chemistry of molten salts had begun and continues to flourish.

Until 2001 the halogenoaluminate (III) (in particular [emim]$^+$AlCl$_4^-$, which contains the cation 1-ethyl-3-methylimidazolium and the smaller anion tetrachloroaluminate) and the closely related alkylhalogenoaluminate (III) IL have been by far the most widely studied.
Nowadays 1,3-dialkylimidazolium salts are the most popular and investigated classes of RTIL.\textsuperscript{5,6} Research into the use of IL as solvents, reagents, catalysts and materials will continue to grow.

1.1.2 What are ionic liquids?

The terms RTIL, non-aqueous IL, molten salt, liquid organic salt, and fused salt have all been used to describe salts in the liquid phase.\textsuperscript{1}

RTIL’s are ionic media resulting from the combination of organic cations and various anions, as shown in Fig. 1.1; they are liquids at room temperature and represent a new class of non-aqueous but polar solvents which are able to dissolve many compounds.\textsuperscript{7}

Conventional molten salts exhibit a high melting point (801°C for sodium chloride and 614°C for lithium chloride), which greatly limits their use as solvents in most applications.\textsuperscript{8} RTIL’s have melting points below 100°C, and sometimes as low as -96°C, so that they can be used as solvents under conventional organic liquid-phase reaction conditions.

These low melting points are a result of the chemical composition of RTIL’s, which contain larger asymmetric organic cations compared to their inorganic counterparts of molten salts: the asymmetry lowers the lattice energy, and hence the melting point, of the resulting ionic medium. In some cases, even the anions are relatively large and play a role in lowering the melting point.

As seen from Fig. 1.1 various combinations of organic cations with specified anions are possible in order to form the IL with particular chemical and physical properties.\textsuperscript{9}
Most commonly used cations:

1-alkyl-3-methylimidazolium

N-Alkylpyridinium

Tetraalkylammonium

(\text{where } R_{1,2,3,4} = \text{alkyl})

Tetraalkylphosphonium

Some possible anions:

\[[PF_6]^\cdot \quad [BF_4]^\cdot \quad [CH_3CO_2]^\cdot \]

\[[CF_3SO_2]_2N^\cdot \quad [CF_3SO_3]^\cdot \quad [CF_3CO_2]^\cdot, [NO_3]^\cdot \]

Br^\cdot, Cl^\cdot, I^\cdot

[Al_2Cl_7]^\cdot, [AlCl_4]^\cdot

\textbf{Fig. 1.1} The building blocks of IL

The composition and associated properties of IL depend on the cation and anion combinations: there are literally millions of different structures that may form an IL, the combinations cation-anion is estimated to be as high as $10^{18}$.
1.1.2.1 Fluorous Anions

- PF$_6^-$, BF$_4^-$

Most prominent among these is PF$_6^-$ and BF$_4^-$: Little variation in properties might be expected between same-cation salts of these species; however the actual differences can be dramatic: for example, [bmim]PF$_6$ is immiscible with water, whereas [bmim]BF$_4$ is miscible with water. This sort of variation arises from different ion pairing giving rise to IL's description as "designer solvents".

- CF$_3$SO$_3^-$, (CF$_3$SO$_3$)$_2$N$^-$

Despite their widespread use, IL featuring PF$_6^-$ and BF$_4^-$ have been reported to sometimes decompose when heated in the presence of water, giving off HF. This drawback has prompted the introduction of alternative anions, though many of these still contain fluorine. However in these, the fluorine of the anion is bonded to carbon, the C-F bond being inert to hydrolysis. Thus, IL based upon CF$_3$SO$_3^-$, (CF$_3$SO$_3$)$_2$N$^-$ and related anions are being marketed.

For reactions involving the use of a metal catalyst in an IL, a low capacity for coordination on the part of the anion is essential. Fluorous species like PF$_6^-$ or (CF$_3$SO$_3$)$_2$N$^-$ will probably remain the best in that regard. However, fluorinated anions such as these tend to be expensive, especially for use on larger scales.

1.1.2.2 Non-fluorous Anions

In response to safety and cost concerns, new IL's with non-fluorous anions have been introduced. Among the most interesting are salts in which the anions are derived from inexpensive bulk chemicals.

- Alkylsulfate anions

Alkylsulfate anions are likely to be reasonably non-toxic and biodegradable. One specific ionic liquid, ECOENG 500 (Peg-5 cocomonium methosulfate), is the first commercially available IL for which full toxicological data is available.
The docusate (dioctylsulfosuccinate) anion (Fig. 1.2 and 1.3) is known to exhibit low mammalian toxicity, and is widely used in food, drug and cosmetic applications. In contrast to other IL, many incorporating docusate are highly lipophilic, some being fully miscible with hydrocarbons.

Fig. 1.2 (a) n-Octyl sulfate and (b) docusate

Fig. 1.3 The IL methyl-tri-n-butylammonium docusate on the left and 1-butyl-3-methylimidazolium diethylene glycolmonomethylethersulfate on the right
Not all IL are liquid at room temperature. Referring to Fig. 1.3, on the left is methyl-tri-$n$-butylammonium docusate, with a melting point of ca. 40°C; on the right is a RTIL, 1-butyl-3-methylimidazolium diethylene glycolmonomethylethersulfate. Note that some IL are colourless, while others are pale yellow-to-orange in colour.

1.1.2.3 Non-conventional Anions

A survey of chemical catalogs uncovers over one hundred commercially available salts that melt below 150°C. Many others melt just above this temperature, suggesting that many new IL might be readily created by matching a desired cation from such a salt with a different anion, or vice-versa. These compounds constitute *incognito* IL. The availability of incognito IL is due to their existing use in some other type of application. Naturally, such pre-existing applications point to potential uses as IL for the compounds themselves or salts related to or derived from them.

- **Acetylcholine chloride**

  This salt, a non-toxic natural product, melts between 147°C–149°C, making it an "ionic liquid". Davies\(^6\) has recently demonstrated that, when combined with selected inorganic salts, it forms eutectics with even lower melting points. These eutectics, themselves composed wholly of ions, are interesting new IL with built-in, water-stable Lewis acidic character.

- **Amino acid derivatives**

  *L-alanine ethyl ester hydrochloride* (mp 78°C) and *L-serine methyl ester hydrochloride* (106°C) are not IL in a strict sense. Melts likely manifest neutral species, meaning that they are not composed only of ions. However, as melts in contact with a secondary, low-polarity organic phase, it is doubtful that any neutral melt component would partition into the latter, allowing the melt to function in a fashion similar to a true IL.
1.1.3 Preparation and Purification of ionic liquids

The imidazolium-based RTIL used in this study are derived from a precursor, the 1-alkyl-3-methylimidazolium halide, in most cases the chloride. The chloride is prepared by heating distilled 1-methylimidazole and distilled 1-chlorobutane under reflux at 80°C for 26 h (Scheme 1.1).

The chloride is then used either in a metathesis reaction, where the 1-alkyl-3-methylimidazolium halide is reacted with a group I metal salt or a silver salt of the desired anion, or in an acid-base neutralization reaction.

The metathesis and acid-base methods are carried out in water at room temperature, although they can be carried out in organic solvents such as acetone. Depending on the anion chosen, the resulting IL forms either a biphasic system with water or a homogeneous solution. If the resulting IL forms a biphasic system with water (that is if the anion is \([\text{PF}_6]^-\) or \([(\text{CF}_3\text{SO}_2)_2\text{N}]^-)\), an aqueous extraction follows to remove the halide, resulting in halide free IL. For water-miscible IL, the purification of the metathesis reaction involves the removal of water under reduced pressure with addition of chloroform, followed by several filtration steps. The purification of the water-miscible IL prepared by the acid-base method includes repetitive addition of water and removal of water/acid under reduced pressure.

The methods explained are the general preparation procedures for the synthesis of IL. The method chosen to prepare IL in this project is the metathesis route with the addition of sodium tetrafluoroborate, sodium hexafluorophosphate and lithium trifluoromethane sulfonamide to the chloride precursor (Scheme 1.2).
Scheme 1.1 Preparation and purification of IL$^9$
**Scheme 1.2**  Preparation of IL from starting material 1-methylimidazole

1.1.4  Physical and Chemical Properties of ionic liquids

RTIL exhibit many properties\(^{11-13}\) which make them potentially attractive media for various applications:

- By combining different anions and cations, it is possible to generate a large number of different IL, each with their own specific solvation properties.
- They are non-volatile and non-flammable and therefore can be used in high vacuum systems which eliminates many containment problems.
- They generally have reasonable thermal stability with liquid ranges up to 300°C.
- They have relatively high viscosity compared to traditional organic solvents.
- They have higher conductivity than the traditional organic solvents.
- They have wide electrochemical windows which is the range between the anodic and cathodic decomposition potential limits.
• They can act as both solvent and catalyst for specific chemical applications.
• They are good solvents for a wide range of both inorganic and organic materials.
• They are immiscible with a number of organic solvents and provide a non-aqueous, polar alternative for two-phase systems. Hydrophobic IL can also be used as immiscible polar phases with water.
• They are often composed of weakly coordinating anions, e.g. $\text{BF}_4^-$ and $\text{PF}_6^-$ and, hence, have the potential to be highly polar yet non-coordinating solvents. They can be expected, therefore, to have a strong rate-enhancing effect on reactions.
• Those which are stable can be recycled and reused therefore leading to waste reduction.
• They are water-sensitive, therefore must be used under an inert atmosphere in a nitrogen box.

1.1.5 The Global Need for Ionic liquids

Volatile organic solvents (VOC’s) are used in a variety of industrial applications such as in the production of pharmaceuticals, the manufacture of electronic components, processing of polymers, refrigeration systems, electrodeposition\textsuperscript{14}, batteries\textsuperscript{15}, electrochemical sensors\textsuperscript{16}, capacitors\textsuperscript{17} and the synthesis of chemicals. As a result of their volatile nature, such solvents easily evaporate into the environment.

The use of VOC’s poses a risk to people working with them or living in close proximities to facilities using them. In addition VOC’s have been heavily implicated in causing changes to the global climate, the formulation of smog as well as being identified as a source of ozone depletion.\textsuperscript{18}

It is estimated that the current usage of VOC’s world-wide is worth some £4,000,000,000 per annum representing a massive global market. The Montreal
Protocol has forced many industries and organizations to re-evaluate their chemical operations, due to the adverse environmental impact caused by the use of VOC’s by investing in clean technology that reduces waste and by-products from industrial processes to a minimum. It is from this background that the pioneering work on IL was commenced.\textsuperscript{18}

Specific IL have the potential to be classified as ideal green solvents as they have negligible vapour pressure and do not evaporate into the atmosphere.

\subsection*{1.1.6 Impurities in ionic liquids}

The synthesis of an IL is in principle quite simple organic chemistry. However, the preparation and purification of an IL of a specific quality requires expert know-how and experience. During the preparation of the IL, the [bmim]Cl, which is a solid, can be recrystallized to remove impurities before continuing with the metathesis or acid-base step of the preparation.

\subsubsection*{1.1.6.1 Organic starting materials and other volatiles}

Volatile impurities in an IL may have different origins. They may result from solvents used in the extraction steps during the synthesis, from the unreacted starting materials, from the alkylation reaction or from any VOC previously dissolved in the IL.

Volatile impurities can easily be removed from the non-volatile IL by simple evaporation. However, this process can sometimes take a considerable time. Factors that influence the time required for the removal of all volatiles from an IL (at a given temperature and pressure) are:
• the amount of volatiles,
• their boiling points,
• their interactions with the IL,
• the viscosity of the IL, and
• the surface of the IL.

An example of a volatile impurity can be found as one of the main impurities in low-quality IL with 1-alkyl-3-methylimidazolium cations, is the 1-methylimidazole starting material. Because of its high boiling point (198°C) and its strong interactions with the IL, this compound is very difficult to remove from an IL even at elevated temperature and under high vacuum. It is therefore important to make sure, by use of appropriate alkylation conditions that no unreacted 1-methylimidazole is left in the final product.

Traces of 1-methylimidazole in the final IL can play an unfavorable role in some common applications of IL. A number of different methods to monitor the amount of this starting material in the final IL are known. NMR spectroscopy is used by most research groups, but has a detection limit of only ca. 1 mol%.¹⁹

1.1.6.2 Halide Impurities ¹⁹

Many IL are still made in a two-step synthesis as described in section 1.1.3. In the first step, alkyl halides are frequently used as alkylation agents, forming halide salts of the desired cation. To obtain a non-halide IL, the halide anions are exchanged in a second step. This can be achieved variously by addition of the alkali salt of the desired anions by treatment with a strong acid or by use of an ion-exchange resin.

All halide exchange reactions cause greater or lesser quantities of halide impurities in the final product. The choice of the best procedure to obtain complete exchange depends mainly on the nature of IL that is being produced. There is no general method to obtain a halide-free IL that can be used for all types of IL.
Halide impurities can seriously affect the usefulness of the material as a solvent for a given chemical reaction. Apart from the point that some physicochemical properties are highly dependent on the presence of halide impurities, the latter can chemically act as catalyst poisons, stabilizing ligands, nucleophiles, or reactants, depending on the chemical nature of the reaction. It is necessary to have an IL free of halide impurities to investigate its properties for any given reaction.

Quantitative analysis of the residual chloride impurities can be determined with the use of ICP-MS Inductively Coupled Plasma-Mass Spectroscopy (Fig. 1.4).20
1.1.6.3 Water

Without special drying procedures and complete inert handling, water is omnipresent in IL. Imidazolium halide salts in particular are known to be extremely hygroscopic, one of the reasons why it is so difficult to make completely proton-free chloroaluminate IL.

For commercial IL production, this clearly means that all products contain a small percentage of water. Also depending on the production conditions and the logistics, the IL can reasonably be expected to come into some contact with traces of water.

Water in an IL may be a problem for some applications, but not for others. However, one should in all cases know the approximate amount of water present in the IL used. One should be aware of the fact that water in the IL may not be inert and, furthermore, that the presence of water can have significant influence on the physicochemical properties of the IL, on its stability (some wet IL may undergo hydrolysis with formation of protic impurities), and on the reactivity of the catalyst dissolved in the IL.

It should be kept in mind, especially when the IL is used as solvent in reactions, that efficient drying and anhydrous handling has to be ensured (under reduced pressure at 70°C for 8 h).

The water content in the IL can be determined with the use of the Karl Fischer (Fig. 1.5) with Hydranal 5 Composite as titrant and HPLC grade methanol as the base.
Karl Fischer titrator can be used for the determination of the water content in the IL.

1.2 Chemical Applications of ionic liquids

1.2.1 Organic reactions

1.2.1.1 Diels-Alder reactions

The first study was the reaction of cyclopentadiene with methyl acrylate and methyl vinyl ketone in [EtNH₃][NO₃]. These reactions lead to a mixture of exo and endo products, and the solvent influences the exo/endo selectivity of the reaction. The word exo and endo are used to indicate relative stereochemistry when referring to bicyclic structures. A substituent on one bridge is said to be exo if it is anti (trans) to the larger of the other two bridges, and is said to be endo if it is syn (cis) to the larger of the other two bridges (Fig. 1.6).
The effect can be attributed to solvophobic interactions that generate an “internal pressure” and promote the association of the reagents in a “solvent cavity” during the activation process. The reactions showed a strong preference for the endo product and an acceleration of the reaction in comparison to nonpolar organic solvents. Although the increased rates and selectivities were not as great as those seen in water, the IL has the advantage that moisture-sensitive reagents may be used (Scheme 1.3).

**Scheme 1.3**  Diels-Alder cycloaddition of cyclopentadiene and methyl acrylate

The same reaction has been investigated in a number of different IL ([emim][BF₄], [emim][ClO₄], [emim][CF₃SO₃], [emim][NO₃] and [emim][PF₆]), all of which show the
same trend.\textsuperscript{22} The effect was slightly weaker in these IL, and this may be due to stronger (N-H) hydrogen bonding leading to stronger solvophobic effects in [EtNH$_3$][NO$_3$].

\section*{1.2.2 Transition Metal Mediated Catalysis}

\subsection*{1.2.2.1 Biphasic Catalysis}

The great advantage of homogeneous catalysis over heterogeneous catalysis is that all of the metal centres are available to the reagents, and so it is inherently more efficient. Biphasic catalysis represents a method to heterogenize a catalyst and product into two separated and immiscible phases without losing the selectivity and efficiency inherent in homogeneous catalysis.\textsuperscript{23} The catalyst resides in solutions in one of the two phases, and the substrate resides in the other phase. During reactions, the two layers are vigorously stirred, thus allowing suitable interaction of catalyst and substrate. Once the reaction has reached the appropriate stage, the stirring is stopped and the mixture of phases separates into two layers, one containing the product and the other the catalyst. Separation is carried out by simple decantation, and in principle, the catalyst solution is available for immediate reuse.

There are three main areas of interest in biphasic catalysis. The main biphasic system used is comprised of an aqueous-organic mixture, and such processes are very effective and have been implemented in commercial processes for both oligomerization and hydroformylation reactions. Another system uses fluorinated solvents to generate fluorous-organic biphasic reaction conditions.\textsuperscript{24} Here, the affinity of the fluorous phase for highly fluorinated solutes is used to isolate the catalysts in the fluorous layer. This allows the use of water-sensitive materials, but requires the use of specially prepared catalysts and expensive solvents. The third system is the IL-organic system.
1.2.2.2 Hydrogenation Reactions

The hydrogenation reaction of sp\(^2\) hybridized C=C bonds catalyzed by transition-metal complexes is probably one of the most widely studied vinylic homogeneous catalysis; however, the separation of products from reactants remains problematic. Initial experiments using [Rh(nbd)PPh\(_3\)][PF\(_6\)] (where nbd = norbornadiene) as the catalyst for the hydrogenation of pent-1-ene in a variety of IL showed their potential as solvents for isolating the catalyst.\(^{25}\) For both [SbF\(_6\)]\(^-\) and [PF\(_6\)]\(^-\) IL, hydrogenation rates were significantly greater than that seen for the same catalyst in acetone, presumably due to the stabilization of the Rh(III) intermediate. In the IL, the cationic catalyst is in direct contact with neighboring anions, whereas in a conventional solvent they will be solvent separated. It is probably this close contact that leads to the influence of the anion on the product distribution.

RhCl(PPh\(_3\))\(_3\) and [Rh(cod)\(_2\)][BF\(_4\)] (where cod = cyclooctadiene) have also been used for the hydrogenation of cyclohexene in [bmim][BF\(_4\)].\(^{26}\) Although RhCl(PPh\(_3\))\(_3\) gave higher turnover rates, the use of [Rh(cod)\(_2\)][BF\(_4\)] led to higher overall conversion of cyclohexene to cyclohexane. It is also notable that ionic [Rh(cod)\(_2\)][BF\(_4\)] showed greater solubility in [bmim]BF\(_4\) than RhCl(PPh\(_3\))\(_3\).

RuCl\(_2\)(PPh\(_3\))\(_3\) is also an effective hydrogenation catalyst in [bmim][BF\(_4\)].\(^{26}\) Hex-1-ene, cyclohexene, and 1,3-butadiene, produced a mixture of but-1-ene, but-2-enes and \(n\)-butane, are all reduced. The use of [bmim]\(_3\)[Co(CN)\(_5\)] to hydrogenate 1,3-butadiene, leads to 100% selectivity, to form but-1-ene.\(^{27}\) The chiral catalyst [RuCl\(_2\)-(S)-BINAP]\(_2\).NE\(_3\) has been used to asymmetrically hydrogenate 2-phenyl-acrylic acid and 2-(6-methoxy-2-naphthyl)acrylic acid, (Scheme 1.4).\(^{28}\)
Palladium(II) chloride has been used in molten [Bu$_4$N]Cl (mp = 42°C) to hydrogenate CCl$_4$ to give a mixture of C$_1$-C$_5$ paraffins and C$_2$-C$_4$ olefins and small amounts of partially hydrogenated products. The catalyst quickly deactivates, but its life time can be extended if CoCl$_2$ or CuCl$_2$ is added to the reaction mixture. Almost certainly [PdCl$_4$]$^{2-}$ is formed on initial dissolution of the PdCl$_2$ in the [Bu$_4$N]Cl.

### 1.2.2.3 Oxidation

Recently results by Song and Roh indicate that the use of IL is also of advantage in selective oxidation reactions. The epoxidation of, for example, 2,2-dimethylchromene with a chiral Mn$^{III}$ (salen) complex ([N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine]manganese(III)chloride) in a mixture of [bmim][PF$_6$] and CH$_2$Cl$_2$ (1:4 v/v) was investigated (Scheme 1.5).

**Scheme 1.4** Formation of (S)-naproxen in [bmim][BF$_4$]

**Scheme 1.5** The epoxidation of 2,2-dimethylchromene in [bmim][PF$_6$]/CH$_2$Cl$_2$
A clear enhancement of the catalyst activity by the addition of the IL to the organic solvent was described. In the presence of the IL, an 86 % conversion of 2,2-dimethylchromene was observed after 2 h. Without the IL the same conversion was obtained only after 6 h. In both cases the enantiomeric excess was as high as 96 %.

The use of IL solvent allows an easy catalyst recycle without the need of any catalyst modification. By washing the organic phase with water followed by extraction of the product with hexane, the ionic catalyst solution is recovered after reaction and can be reused. After five recycles the conversion drops from 83 % to 53 % under identical reaction conditions. The example by Song and Roh is the first published example of a transition metal catalyzed oxidation reaction in an IL. This is quite surprising, taking into account that the IL concept appears particularly suitable for oxidation reactions.

It is known from electrochemical studies that some IL show high oxidation stability. Moreover, recent studies showed that low melting imidazolium and pyridinium salts are stable even versus highly oxidizing media such as fuming sulfuric acid (30 % SO₃) if short alkyl chains are chosen as the cation. The investigation of further oxidation reactions in IL looks therefore quite promising.

1.2.2.4 Dimerization of Butadiene

Palladium(II)chloride, palladium(II)acetate and palladium(II)acetylacetonate in [bmim][BF₄] or [bmim][PF₆] IL have been used for the hydrodimerization of butadiene to form octa-2,7-dien-1-ol as the major product and 1,3,6-octatriene as the minor product. The reaction mixture was homogeneous under the reaction conditions (70°C), but the products could easily be separated by cooling the mixture to below 5°C. The recovered IL and catalyst could be reused. In this reaction system hydrodimerization was achieved in the absence of CO₂, which is necessary for reaction to occur in conventional molecular solvents, although both the degree of conversion of the 1,3-butadiene and the turnover frequencies were greatly improved.
by its addition. In this case, the active catalyst is the neutral trans-bis(methyl-imidazole)palladium(II)dichloride, which is formed from the ionic precursor [bmim][PdCl$_4$] when water is added to its solution in the IL.$^{32}$

The cyclodimerization of butadiene to 4-vinylcyclohexene using Fe(NO)$_2$ in [bmim][AF$_6$] (A=P or Sb) IL has been reported to show a remarkable solvent effect.$^{33}$ Fe(NO)$_2$ was produced by the chemical or electrochemical reduction of Fe$_2$(NO)$_4$Cl$_2$ to yield the catalyst for this Diels-Alder dimerization.

1.2.2.5 Heck Reaction

Palladium(II)chloride and palladium(II)acetate have also been used as precatalysts in a number of tetraalkylammonium and phosphonium bromide salts for palladium(0)-catalyzed C-C coupling, Heck reactions.$^{34}$ Since the reactions were conducted at 100°C, it did not matter if the solvents were liquids at room temperature. In the Heck reaction, C-C coupling of aromatic and vinylic systems occurs. The reaction of bromobenzene with butyl acrylate to provide butyl cinnamate, succeeded in high yield, in molten tetraalkylammonium and tetraalkylphosphonium bromide salts (Scheme 1.6).$^{34}$
When the complexes dichlorobis(triphenylphosphine)palladium(II) and palladium(II)-acetate were used as the catalyst precursors, stable solutions were formed which could be reused after the reaction without loss of catalytic activity for at least two further runs. The products were removed from the solution by distillation. High levels of conversion were observed in these IL (over 99 % in some cases). When palladium(II)chloride was used, precipitation of a palladium cluster which was deactivated toward the catalysis occurred after some hours.

1.2.2.6 Trost-Tsuji Couplings

The nucleophilic, allylic substitution catalyzed by palladium(0) complexes is an attractive way to form carbon-carbon bonds in organic synthesis. The reaction could be successfully carried out in IL as well. Xiao et al. described the monophasic reaction of 3-acetoxy-1,3-diphenylprop-1-ene with dimethyl malonate in [bmim][BF₄].³⁵ The reaction proceeded in 5 h (80°C) to complete conversion with Pd(OAc)₂/PPh₃ as catalyst system and K₂CO₃ as base. The desired coupling product could be isolated in 91 % yield. The possibility of generating the nucleophile in situ is regarded as a special advantage of the use of the IL solvent.

De Bellefon et al. investigated biphasic Trost-Tsuji coupling reactions.³⁶ Ethyl cinnamyl carbonate was reacted with ethyl acetoacetate in [bmim]Cl/methyl-cyclohexane and the results compared to the identical reaction in butyronitrile/water (Scheme 1.7). Evidently, the reaction in the solvent incorporating the IL shows clear advantages over the reaction in the aqueous biphasic solvent.
Scheme 1.7 The reaction of cinnamyl carbonate with ethyl acetoacetate in [bmim]Cl/methylcyclohexane

An enhancement of the catalytic activity by a factor of ten is observed in the IL mainly due to the much better solubility of the substrate molecules in the IL. The reaction in [bmim]Cl/methylcyclohexane shows significantly improved selectivity since the formation of cinnamyl alcohol (by reaction of water as nucleophile) and the formation of phosphonium salts (by reaction of the Pd-allyl complex with trisulfonated triphenylphosphine (tppts) as ligand) is suppressed and very much decreased in the IL.

1.2.3 Organometallic reactions in chloroaluminate(III) ionic liquids

An interesting Friedel-Crafts reaction performed in RTIL’s involves the acylation of ferrocene. The acylation of ferrocene with acetic anhydride in an [emim]-AlCl₃ IL and in the liquid clathrate, prepared from the addition of toluene to the IL has been reported. It was claimed that monoacetylferrocene was the only product of the acylation reaction using both reaction media, with the highest yields being acquired using the liquid clathrate.

Arene exchange reactions of ferrocene are well known to be catalyzed by aluminum (III) chloride. Hence, the [bmim]Cl-AlCl₃ has been used to prepare a number of arene(cyclopentadienyl)iron(II) complexes, [Fe(C₅H₅)ⁿ(arene)⁺⁻⁻][] from ferrocene. The IL acts as a solvent and Lewis acid source. However, since the IL used were completely aprotic, the products were only formed on addition of a proton source,
[bmim][HCl₂]. This would probably have been unnecessary if commercial aluminum (III) chloride had been used without sublimation (Scheme 1.8).

**Scheme 1.8** Arene exchange reactions of ferrocene

1.3 **Electrochemical applications of ionic liquids**

There are a number of potential applications for IL in the area of electrochemistry and this includes the following: fuel cells, Li batteries, photoelectrochemical cells, electrochemical capacitors, electrodeposition of metals and electrochemical polymerization. In section 1.3.1, the use of IL in electrochemical capacitors and Li batteries will be explained.

1.3.1 **Ionic liquids as electrolytes for electrochemical capacitors**

IL are being considered for use as liquid electrolytes for electrochemical energy devices because they can increase device safety by their non-volatile and non-flammable properties.³⁹ The double-layer capacitor (DLC) has shown the most promise as an electrochemical energy storage device for hybrid electric vehicles and hybrid fuel cell vehicles. This is because it has higher pulse power capability than conventional rechargeable batteries.⁴⁰ Commercial double-layer capacitors use
activated carbon electrodes, a non-aqueous solution such as 0.5 to 1 M Et$_4$NBF$_4$ in propylene carbonate (PC) or an aqueous solution such as 3.7 to 4.5 M (30~35 wt %) H$_2$SO$_4$ is used.\textsuperscript{41} The advantages of non-aqueous IL electrolytes are as follows:

- High decomposition voltage.
- Wide operational temperature range.
- Non-corrosive which allows the use of low cost metals such as Al in components.

The disadvantages are as follows:

- Low electrolytic conductivity.
- Need to be kept in an inert atmosphere and away from atmospheric moisture.
- High environmental impact.
- High cost.

Based on these properties, the double-layer capacitor consisting of a pair of activated carbon electrodes and the non-aqueous IL electrolyte is the most favorable one from the viewpoint of energy density.

1.3.2 Application of ionic liquids in Li batteries

The exothermic reaction at the first stage of thermal runaway of a Li-ion battery with an organic electrolyte involves electrolyte decomposition and an electrolyte-electrode reaction which accelerates the rising heat.\textsuperscript{42} Because the organic electrolyte contains volatile solvents, such as propylene carbonate, dimethylcarbonate, and dimethoxyethane, the inner pressure of the battery increases causing the battery to explode.

Once the battery is open to air, the organic electrolytes work as a fuel because they are flammable. Even if the battery could stay unopened at the elevated temperature,
the positive electrode material in the charged state begins to decompose at ca. 200°C and provides oxygen inside the battery in the presence of organic solvent.

It is therefore important to find a replacement for the volatile and flammable electrolytes. IL could be the ideal material for use as an electrolyte because they are non-volatile and flame resistant. These properties will make the battery safer. Interesting properties of IL that pertain to battery application are listed below:

- Liquid over a wide temperature range, including ambient temperature.
- Thermal stability, non-volatility, flame-resistance.
- Wide electrochemical window.
- Higher conductivity than traditional organic solvents.
- Chemical stability.

1.3.3 Electrochemical synthetic applications

1.3.3.1 Organic Industry

The industrial electrosynthesis reaction of greatest impact must be the Monsanto process for the hydrodimerization of acrylonitrile to adiponitrile, one of the steps in the fabrication of nylon 66. Chemical synthesis routes, such as gas-phase catalysis of butane exist and are used but the feedstock is more expensive than for the electrochemical route.

The electrode reactions are shown in Scheme 1.9.
Scheme 1.9 The electrode reaction in the Monsanto process

At the cathode, other reactions are possible such as reaction of acrylonitrile with OH$^-$ or direct protonation of the radical anion [CH$_2$=CHCN]$^-$ to give propionitrile. The existence of several possible pathways is general in the synthesis of organic compounds, and optimized experimental conditions, such as choice of electrode potentials that minimize unwanted lateral reactions, must be sought. In this case the pH control is also of importance in minimizing the unwanted reactions.

The Monsanto process is shown schematically in Fig. 1.7. The solution is an emulsion of acrylonitrile and 10-15 % disodium hydrogenphosphate in water containing a quaternary ammonium salt, hexamethylene-bis(ethyl-di-butylammonium) phosphate, to conduct the current. The anode is carbon steel and the cathode is cadmium (a sheet fixed onto the anode); this cell is a good example of the use of bipolar electrodes. EDTA and borax are added in small quantities to minimize anode corrosion. The cell potential is -3.8V and the selectivity is 88 %.
Aluminium is one of the most abundant elements in the earth’s crust, but, under feasible industrial conditions, can only be extracted by electrolysis. The process used is the electrolysis of aluminium hydroxide in molten cryolite (Na$_3$AlF$_6$) at 970°C. Pure aluminium hydroxide is prepared from the mineral bauxite (hydrated aluminium oxide containing silica and some metal oxides such as iron) by the Bayer process. The cathode is carbon covered molten aluminium metal and the anode is carbon, the total reaction being Eq 1 (Scheme 1.10), which consumes the anode. This is the Hall-Heroult process $^{45}$, represented in Fig. 1.8.

Fig. 1.7  The Monsanto process for the hydrodimerization of acrylonitrile

1.3.3.2  Inorganic Industry$^{43}$
The molten cryolite is ionized. The reactions (Eq 2 to Eq 5) in Scheme 1.10 involves the complex ion formation. At the cathode, there is evidence that the complex ions AlF$_6^{-3}$ and AlF$_4^{-}$ dismute, then followed by reduction of Al$^{3+}$ to Al (Eq 6 to Eq 8). Na$^{+}$ is not reduced and F$^{-}$ produced by the cathode reactions neutralizes the charge of the sodium ions. At the anode the electrode reactions involve the aluminium oxyfluoride complex ion (Eq 9 and Eq10) in Scheme 1.10.
<table>
<thead>
<tr>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2 )</td>
</tr>
<tr>
<td>( \text{Na}_3\text{AlF}_6 \rightarrow 3\text{Na}^+ + \text{AlF}_6^{3-} )</td>
</tr>
<tr>
<td>( \text{AlF}_6^{3-} \rightarrow \text{AlF}_4^- + 2\text{F}^- )</td>
</tr>
<tr>
<td>( 4\text{AlF}_6^{3-} + \text{Al}_2\text{O}_3 \rightarrow 3\text{Al}_2\text{OF}_6^{2-} + 6\text{F}^- )</td>
</tr>
<tr>
<td>( 2\text{AlF}_6^{3-} + 2\text{Al}_2\text{O}_3 \rightarrow 3\text{Al}_2\text{O}_2\text{F}_4^{2-} )</td>
</tr>
<tr>
<td>( \text{AlF}_6^{3-} \rightarrow \text{Al}^{3+} + 6\text{F}^- )</td>
</tr>
<tr>
<td>( \text{AlF}_4^- \rightarrow \text{Al}^{3+} + 4\text{F}^- )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} \rightarrow \text{Al} + 3\text{e}^- )</td>
</tr>
<tr>
<td>( \text{AlO}_2\text{F}_4^{2-} + 2\text{AlF}_6^{3-} + \text{C} \rightarrow 4\text{AlF}_4^- + \text{CO}_2 + 4\text{e}^- )</td>
</tr>
<tr>
<td>( 2\text{AlOF}_6^{2-} + 2\text{AlF}_6^{3-} + \text{C} \rightarrow 6\text{AlF}_4^- + \text{CO}_2 + 4\text{e}^- )</td>
</tr>
</tbody>
</table>

**Scheme 1.10** Equations used in the Hall-Heroult process

Under typical conditions the cell potential is

- reversible potential: -1.2 V
- anode overpotential: -0.5 V
- \( IR \) drops: at electrodes: -1.1 V
- in electrodes: -1.5 V
- 4.3 V

Thus only 30% of the total potential is used for the electrode reactions. It would clearly be very advantageous if there were another more energy-efficient process, preferably at a lower temperature.
1.4 Electro-oxidation coupling of 2,6-di-t-butylphenol

Electro-oxidations involve electron transfer between an organic reactant and the anode of an electrochemical cell. This results in an intermediate which then reacts further to form the product. The characteristic features of electro-oxidations are as follows:

- Electrochemical methods can be used to synthesize a wide variety of organic chemicals: any oxidation that can be carried out using conventional chemical oxidizing agents can theoretically be carried out in an electrochemical cell.

- The selectivity of the electrochemical step can be greatly increased by careful selection of the conditions at the phase boundary, e.g. potential, current densities, etc.

- Electrochemical syntheses often have a lower environmental impact than conventional oxidation methods since electrolytic routes often replace toxic reagents and hazardous process conditions.

The main reaction studied in chapter 4 is the oxidative coupling of 2,6-di-t-butylphenol in an IL medium contained in an electrochemical cell, in order to produce the biphenyl compound. The reaction is given in Scheme 1.11, which shows that mild oxidation firstly causes the formation of the biphenyl compound, which can be further oxidized to the corresponding diphenoquinone. There is a reversible equilibrium between the two dimeric forms.

In Chapter 4, the electro-oxidation of 2,6-di-t-butylphenol will be investigated in conventional organic solvents such as methanol and dichloromethane with lithium perchlorate as supporting electrolyte. The use of IL will also be investigated where the electro-oxidation will be carried out in three different IL and compared to the commercial IL.
Scheme 1.11  Electro-oxidation coupling of 2,6-di-t-butylphenol
CHAPTER 2

EXPERIMENTAL

2.1 Materials

2.1.1 Reagents for synthesis of ionic liquids

All reagents used in the organic synthesis procedures for IL together with their sources and respective grades, are listed in Table 2.1 and were used as received.

Table 2.1 Reagents for synthesis of IL

<table>
<thead>
<tr>
<th>CHEMICAL NAME</th>
<th>CHEMICAL FORMULA</th>
<th>SOURCE</th>
<th>GRADE&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-methylimidazole</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>Calcium hydride</td>
<td>CaH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>1-chlorobutane</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;Cl</td>
<td>Fluka</td>
<td>AR</td>
</tr>
<tr>
<td>Sodium tetrafluoroborate</td>
<td>NaBF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>Sodium hexafluorophosphate</td>
<td>NaPF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>Lithium trifluoromethane Sulfonimide</td>
<td>Li N(CF&lt;sub&gt;3&lt;/sub&gt;SO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O</td>
<td>Saarchem</td>
<td>AR</td>
</tr>
<tr>
<td>Acetone</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;O</td>
<td>SMM Instruments</td>
<td>AR</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Saarchem</td>
<td>AR</td>
</tr>
</tbody>
</table>

<sup>a</sup> AR = Analytical grade reagent

2.1.2 Reagents for synthesis of HPLC standards

All reagents used in the organic synthesis of HPLC standards, together with their sources and respective grades, are listed in Table 2.2 and 2.3 and were used as received.
### 2.1.2.1 Reagents for synthesis of 3,3′,5,5′-tetra-t-butyldiphenoquinone

Table 2.2 Reagents for synthesis of 3,3′,5,5′-tetra-t-butyldiphenoquinone

<table>
<thead>
<tr>
<th>CHEMICAL NAME</th>
<th>CHEMICAL FORMULA</th>
<th>SOURCE</th>
<th>GRADE^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6-di-t-butylphenol</td>
<td>C₁₄H₂₂O₂</td>
<td>Fluka</td>
<td>AR</td>
</tr>
<tr>
<td>Silver Oxide</td>
<td>Ag₂O</td>
<td>Fluka</td>
<td>AR</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>BDH</td>
<td>HPLC</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₆H₅CH₃</td>
<td>Rochelle</td>
<td>AR</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>C₄H₈O₂</td>
<td>Saarchem</td>
<td>AR</td>
</tr>
<tr>
<td>Petroleum Ether</td>
<td>Unavailable</td>
<td>Saarchem</td>
<td>Distilled 60-80°C</td>
</tr>
</tbody>
</table>

^a AR = Analytical grade reagent, HPLC = High Performance Liquid Chromatography

### 2.1.2.2 Reagents for synthesis of 3,3′,5,5′-tetra-t-butyl-4,4′-dihydroxybiphenyl

Table 2.3 Reagents for synthesis of 3,3′,5,5′-tetra-t-butyl-4,4′-dihydroxybiphenyl

<table>
<thead>
<tr>
<th>CHEMICAL NAME</th>
<th>CHEMICAL FORMULA</th>
<th>SOURCE</th>
<th>GRADE^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,3′,5,5′-tetra-t-butylidiphenoquinone</td>
<td>C₂₈H₄₀O₂</td>
<td>Synthesis</td>
<td></td>
</tr>
<tr>
<td>Sodium dithionite</td>
<td>Na₂S₂O₄</td>
<td>SAJ</td>
<td>AR</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>Saarchem</td>
<td>AR</td>
</tr>
<tr>
<td>Magnesium Sulphate Anhydrous</td>
<td>MgSO₄</td>
<td>Fluka</td>
<td>AR</td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td>H₂SO₄</td>
<td>Saarchem</td>
<td>AR</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>C₄H₁₀O</td>
<td>Saarchem</td>
<td>AR</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl₃</td>
<td>Saarchem</td>
<td>AR</td>
</tr>
<tr>
<td>Hexane</td>
<td>C₆H₁₄</td>
<td>Saarchem</td>
<td>AR</td>
</tr>
</tbody>
</table>

^a AR = Analytical grade reagent, HPLC = High Performance Liquid Chromatography
2.1.3 Reagents for electro-organic synthesis

All the reagents used in the electro-organic synthesis studies are listed in Table 2.4. The preparation of the compounds used for electro-organic standards are described in section 2.2.2 and 2.2.3.

**Table 2.4** Reagents for electro-organic synthesis

<table>
<thead>
<tr>
<th>CHEMICAL NAME</th>
<th>CHEMICAL FORMULA</th>
<th>SOURCE</th>
<th>GRADE*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6-di-t-butylphenol</td>
<td>C_{14}H_{22}O</td>
<td>Fluka</td>
<td>AR</td>
</tr>
<tr>
<td>Lithium perchlorate</td>
<td>LiClO_4</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH_3OH</td>
<td>BDH</td>
<td>HPLC</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>CH_2Cl_2</td>
<td>SMM</td>
<td>AR</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Instrument</td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>CH_3CN</td>
<td>BDH</td>
<td>HPLC</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>C_4H_8O_2</td>
<td>Saarchem</td>
<td>AR</td>
</tr>
<tr>
<td>1-butyl-3-methyl imidazolium</td>
<td>[C_8H_15N_2][BF_4]</td>
<td>Synthesis</td>
<td></td>
</tr>
<tr>
<td>Imidazolium tetrafluoroborate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-butyl-3-methylimidazolium</td>
<td>[C_8H_15N_2][PF_6]</td>
<td>Synthesis</td>
<td></td>
</tr>
<tr>
<td>hexafluorophosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-butyl-3-methylimidazolium trifluoromethane sulfonimide</td>
<td>[C_8H_15N_2][N(CF_3SO_2)_2]</td>
<td>Synthesis</td>
<td></td>
</tr>
</tbody>
</table>

*AR = Analytical grade reagent, HPLC = High Performance Liquid Chromatography
2.1.4 Additional reagents for electro-organic synthesis

Additional reagents used in the physical and chemical studies of the IL, together with their sources and respective grades, are listed in Table 2.5, and were used as received.

Table 2.5 Reagents for physical and chemical studies

<table>
<thead>
<tr>
<th>CHEMICAL NAME</th>
<th>CHEMICAL FORMULA</th>
<th>SOURCE</th>
<th>GRADE a</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-butylammonium hexafluorophosphate</td>
<td>C₁₆H₃₆F₆NP</td>
<td>BAS</td>
<td>AR</td>
</tr>
<tr>
<td>Hydralan 5 composite</td>
<td></td>
<td>Riedel-de</td>
<td>AR</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Haën</td>
<td></td>
</tr>
<tr>
<td>Silver nitrate</td>
<td>AgNO₃</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>d-Chloroform</td>
<td>CDCl₃</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>Acetone</td>
<td>C₃H₆O</td>
<td>SMM</td>
<td>AR</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Instruments</td>
<td></td>
</tr>
<tr>
<td>1-butyl-3-methyl imidazolium chloride</td>
<td>C₈H₁₅N₂Cl</td>
<td>Synthesis</td>
<td></td>
</tr>
</tbody>
</table>

a AR = Analytical grade reagent
2.2 Synthetic procedures

2.2.1 Synthesis of ionic liquids

2.2.1.1 Synthesis of 1-butyl-3-methylimidazolium chloride

1-Methylimidazole (75 g, 0.91 mol) was first heated under reflux for 10 min in a pre-weighed 100 mL RB flask with CaH$_2$ (2.0 g, 0.048 mol), to remove any traces of water. The reacted CaH$_2$ changed colour from grey to white. After heating under reflux, the 1-methylimidazole (b.p = 198°C) was distilled (0.8 mbar, 56°C) to remove the reacted CaH$_2$.

The distilled 1-methylimidazole (62.82 g, 0.77 mol) and a 20 % molar excess of 1-chlorobutane (75.17 g, 0.92 mol) was placed in an 100 mL two-necked RB flask, equipped with a thermometer, magnetic stirrer bar, water-cooled condenser and drying tube (Fig. 2.1). The flask was placed in an oil bath and its solution heated under reflux at 80°C for 48 h (after 2 h, the mixture turned cloudy).
Fig. 2.1  Apparatus for the preparation of 1-butyl-3-methylimidazolium chloride

After heating under reflux, the hot solution was poured into a porcelain mortar, in a nitrogen glove box. Diethyl ether was added to the solution while stirring until the solution solidified. The solid was then crushed into a fine powder and placed in a 250 mL preweighed RB flask. The flask was then placed on a high vacuum system to remove all traces of solvent. The 1-butyl-3-methylimidazolium chloride solid was weighed and then stored under a nitrogen atmosphere. Table 2.6 summarizes the experimental data obtained.
$^1$H-NMR (CDCl$_3$) 10.50 (1H, s, ArH), 7.62 (2H, s, ArH), 4.19 (2H, t, CH$_2$), 3.98 (3H, s, CH$_3$), 1.75 (2H, t, CH$_2$), 1.22 (2H, t, CH$_2$), 0.79 (3H, t, CH$_3$); $^{13}$C-NMR (CDCl$_3$) 137.94, 124.11, 122.42, 49.98, 36.78, 32.45, 19.71, 13.74.

Table 2.6  Yields for 1-butyl-3-methylimidazolium chloride

<table>
<thead>
<tr>
<th>Mass of starting N-methyl-imidazole</th>
<th>Mass of distilled N-methyl-imidazole</th>
<th>Mass of 1-clorobutane added</th>
<th>Mass of [bmim]Cl obtained</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>75.00 g (0.91 mol)</td>
<td>62.82 g (0.77 mol)</td>
<td>75.17 g (0.81 mol)</td>
<td>123.86 g (0.71 mol)</td>
<td>93.0 %</td>
</tr>
<tr>
<td>75.00 g (0.91 mol)</td>
<td>52.03 g (0.76 mol)</td>
<td>70.85 g (0.77 mol)</td>
<td>110.18 g (0.63 mol)</td>
<td>99.5 %</td>
</tr>
<tr>
<td>75.18 g (0.92 mol)</td>
<td>67.67 g (0.83 mol)</td>
<td>90.09 g (0.97 mol)</td>
<td>135.01 g (0.77 mol)</td>
<td>93.8 %</td>
</tr>
</tbody>
</table>

2.2.1.2  Synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate

2.2.1.2.1  Synthesis with water as solvent

In a pre-weighed 500 mL RB flask, [bmim]Cl (50.49 g, 0.29 mol) and sodium tetrafluoroborate (31.94 g, 0.29 mol), in water (50 mL), were stirred for 48 h. The water was then removed with a rotavap for 2 h. The resulting yellow oil was dissolved in chloroform (50 mL) and the white precipitate, sodium chloride, removed by vacuum filtration. The liquid was placed on the rotavap to remove the chloroform, and then
placed on the trolley pump overnight to remove the remaining solvent then stored under a nitrogen atmosphere. Table 2.7 contains the experimental data obtained.

$^1$H-NMR (CDCl$_3$) 8.82 (1H, s, ArH), 7.43 (2H, s, ArH), 4.18 (2H, t, CH$_2$), 3.91 (3H, s, CH$_3$), 1.80 (2H, t, CH$_2$), 1.34 (2H, t, CH$_2$), 0.93 (3H, t, CH$_3$); $^{13}$C-NMR (CDCl$_3$) 136.34, 123.93, 122.85, 49.96, 36.39, 32.22, 19.62, 13.64.

2.2.1.2.2 Synthesis with acetone as solvent

In a pre-weighed 500 mL RB flask, [bmim]Cl (50.31 g, 0.29 mol) and sodium tetrafluoroborate (37.95 g, 0.34 mol), in water (200 mL), were stirred for 48 h. The precipitate, sodium chloride, was removed by vacuum filtration and the solvent removed on the rotavap. The IL was washed with acetone, vacuum filtered and placed on the rotavap to remove more sodium chloride. The process was continued until no further sodium chloride precipitated. The IL was placed on the trolley pump overnight, then weighed and stored under a nitrogen atmosphere. Table 2.7 provides a comparison of the yields obtained using the two different methods. It can be seen that the acetone method produced the better yield.

$^1$H-NMR (CDCl$_3$) 8.82 (1H, s, ArH), 7.33 (2H, s, ArH), 4.21 (2H, t, CH$_2$), 3.96 (3H, s, CH$_3$), 1.82 (2H, t, CH$_2$), 1.37 (2H, t, CH$_2$), 0.95 (3H, t, CH$_3$); $^{13}$C-NMR (CDCl$_3$) 136.89, 123.97, 122.41, 50.24, 36.70, 31.36, 19.77, 13.71.
Table 2.7  Yields obtained for 1-butyl-3-methylimidazolium tetrafluoroborate prepared using the two different methods

<table>
<thead>
<tr>
<th>Volume Solvent used</th>
<th>Mass of [bmim]Cl</th>
<th>Mass of NaBF$_4$ added</th>
<th>Mass of [bmim]BF$_4$ obtained</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ml Water</td>
<td>50.49 g (0.29 mol)</td>
<td>31.94 g (0.29 mol)</td>
<td>60.49 g (0.27 mol)</td>
<td>93 %</td>
</tr>
<tr>
<td>200 ml Acetone</td>
<td>50.31 g (0.29 mol)</td>
<td>37.95 g (0.34 mol)</td>
<td>63.88 g (0.28 mol)</td>
<td>98 %</td>
</tr>
</tbody>
</table>

2.2.1.3. Synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate

In a pre-weighed 500 mL RB flask, [bmim]Cl (50.05 g, 0.29 mol) and an equimolar quantity of sodium hexafluorophosphate (48.09 g, 0.29 mol), dissolved in distilled water (50 mL), were stirred for 26 h. After this time, the solution was placed on the rotavap for 2 h to remove the water. The IL was dissolved in dichloromethane and the white precipitate, sodium chloride, removed by vacuum filtration. The liquid was placed on the rotavap to remove the dichloromethane, and then placed on the trolley pump overnight at 0.8 mbar to remove the remaining solvent. The IL was weighed then stored under a nitrogen atmosphere. Table 2.8 contains the experimental data obtained.

$^1$H-NMR (CDCl$_3$) 8.37 (1H, s, ArH), 7.30 (2H, s, ArH), 4.13 (2H, t, CH$_2$), 3.85 (3H, s, CH$_3$), 1.81 (2H, t, CH$_2$), 1.29 (2H, t, CH$_2$), 0.87 (3H, t, CH$_3$); $^{13}$C-NMR (CDCl$_3$) 135.97, 123.95, 122.70, 49.99, 36.26, 31.99, 19.51, 13.48.
Table 2.8  Yields obtained for 1-butyl-3-methylimidazolium hexafluorophosphate

<table>
<thead>
<tr>
<th>Volume water used</th>
<th>Mass of [bmim]Cl</th>
<th>Mass of NaPF₆ added</th>
<th>Mass of [bmim]PF₆ obtained</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ml</td>
<td>50.05 g (0.29 mol)</td>
<td>48.09 g (0.29 mol)</td>
<td>74.24 g (0.26 mol)</td>
<td>91.2 %</td>
</tr>
</tbody>
</table>

2.2.1.4  Synthesis of 1-butyl-3-methylimidazolium trifluoromethane sulfonimide

In a 250 mL RB flask, [bmim]Cl (15.13g, 0.09 mol) and an equimolar quantity of lithium trifluoromethane sulfonimide (24.98g, 0.09 mol), in distilled water (50 mL), were stirred for 48 h. Two layers formed upon standing, then the IL was separated from the aqueous layer with the use of a separating funnel. The IL was washed with distilled water to remove the residual lithium chloride.

The remaining water was removed using the rotavap after the water was tested for halide (Cl⁻) until there was no further precipitation with silver nitrate (AgNO₃). The IL was washed with chloroform and then placed on the rotavap to remove the solvent. The IL was then placed on the high vacuum system overnight at 0.8 mbar to remove the remaining solvent. The IL was weighed and then stored under a nitrogen atmosphere. Table 2.9 contains the experimental data.

¹H-NMR (CDCl₃) 8.51 (1H, s, ArH), 7.32 (2H, s, ArH), 4.10 (2H, t, CH₂), 3.86 (3H, s, CH₃), 1.79 (2H, t, CH₂), 1.29 (2H, t, CH₂), 0.89 (3H, t, CH₃); ¹³C-NMR (CDCl₃) 136.03, 124.08, 122.77, 50.14, 36.45, 32.19, 19.70, 13.59.
Table 2.9  Yields obtained for 1-butyl-3-methylimidazolium trifluoromethane sulfonimide

<table>
<thead>
<tr>
<th>Volume water used</th>
<th>Mass of [bmim]Cl</th>
<th>Mass of Li[N(CF₃SO₂)₂]</th>
<th>Mass of [bmim] N(CF₃SO₂)₂ obtained</th>
<th>% Yield obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ml</td>
<td>15.13 g (0.087 mol)</td>
<td>25.00 g (0.087 mol)</td>
<td>23.72 g (0.057 mol)</td>
<td>65.3 %</td>
</tr>
</tbody>
</table>

2.2.2  Synthesis of 3,3',5,5'-tetra-t-butyl dichenoquinone

2,6-di-t-butylphenol (0.49 g, 2.38 mmol) was added to silver oxide (1.03 g, 4.45 mmol) in methanol (50 mL), and then stirred for 1 h. The resulting solid was removed by vacuum filtration and washed with hot toluene, the toluene then being combined with the filtrate. This solution was then concentrated down on the rotavap to afford crude 3,3',5,5'-tetra-t-butyl diphenoquinone, which was further purified by recrystallization using ethyl acetate/petroleum ether (b.p. 60–80°C). Table 2.10 shows the experimental results obtained.

The presence of an isomer was detected in the ¹H-NMR spectrum. Thin layer chromatography plates were used to separate the major product from the isomer, using a solvent mixture consisting of hexane: chloroform in a 3:1 ratio.

The desired product, 3,3',5,5'-tetra-t-butyl diphenoquinone, was thus obtained, and had m.p. 247-248°C (lit. 66, m.p. 248°C); ¹H-NMR (CDCl₃) 7.72 (4H, s, ArH), 1.38 (36 H, s, CH₃); ¹³C-NMR (CDCl₃) 186.88, 150.83, 136.53, 126.43, 36.44, 29.99; m/z 409 (M⁺), 393 (M⁺-15), 366 (M⁺-42), 351 (M⁺-57), 309 (M⁺-99).
Table 2.10 Yields obtained for the synthesis of 3,3',5,5'-tetra-\textit{t}-butyldiphenoquinone

<table>
<thead>
<tr>
<th>Mass of 2,6-di-\textit{t}-butylphenol</th>
<th>Mass of silver oxide</th>
<th>Mass of 3,3',5,5'-tetra-\textit{t}-butyldiphenoquinone Obtained</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.49 g (2.38 mmol)</td>
<td>1.03 g (4.45 mmol)</td>
<td>0.37 g (0.91 mmol)</td>
<td>76.3 %</td>
</tr>
<tr>
<td>2.53 g (12.26 mmol)</td>
<td>5.03 g (21.71 mmol)</td>
<td>1.98 g (4.85 mmol)</td>
<td>79.2 %</td>
</tr>
</tbody>
</table>

2.2.3 Synthesis of 3,3',5,5'-tetra-\textit{t}-butyl-4,4'-dihydroxybiphenyl

To a suspension of 3,3',5,5'-tetra-\textit{t}-butyldiphenoquinone (0.28 g, 0.69 mmol) in ether (50 mL) was added a solution of sodium dithionite (2.03 g, 11.66 mmol) in aqueous NaOH (1.0 M, 100 mL). After stirring the reaction mixture for 1 h, the aqueous layer was acidified with concentrated H$_2$SO$_4$ (3.75 mL). The organic layer was separated, dried with MgSO$_4$ and concentrated to afford 3,3',5,5'-tetra-\textit{t}-butyl-4,4'-dihydroxybiphenyl, which was further purified by recrystallization using ethyl acetate/petroleum ether (b.p. 60-80°C). Table 2.11 shows the experimental data for this synthesis.

The presence of an isomer was detected in the $^1$H-NMR spectrum. Thin layer chromatography plates were used to separate the major product from the isomer, using a solvent mixture consisting of hexane: chloroform in a 3:1 ratio.
The desired product, 3,3’,5,5’-tetra-\(t\)-butyl-4,4’-dihydroxybiphenyl, was thus obtained, and had m.p. 180-183°C (lit.\(^{67}\), m.p. 185-186°C); \(^1\)H-NMR (CDCl\(_3\)) 7.38 (4H, s, ArH), 1.51 (36 H, s, CH\(_3\)); \(^{13}\)C-NMR (CDCl\(_3\)) 153.19, 136.33, 134.31, 124.48, 34.83, 30.75; m/z 410 (M\(^+\)), 395 (M\(^+\)-15), 190 (M\(^+\)-220), 162 (M\(^+\)-248).

**Table 2.11** Yields obtained for the synthesis of 3,3’,5,5’-tetra-\(t\)-butyl-4,4’-dihydroxybiphenyl

<table>
<thead>
<tr>
<th>Mass of 3,3’,5,5’-tetra-(t)-butyl-diphenoquinone</th>
<th>Mass of sodium dithionite added</th>
<th>Mass of 3,3’,5,5’-tetra-(t)-butyl-4,4’-dihydroxybiphenyl</th>
<th>Reaction time</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.28 g (0.69 mmol)</td>
<td>2.03 g (11.66 mmol)</td>
<td>0.10 g (0.24 mmol)</td>
<td>1 h</td>
<td>35.5 %</td>
</tr>
<tr>
<td>0.52 g (1.27 mmol)</td>
<td>8.02 g (46.06 mmol)</td>
<td>0.17 g (0.41 mmol)</td>
<td>2 h</td>
<td>32.5 %</td>
</tr>
</tbody>
</table>

**2.3 Experimental Procedure**

**2.3.1 Apparatus for electrochemical oxidation procedures**

The electrochemical cell shown in Fig. 2.2 was used in all oxidation procedures. It consists of a 10 mL glass vial that was stoppered to prevent introduction of atmospheric moisture. The electrodes were two platinum flag electrodes (area of 2.88 cm\(^2\) per electrode) acting as anode and cathode. A constant current power supply was used to regulate the current supplied and a heater/stirrer was used to control stirring of the solution.
2.3.2 Oxidation of 2,6-di-t-butylphenol using the electrochemical cell

The substrate 2,6-di-t-butylphenol was weighed into the electrochemical cell and dissolved in the appropriate IL (3 mL). This electrolysis reaction was carried out in either the IL by themselves or with the IL suitably diluted with a solvent to increase conductivity. The vial was stoppered with a stopper containing the electrodes. The electrolysis was conducted under constant current conditions in order to achieve the required current density and controlled by a Lodestar DC Power Supply.

After completion of the electrolysis, the electrodes were removed from the reaction mixture and the solvent was removed from the IL using a rotavap. A solution of IL (0.1M) containing the product with acetonitrile was prepared with a known amount of nitrobenzene for HPLC internal standard quantification.
2.4 Analytical Techniques

Several analytical procedures were employed for the analysis of the IL and the products after electrolysis. Each analytical technique will be described separately.

2.4.1 Nuclear Magnetic Resonance (NMR)

Proton and carbon NMR spectra were recorded on a NMR Bruker Spectrospin (300 MHz) spectrometer using D-chloroform (CDCl₃) as solvent.

2.4.2 Gas Chromatography - Mass spectroscopy (GC-MS)

GC-MS analysis was used mainly for qualitative analysis. Use was made of a Thermo Finnigan Trace MSplus Gas Chromatograph. Separation was achieved with the aid of 15m x 0.25 mm x 0.25 μm Rtx 5MS column. Other important chromatographic conditions used are summarized in Table 2.12.

Table 2.12 GC-MS analysis conditions

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial column temperature</td>
<td>70 °C</td>
</tr>
<tr>
<td>Initial column hold time</td>
<td>5 min</td>
</tr>
<tr>
<td>Heating rate</td>
<td>10 °C/min</td>
</tr>
<tr>
<td>Final column temperature</td>
<td>270 °C</td>
</tr>
<tr>
<td>Final column hold time</td>
<td>5 min</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>250 °C</td>
</tr>
</tbody>
</table>
2.4.3 High Pressure Liquid Chromatography (HPLC)

HPLC analyses were carried out on a Hewlett Packard 1100 series HPLC chromatograph with a dual pump system, equipped with a variable UV-Visible detector and an auto sampler unit. Data was acquired with a Mecer Personal computer loaded with HP Chemstation for LC software. All solvents were HPLC grade and were degassed prior to analysis with a Millipore vacuum-degassing unit. A 3.9 mm x 300 mm x 10μm Waters μBondapak C$_{18}$ (serial no. WAT027324) column was used for the analysis of the reaction samples.

An internal standard method, with nitrobenzene as standard, was used for the analysis of individual components, 2,6-di-$t$-butylphenol and reaction mixtures. Response factors for the compounds of interest were determined by means of a three-level calibration using standard solutions containing known amounts of the analytes and internal standards. HPLC conditions are summarized in Table 2.13.

<table>
<thead>
<tr>
<th>Table 2.13</th>
<th>HPLC analysis conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injector volume</td>
<td>1.00 μL</td>
</tr>
<tr>
<td>Analysis time</td>
<td>10 min</td>
</tr>
<tr>
<td>Column</td>
<td>3.9 x 300 mm C$_{18}$ column</td>
</tr>
<tr>
<td>Wavelength</td>
<td>267 nm</td>
</tr>
<tr>
<td>Flow rates</td>
<td>0.7 mL/min</td>
</tr>
<tr>
<td>Mobile phase</td>
<td>Acetonitrile</td>
</tr>
</tbody>
</table>
2.4.4 Cyclic and linear sweep voltammetry

The most common methods used for determining the potential window of an IL is cyclic voltammetry (Fig. 2.3) or linear sweep voltammetry. CV studies were performed on a BAS CV50 cyclic voltammetry system (Fig. 2.3). A Gateway 2000 personal computer, running CV50 software, was used for both instrumental control and data acquisition. The electrochemical cell was equipped with glassy carbon working electrode, a platinum wire auxiliary electrode and a non-aqueous Ag/AgNO₃ reference electrode.

In the three-electrode system, the potential of an inert working electrode (glassy carbon) is scanned out to successively greater positive (anodic) and negative (cathodic) potentials until background currents rise dramatically due to oxidation and reduction of the IL. The oxidative and reductive potential limits are assigned when the background current reaches a threshold value. The electrochemical potential window is the difference between these anodic and cathodic potential limits.

The potential of the working electrode was scanned over a potential of -3.0 V to +3.0 V at a scan rate of 100 mV/s and a sensitivity of 0.1 mV/s. Cyclic voltammograms were recorded for the substrate, intermediate and product, so as to determine their oxidation potentials.
Fig. 2.3  (a) is the C2 cell stand that are controlled by CV-50W analyzer and (b) the cell setup of the Cyclic Voltammetry instrument.

Linear sweep voltammograms were recorded to determine the electrochemical window of the IL. The threshold value was set at 1 mA/cm². In Section 3.2.1, Fig. 3.2, illustrates the determination of the potential window for an IL.

2.4.5 Conductivity

Conductivity measurements of the IL were performed on a Metrohm 660 conductivity meter equipped with two platinum black electrodes. The cell constant (calculated to be 0.852 cm⁻¹) was determined from a KCl solution (0.1M).
2.4.6 Density Meter

The density of all the IL was determined with an Anton Paar DMA 35 N density meter at room temperature.

2.4.7 Halide Determination

The halide content (Cl⁻) in the IL was determined with a Perkin-Elmer Sciex Elan 6100 ICP-MS using a Perkin-Elmer As-90 autosampler (see section 1.1.6.2, Fig 1.6). Standards of concentration 0.1, 0.5, 1, 5, 10, 20 mg/L Cl were prepared from a SpectraScan multi-element standard 8550. Standards were prepared in 1 % (v/v) sub-boiled HNO₃ medium using high purity distilled & de-ionized water. The Cl 35 isotope was analyzed with an integration time of 3 s and ten replicates were recorded.

2.4.8 Water Determination

The water content in the IL was determined with a Karl Fischer model-701 KF Titrino (see section 1.1.6.3, Fig. 1.5). It made use of Hyranal Composite 5 as the titrant and HPLC grade methanol as the base.

2.4.9 Viscosity

The viscosity of the IL could not be determined using a viscometer, such as a Brookfield, since only a small amount of IL was available. An alternative method was therefore derived making use of a graduated 2 mL pipette and measuring the time it took for the liquid to empty the pipette. This time was them compared to the time it took 2 mL of glycerol to run freely from the pipette, under the same conditions. All measurements were carried out in triplicate.
The following formula was used to calculate the viscosity of the IL\textsuperscript{47}:

\[
\frac{\eta_1}{\eta_2} = \frac{t_1 \times d_1}{t_2 \times d_2}
\]

where \( \eta_1 \) = viscosity of glycerol
\( \eta_2 \) = viscosity of IL
\( t_1 \) = delivery time for glycerol
\( t_2 \) = delivery time for the IL
\( d_1 \) = density of glycerol
\( d_2 \) = density of IL
CHAPTER 3

PHYSICAL AND CHEMICAL PROPERTIES OF THE IONIC LIQUIDS

3.1 Introduction

The physical and chemical properties of the three synthesized IL were investigated (Fig. 3.1). The following physical properties were measured: conductivity, density, viscosity and the electrochemical window. In addition, some aspects relating to purity such as the percentage halide and water in the IL were also determined. The measured properties of the IL were compared to those of commercial IL. In addition the quality of the IL were examined using NMR.

![Chemical structures of ILs](image)

**Fig. 3.1** IL synthesized and purchased for electro-oxidation studies

The electrochemical stability of the IL was also investigated to determine possible break-up of the structure of the IL. Ionic liquids have high ion conductivities, but addition of organic solvents, such as acetonitrile, increases the conductivity to its
maximum. A conductivity study was carried out to determine the best solvent-IL combination, a system which gives the highest conductivity with the smallest amount of added organic solvent.

3.2 Physical properties of the ionic liquids

IL possess a variety of properties that make them desirable as solvents for investigation of electrochemical processes. They often have wide electrochemical potential windows; they have reasonably good electrical conductivity and solvent transport properties; they are thermally stable up to 300°C, and they are able to solvate a wide variety of inorganic, organic and organometallic species.

3.2.1 Electrochemical Windows

3.2.1.1 Introduction to electrochemical windows

The most common method used for the determination of the potential window of an IL is cyclic voltammetry (Section 2.4.4, Fig. 2.3) and linear sweep voltammetry (Fig. 3.2). In a three-electrode system, the potential of an inert working electrode (glassy carbon) is scanned out to successively greater positive (anodic) and negative (cathodic) potentials until background currents rise dramatically due to oxidation and reduction of the IL. The oxidative and reductive potential limits are assigned when the background current reaches a threshold value. The electrochemical potential window is the difference between these anodic and cathodic potential limits.

In the case of IL, the potential window depends primarily on the resistance of the cation to reduction and the resistance of the anion to oxidation. In addition, the presence of impurities (water and halide) can play an important role in limiting the potential windows of IL.
Fig. 3.2  Linear sweep voltammogram of RTIL (two separate voltammograms are indicated here) \(^{48}\)

Note that both the reduction and oxidation current increase with the potential sweep in the cathodic and anodic directions.\(^{48}\) In Fig. 3.2, the reduction or the oxidation potential, the cathodic limiting or anodic limiting potential, which are denoted as \(E_{\text{CL}}\) and \(E_{\text{AL}}\), respectively, is evaluated when the reduction or oxidation current density reaches 1.0 mA/cm\(^2\). In many studies, the cut-off current density is selected between 0.1 and 1.0 mA/cm\(^2\). The scan rate is an important parameter for potential sweep methods, such as CV or linear sweep voltammetry (LSV). The current is proportional to the square root of the scan rate in all electrochemical systems (irreversible, reversible, and quasi-reversible systems).

It must be noted that impurities in the IL can have a profound impact on the potential limits and the corresponding electrochemical window. During the synthesis of IL, residual halide and water may remain in the final product.
Halide ions (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) are more easily oxidized than the fluorine-containing anions in some IL. Consequently, the observed anodic potential limit can be appreciably reduced if significant concentrations of halide ions are present. Contamination of an IL with significant amounts of water can affect both the anodic and the cathodic potential limits, as water can be both reduced and oxidized with the potential limits of many IL.

Recent work by Schröder et al. demonstrated considerable reduction in both the anodic and cathodic limits of several IL upon the addition of 3 % water (by weight).<sup>49</sup> For example, the electrochemical window of ‘dry’ [bmim][BF<sub>4</sub>] was found to be 4.10 V, while that for the IL with 3 % water by weight was reduced to 1.95 V.

In addition to its electrochemistry, water can react with the IL components (especially anions) to produce products that are electroactive in the electrochemical potential window. This has been documented for the chloroaluminate IL, in which water will react to produce electroactive proton-containing species (e.g., HCl and [HCl<sub>2</sub>]<sup>-</sup>). In addition, water appears to react with some of the anions commonly used in the non-haloaluminate IL. The [PF<sub>6</sub>]<sup>-</sup> anion, for example, is known to react with water to form HF.<sup>50; 51</sup>

Glassy Carbon (GC), platinum (Pt), and tungsten (W) are the most common working electrodes used to evaluate electrochemical windows in IL. The choice of the working electrode has some impact on the overall electrochemical window. This is due to the effect of the electrode material on the irreversible electrode reactions that take place at the oxidative and reductive limits. In addition, GC (and to lesser extent W) exhibit a large overpotential for proton reduction.

Under normal circumstances, the electrochemistry of protonic impurities (i.e. water) is not observed in the IL electrochemical window with GC. Platinum on the other hand, exhibits good electrochemical behavior for proton activity. Comparison of the background electrochemical behavior of an IL at both Pt and GC working electrodes
can be an excellent qualitative tool for determining if significant amounts of protonic impurities (water impurity) are present.

Table 3.1 contains electrochemical potential windows for a wide variety of IL. Only limited information concerning the purity of the IL listed is available, so these electrochemical potential windows must be treated with caution, as it is likely that many of the IL would have had residual halides and water present.

**Table 3.1** The electrochemical potential windows for a variety of IL

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion(s)</th>
<th>Working electrode</th>
<th>Window (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ammonium</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-butyl-1-methyl-pyrrolidinium</td>
<td>[(CF₃SO₂)₂N]⁻</td>
<td>GC</td>
<td>5.5</td>
</tr>
<tr>
<td><strong>Sulfonium</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(n-C₄H₉)₃S]⁺</td>
<td>[(CF₃SO₂)₂N]⁻</td>
<td>GC</td>
<td>4.8</td>
</tr>
<tr>
<td><strong>Imidazolium</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[bmim]⁺</td>
<td>[BF₄]⁻</td>
<td>Pt</td>
<td>4.1</td>
</tr>
<tr>
<td>[bmim]⁺</td>
<td>[PF₆]⁻</td>
<td>Pt</td>
<td>4.2</td>
</tr>
<tr>
<td><strong>Pyrazolium</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-dimethyl-4-fluoropyrazolium</td>
<td>[BF₄]⁻</td>
<td>GC</td>
<td>4.1</td>
</tr>
<tr>
<td><strong>Pyridinium</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[BP]⁺</td>
<td>[BF₄]⁻</td>
<td>Pt</td>
<td>3.4</td>
</tr>
</tbody>
</table>
The following observation can be seen in Table 3.1:

- The trend in the electrochemical stabilities of the types of IL cations is:
  
  pyridinium < pyrazolium < imidazolium < sulfonium < ammonium

- The anion stabilities towards oxidation appear to follow the order:
  
  
  halide      fluorinated ions      triflate/triflyl ions

3.2.1.2 Results of the electrochemical windows obtained

Table 3.2 shows the results for the electrochemical windows of the IL obtained with linear sweep voltammetry and compared to the electrochemical windows in Table 3.1. The linear sweep scan was carried out with the use of glassy carbon as the working electrode, platinum wire as the auxiliary and a non-aqueous Ag/AgNO_3 as the reference electrode.

The potential of the working electrode was scanned over a potential of -3.0 V to +3.0 V at a scan rate of 100mV/s and a sensitivity of 0.1 mV/s. The cut-off current used for the determination of the electrochemical window of the IL was 0.1 mA/cm².
**Table 3.2** Results for the electrochemical windows of the IL obtained with linear sweep voltammetry

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>Oxidation potential (V)</th>
<th>Reduction potential (V)</th>
<th>Electrochemical window (V)</th>
<th>Reference Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]BF$_4$ ^1</td>
<td>1.79</td>
<td>2.05</td>
<td>3.84</td>
<td>4.1</td>
</tr>
<tr>
<td>[bmim]BF$_4$ ^2</td>
<td>1.74</td>
<td>2.51</td>
<td>4.25</td>
<td>4.1</td>
</tr>
<tr>
<td>[bmim]PF$_6$ ^3</td>
<td>1.83</td>
<td>2.40</td>
<td>4.23</td>
<td>4.2</td>
</tr>
<tr>
<td>[bmim]N(CF$_3$SO$_2$)$_2$ ^4</td>
<td>1.88</td>
<td>2.49</td>
<td>4.37</td>
<td>4.6</td>
</tr>
<tr>
<td>[bmim]BF$_4$ ^5</td>
<td>1.92</td>
<td>2.43</td>
<td>4.35</td>
<td>4.1</td>
</tr>
<tr>
<td>[bmim]N(CF$_3$SO$_2$)$_2$ ^5</td>
<td>2.14</td>
<td>2.49</td>
<td>4.63</td>
<td>4.6</td>
</tr>
</tbody>
</table>

^1 [bmim]BF$_4$ was synthesized by the water method  
^2 [bmim]BF$_4$ was synthesized by the acetone method  
^3 [bmim]PF$_6$ was synthesized by the water method  
^4 [bmim]N(CF$_3$SO$_2$)$_2$ was synthesized by the water method  
^5 IL’s were commercial products

With respect to the results obtained in Table 3.2, the following conclusions can be made:

- The IL [bmim]N(CF$_3$SO$_2$)$_2$ produced the widest electrochemical window due to its anion stability. The anion N(CF$_3$SO$_2$)$_2$ are the most stable compared to the other anions, followed by the fluorinated anions and then the halides.

- The electrochemical windows of the IL that is lower than the reference window can be due to the small amount of water present in the IL. Water has a major effect on the electrochemical window which is why it is important to remove the
water before electrolysis. IL are hygroscopic and therefore normally contain trace amounts of water.

- The presence of halide, Cl\(^-\), also has an effect on the electrochemical window. The anodic potential limit (oxidation potential) is reduced due to the presence of halide in the IL. A small amount of the residual halide can remain during the synthesis of the IL.

- The electrochemical windows of the IL synthesized in the laboratory compared well to those of the commercial products.

3.2.2 Conductivity and Viscosity

3.2.2.1 Introduction to the conductivity and viscosity

The conductivity of IL depends on the ion mobility which is related to the viscosity, according to the Stokes-Einstein equation.\(^{52}\) The viscosity of IL strongly depends on temperature. Table 3.3 provides details of the temperature dependent viscosity data of [bmim]PF\(_6\).\(^{53}\) The viscosity significantly increases when temperature decreases. A 27 \% increase in the viscosity of [bmim]PF\(_6\) has been reported when the temperature is lowered from 298 to 293 K.\(^{53}\)
Table 3.3 Effect of temperature on the viscosity of [bmim]PF$_6$\textsuperscript{53}

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>286 ± 6</td>
</tr>
<tr>
<td>298</td>
<td>207 ± 11</td>
</tr>
<tr>
<td>304</td>
<td>153 ± 1</td>
</tr>
<tr>
<td>308</td>
<td>116 ± 6</td>
</tr>
<tr>
<td>313</td>
<td>94 ± 0</td>
</tr>
<tr>
<td>318</td>
<td>73 ± 1</td>
</tr>
<tr>
<td>323</td>
<td>58 ± 1</td>
</tr>
<tr>
<td>328</td>
<td>46 ± 1</td>
</tr>
<tr>
<td>333</td>
<td>40 ± 1</td>
</tr>
<tr>
<td>338</td>
<td>35 ± 0</td>
</tr>
<tr>
<td>343</td>
<td>29 ± 1</td>
</tr>
</tbody>
</table>

The physical unit for viscosity is the poise (P) named after Jean Louis Marie Poiseuille. It is more commonly expressed, as centipoise (cP). The centipoise is commonly used because water has a viscosity of 1.0020 cP (at 20°C).

$1$ centipoise = 0.001 Pa.s = 1 mPa.s

Impurities also may have a very significant influence on the viscosity of IL. The presence of water decreases the viscosity of IL, whereas the presence of chloride (added as chloride salts with the cation being the same as that of the IL) increases their viscosity. For example, in the case of [bmim]BF$_4$ (20°C), the solvent viscosity decreases more than 30 % when 10 % (molar fraction) of water is present, and the viscosity increases from 66.5 to 92.4 mPa/s when the concentration of chloride impurity increases from 0.01 to 0.5 mol/kg.\textsuperscript{7}
The conductivity of IL usually exhibits classical Arrhenius behaviour. For example, the conductivity of \([\text{emim}][\text{BF}_4]\) decreases by a factor of ten when the temperature decreases from 375 to 275 K.\(^{19}\)

Viscosity and conductivity data reported for some common IL are summarized in Tables 3.4 and 3.5. This data again should be treated with caution, as even trace contamination by water or chloride, as mentioned previously, may lead to significant uncertainty. For comparison, the viscosity of some conventional solvents is also included.

Data in Table 3.5 reveals that IL are often much more viscous than conventional solvents, e.g. 207 mPa.s for \([\text{bmim}][\text{PF}_6]\) versus 0.89 mPa.s for water. Consequently, the influence of uncompensated resistance (\(R_u\)) may be highly significant. In these instances, use of microdisc electrodes (\(\mu\)m radii) rather than conventional macrodisc electrodes (mm radii) voltammetry under conditions that minimize the influence of ohmic (\(I_{R_u}\)) drop is recommended, particularly for studies of rapid electron transfer reactions and rapid homogeneous chemical reactions coupled to a heterogeneous electron transfer step.

**Table 3.4**  Physiochemical properties of common IL\(^{54}\)

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>Density (g/mL)</th>
<th>Conductivity (mS/cm)</th>
<th>Viscosity (mPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{bmim}][\text{BF}_4])</td>
<td>1.17</td>
<td>1.7</td>
<td>233</td>
</tr>
<tr>
<td>([\text{bmim}][\text{PF}_6])</td>
<td>1.36-1.37</td>
<td>1.4</td>
<td>148-450</td>
</tr>
<tr>
<td>([\text{bmim}][\text{N(CF}_3\text{SO}_2)_2])</td>
<td>1.42</td>
<td>3.9</td>
<td>52</td>
</tr>
</tbody>
</table>
Table 3.5  Viscosity and conductivity of some IL and conventional solvents$^{55}$

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion</th>
<th>Conductivity (mS/cm)</th>
<th>Viscosity (mPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[emim]$^+$</td>
<td>BF$_4^-$</td>
<td>14</td>
<td>34</td>
</tr>
<tr>
<td>[emim]$^+$</td>
<td>PF$_6^-$</td>
<td>5.2</td>
<td>-</td>
</tr>
<tr>
<td>[emim]$^+$</td>
<td>[(CF$_3$SO$_2$)$_2]^-$</td>
<td>8.8</td>
<td>34</td>
</tr>
<tr>
<td>[bmim]$^+$</td>
<td>PF$_6^-$</td>
<td>-</td>
<td>207</td>
</tr>
<tr>
<td>[bmim]$^+$</td>
<td>[(CF$_3$SO$_2$)$_2]^-$</td>
<td>3.9</td>
<td>52</td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
<td>12.86$^a$</td>
<td>0.89</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td></td>
<td>7.58$^b$</td>
<td>0.33</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td></td>
<td>-</td>
<td>0.80</td>
</tr>
<tr>
<td>Benzonitrile</td>
<td></td>
<td>-</td>
<td>1.11</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td></td>
<td>-</td>
<td>0.46</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td></td>
<td>1.38$^b$</td>
<td>0.39</td>
</tr>
</tbody>
</table>

$^a$ 0.1M KCl and measured at 25°C  
$^b$ 0.1M [Bu$_4$N][ClO$_4$] and measured at 22°C

3.2.2.2  Results of the conductivity and viscosity values obtained

Table 3.6 shows the results obtained for the conductivity determination of the IL. The conductivity results of the IL were compared to literature values obtained from Tables 3.4 and 3.5. The conductivity was measured with a Metrohm 660 conductivity meter equipped with two platinum black electrodes. The cell constant (calculated to be 0.852 cm$^{-1}$) was determined from a 0.1 M KCl solution.
Table 3.6  Conductivity results of the IL

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>Conductivity (mS/cm)</th>
<th>Reference Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]BF$_4$</td>
<td>1.4</td>
<td>1.7</td>
</tr>
<tr>
<td>[bmim]BF$_4$</td>
<td>1.6</td>
<td>1.7</td>
</tr>
<tr>
<td>[bmim]PF$_6$</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>[bmim]N(CF$_3$SO$_2$)$_2$</td>
<td>3.3</td>
<td>3.9</td>
</tr>
<tr>
<td>[bmim]BF$_4$</td>
<td>1.4</td>
<td>1.7</td>
</tr>
<tr>
<td>[bmim]N(CF$_3$SO$_2$)$_2$</td>
<td>3.4</td>
<td>3.9</td>
</tr>
</tbody>
</table>

1 [bmim]BF$_4$ was synthesized by the water method
2 [bmim]BF$_4$ was synthesized by the acetone method
3 [bmim]PF$_6$ was synthesized by the water method
4 [bmim]N(CF$_3$SO$_2$)$_2$ was synthesized by the water method
5 IL’s were commercial products

With respect to the results obtained in Table 3.6, the following conclusions can be made:

- The conductivity of the various IL, synthesized and purchased, was determined and compared to reference conductivity values (Table 3.4 and 3.5) and were found to be very similar.

- The conductivity values obtained for the synthesized liquids compared well with those in the purchased products.

- The slight decrease of conductivity of the IL in comparison with the reference values can be due to the presence of water that decreases conductivity reading. Water is always present in the IL, even after a moderate drying
procedure; therefore there will always be a slight deviation in the conductivity results.

Table 3.7 shows the results obtained for the viscosity determination of the IL. The viscosity of the IL synthesized was compared to the commercial IL and was determined as mentioned in section 2.4.10.

**Table 3.7**  Viscosity results of the IL

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>Volume ionic liquid (ml)</th>
<th>Time (sec)</th>
<th>Viscosity (mPa/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]BF$_4$ $^1$</td>
<td>2.00</td>
<td>17.58</td>
<td>682</td>
</tr>
<tr>
<td>[bmim]BF$_4$ $^2$</td>
<td>2.00</td>
<td>12.20</td>
<td>467</td>
</tr>
<tr>
<td>[bmim]PF$_6$ $^3$</td>
<td>2.00</td>
<td>22.06</td>
<td>963</td>
</tr>
<tr>
<td>[bmim]N(CF$_3$SO$_2$)$_2$ $^4$</td>
<td>2.00</td>
<td>8.36</td>
<td>383</td>
</tr>
<tr>
<td>[bmim]BF$_4$ $^5$</td>
<td>2.00</td>
<td>14.49</td>
<td>556</td>
</tr>
<tr>
<td>[bmim]N(CF$_3$SO$_2$)$_2$ $^5$</td>
<td>2.00</td>
<td>9.83</td>
<td>405</td>
</tr>
<tr>
<td>Glycerol $^6$</td>
<td>2.00</td>
<td>37.26</td>
<td>1500</td>
</tr>
</tbody>
</table>

$^1$ [bmim]BF$_4$ was synthesized by the water method

$^2$ [bmim]BF$_4$ was synthesized by the acetone method

$^3$ [bmim]PF$_6$ was synthesized by the water method

$^4$ [bmim]N(CF$_3$SO$_2$)$_2$ was synthesized by the water method

$^5$ IL's were commercial products

$^6$ Glycerol with known viscosity

With respect to the results obtained in Table 3.7, the following conclusions can be made:

- It can be seen that in Table 3.7 there is a variation between the viscosity results of the IL. A more accurate instrument such as a Brookfield or Oswald
viscometer could not be used since it requires at least 100 mL and 50 mL respectively of IL for viscosity determination. The amount of IL available was limited and so a graduated pipette was used. The delivery time of the IL was measured and compared with a standard. The equation in section 2.4.10 was used to calculate the viscosity during the determination.\textsuperscript{47}

- These results should be treated with caution due to the fact that even trace amounts of contamination by water or chloride, may lead to significant changes, in viscosity.

- The presence of water and chloride could be the reason for variation in results.

- The viscosity values for the synthesized and purchased IL are 2-3 times greater than the reference values in Table 3.5. The reason for the inaccurate results can again be due to the method of analysis.

### 3.2.3 Density

Density is defined as the amount of mass in a unit volume of the substance:

\[
\rho = \frac{m}{V}
\]

where \( \rho \) is the object's density (measured in grams per milliliter)

- \( m \) is the object's total mass (measured in grams)

- \( V \) is the object's total volume (measured in milliliter)

Table 3.8 shows the results obtained for the density measurements of the IL. The density measurement was carried out with an Anton Paar DMA 35 N density meter at room temperature. The density of the synthesized IL was compared to the commercial IL and compared to reference values obtained from Table 3.5.
**Table 3.8**  Density results of the IL

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>Density (25°C) (g/ml)</th>
<th>Reference Density (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]BF₄¹</td>
<td>1.22</td>
<td>1.17</td>
</tr>
<tr>
<td>[bmim]BF₄²</td>
<td>1.20</td>
<td>1.17</td>
</tr>
<tr>
<td>[bmim]PF₆³</td>
<td>1.37</td>
<td>1.36</td>
</tr>
<tr>
<td>[bmim]N(CF₃SO₂)₂⁴</td>
<td>1.44</td>
<td>1.42</td>
</tr>
<tr>
<td>[bmim]BF₄⁵</td>
<td>1.20</td>
<td>1.17</td>
</tr>
<tr>
<td>[bmim]N(CF₃SO₂)₂⁵</td>
<td>1.29</td>
<td>1.42</td>
</tr>
</tbody>
</table>

¹ [bmim]BF₄ was synthesized by the water method
² [bmim]BF₄ was synthesized by the acetone method
³ [bmim]PF₆ was synthesized by the water method
⁴ [bmim]N(CF₃SO₂)₂ was synthesized by the water method
⁵ IL’s were commercial products

With respect to the results obtained in Table 3.8, the following conclusions can be made:

- The densities of the IL synthesized and the commercial IL are very similar. The densities of the IL synthesized and the commercial ones are very similar to reference values obtained from Table 3.5.

- Variations in the density results could be due to impurities present such as water or chloride.
3.3 Chemical properties of the ionic liquids

3.3.1 Halide content in ionic liquids

Many IL are still made in two-step syntheses. Alkyl halides are used as alkylating agents, forming halide salts of the desired cation. To obtain a non-halide IL, the halide anions are exchanged in a second step for the desired anion. The presence of halide remaining after synthesis is known as an impurity and will have an influence on their physical properties. Halide impurities can seriously affect the usefulness of the material as a solvent for a given chemical reaction; therefore it is necessary to have an IL free of halide impurities or with a lower possible chloride content to investigate its properties for any given reaction.

Table 3.9 shows the chloride (Cl\textsuperscript{-}) content results obtained for the IL synthesized and commercial products. The results were obtained with the use of an ICP-MS (Fig. 1.4) and a range of standards of concentrations: 0.1, 0.5, 1, 5, 10, 20 mg/L Cl was prepared. The method used for the determination of chloride in IL is mentioned in section 2.4.8.
Table 3.9  The chloride (Cl\textsuperscript{−}) content results obtained for the IL

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>[Cl\textsuperscript{−}] in (ppm)</th>
<th>% Cl\textsuperscript{−} in (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]BF\textsubscript{4} \textsuperscript{1}</td>
<td>19.6211</td>
<td>0.20</td>
</tr>
<tr>
<td>[bmim]BF\textsubscript{4} \textsuperscript{2}</td>
<td>18.5378</td>
<td>0.18</td>
</tr>
<tr>
<td>[bmim]PF\textsubscript{6} \textsuperscript{3}</td>
<td>15.5378</td>
<td>0.15</td>
</tr>
<tr>
<td>[bmim]N(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2} \textsuperscript{4}</td>
<td>15.5719</td>
<td>0.15</td>
</tr>
<tr>
<td>[bmim]BF\textsubscript{4} \textsuperscript{5}</td>
<td>14.6627</td>
<td>0.14</td>
</tr>
<tr>
<td>[bmim]N(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2} \textsuperscript{5}</td>
<td>16.9033</td>
<td>0.17</td>
</tr>
</tbody>
</table>

\textsuperscript{1} [bmim]BF\textsubscript{4} was synthesized by the water method  
\textsuperscript{2} [bmim]BF\textsubscript{4} was synthesized by the acetone method  
\textsuperscript{3} [bmim]PF\textsubscript{6} was synthesized by the water method  
\textsuperscript{4} [bmim]N(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2} was synthesized by the water method  
\textsuperscript{5} IL’s were commercial products

With respect to the results obtained in Table 3.9, the following conclusions can be made:

- The IL contains only trace amounts of chloride as can be seen from the ICP-MS results. The trace amount of chloride present in the IL can have minor effects on the physical property of the IL.

3.3.2  Water content in ionic liquids

All IL contain a certain percentage of water, depending on the synthesis conditions, since the IL can be expected to come into some contact with traces of water. Water in an IL may be a problem for some applications, but not for others. However, one should in all cases know the approximate amount of water present in the IL used.
Table 3.10 contains the water content in the IL determined with the Karl Fischer (Fig. 1.5). Hydranal 5 Composite was used as titrant with HPLC-grade methanol as the base.

**Table 3.10** Water content results obtained for the IL synthesized and purchased.

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>Water content reading 1 (%)</th>
<th>Water content reading 2 (%)</th>
<th>Average Water content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]BF&lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;1&lt;/sup&gt;</td>
<td>1.40</td>
<td>1.46</td>
<td>1.43</td>
</tr>
<tr>
<td>[bmim]BF&lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2&lt;/sup&gt;</td>
<td>1.12</td>
<td>1.49</td>
<td>1.31</td>
</tr>
<tr>
<td>[bmim]PF&lt;sub&gt;6&lt;/sub&gt; &lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.20</td>
<td>0.29</td>
<td>0.25</td>
</tr>
<tr>
<td>[bmim]N(CF&lt;sub&gt;3&lt;/sub&gt;SO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; &lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.28</td>
<td>1.43</td>
<td>1.36</td>
</tr>
<tr>
<td>[bmim]BF&lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;5&lt;/sup&gt;</td>
<td>0.97</td>
<td>0.88</td>
<td>0.93</td>
</tr>
<tr>
<td>[bmim]N(CF&lt;sub&gt;3&lt;/sub&gt;SO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; &lt;sup&gt;5&lt;/sup&gt;</td>
<td>0.91</td>
<td>0.89</td>
<td>0.90</td>
</tr>
</tbody>
</table>

<sup>1</sup> [bmim]BF<sub>4</sub> was synthesized by the water method
<sup>2</sup> [bmim]BF<sub>4</sub> was synthesized by the acetone method
<sup>3</sup> [bmim]PF<sub>6</sub> was synthesized by the water method
<sup>4</sup> [bmim]N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> was synthesized by the water method
<sup>5</sup> IL’s were commercial products

With respect to the results obtained in Table 3.10, the following conclusions can be made:

- The water content in the IL was determined with the use of a Karl Fischer.
- The IL was placed on a high vacuum system at 80°C for about 2 h to remove the water, prior to analysis.
• IL are moisture sensitive and should be handled in a dry atmosphere, such as a nitrogen glove box.

3.4 Electrochemical stability of the ionic liquids

The electrochemical stability of the IL was investigated through constant current electrolysis reactions and the products were analyzed by NMR and GC-MS.

3.4.1 Investigation of the electrochemical stability of ionic liquids

The electrochemical stability of the IL synthesized in our laboratory as well as the commercial products were investigated. The following experimental conditions were used for the electrochemical stability investigation:

• Undivided reaction cell
• Ionic liquid (3 mL)
• Current of 9.2 mA
• Reaction time: 2 h
• Power supply and digital multimeter

An undivided reaction cell, instead of a divided cell, was used due to the small volume of the IL available for the investigation. During the reactions, a colour change from pale yellow to brown occurred. After 2 h, the reaction was stopped and the IL was analyzed with NMR spectroscopy and GC-MS spectrometry. The $^1$H and $^{13}$C NMR spectra for [bmim]BF$_4$ (synthesized) prior to electrolysis are shown in Fig. 3.3 and 3.4. The spectra for the IL after electrolysis are shown in Fig. 3.5 and 3.6, whilst the GC-MS of the IL after electrolysis is shown in Fig. 3.7.
Fig. 3.3  $^1$H NMR spectrum of [bmim]BF$_4$ (synthesized) before electrolysis

The spectrum of [bmim]BF$_4$ (synthesized) before electrolysis: $^1$H-NMR (CDCl$_3$) 8.82 (1H, s, ArH), 7.43 (2H, s, ArH), 4.18 (2H, t, CH$_2$), 3.91 (3H, s, CH$_3$), 1.80 (2H, t, CH$_2$), 1.34 (2H, t, CH$_2$), 0.93 (3H, t, CH$_3$).

Fig. 3.4  $^{13}$C NMR spectrum for [bmim]BF$_4$ (synthesized) before electrolysis

The spectrum of [bmim]BF$_4$ (synthesized) before electrolysis: $^{13}$C-NMR (CDCl$_3$) 135.95, 123.93, 122.63, 49.94, 36.21, 31.96, 19.48, 13.45.
Fig. 3.5  $^1$H NMR spectrum of [bmim]BF$_4$ (synthesized) after electrolysis

The spectrum of [bmim]BF$_4$ (synthesized) after electrolysis: $^1$H-NMR (CDCl$_3$) 8.88 (1H, s, ArH), 7.28 (2H, s, ArH), 4.23 (2H, t, CH$_2$), 3.98 (3H, s, CH$_3$), 2.19 (3H, s, CH$_3$), 1.88 (2H, t, CH$_2$), 1.37 (2H, t, CH$_2$), 0.98 (3H, t, CH$_3$).

Fig. 3.6  $^{13}$C NMR spectrum of [bmim]BF$_4$ (synthesized) after electrolysis

The spectrum of [bmim]BF$_4$ (synthesized) after electrolysis: $^{13}$C-NMR (CDCl$_3$) 135.97, 123.95, 122.70, 53.84, 49.99, 36.26, 31.99, 19.51, 13.48.
Fig. 3.7  GC-MS of [bmim]BF₄ (synthesized) after electrolysis

The spectrum of [bmim]BF₄ (synthesized) after electrolysis: m/z 187.2 (M⁺), 152.2 (M⁺-35), 137.1 (M⁺-50), 122.5 (M⁺-65), 109.2 (M⁺-79), 96.2 (M⁺-93), 81.9 (M⁺-107), 68.2 (M⁺-122).
Fig. 3.8 indicates the imidazolium cation with the approximate chemical shifts of the protons in the $^1$H NMR spectrum before electrolysis.

![Fig. 3.8 Imidazolium cation and their $^1$H NMR positions](image)

In comparing the NMR spectra of [bmim]BF$_4$ (synthesized) in Fig. 3.3–3.6, the following observations can be made:

- The $^1$H NMR spectrum after electrolysis shows the presence of an extra peak containing three hydrogens atoms at 2.19 ppm. The remaining peaks are still the IL with only slight shifting, compared to the spectrum before electrolysis.

- The $^{13}$C NMR spectrum after electrolysis also indicates the presence of an extra peak at 53.84 ppm together with the peaks of the IL.

- The presence of an extra peak with three hydrogens atoms and one carbon atom peak indicates the presence of a methyl group.
The following conclusions can be deducted from the GC-MS in Fig. 3.7:

- The GC spectra for all the IL’s after constant current electrolysis were identical.

- The GC spectrum produced only one peak, around 16 min, which was present for each IL after electrolysis, but was not present initially.

- The fragmentation pattern for this substance in all the IL’s after electrolysis was identical and possibly corresponds to the cation structure in Fig. 3.9.

![Fig. 3.9](image)

**Fig. 3.9** The possible cation structure according to results obtained

- The chloride would originate from impurities after synthesis, which would be the intermediate 1-butyl-3-methylimidazolium chloride.

- The results obtained from spectra after electrolysis, indicates the original ionic liquid with an additional methyl group. The exact structure could not have been determined since further work needs to be implemented.
• The IL cation together with an extra methyl group and chloride atom, has an molecular weight of 187.67 g/mol that corresponds to the GC-MS fragmentation pattern in Fig. 3.7.

• The same results were obtained for both the synthesized and commercial IL’s.

As a conclusion the NMR and GC-MS results indicate that some sort of rearrangement occurred. The products formed, could have been as a result of impurities in the IL’s or the IL’s that are not stable enough for electrolysis and starts rearranging. If more IL were available, the constant current electrolysis could have been studied in an divided cell and compared to literature studies where dimers where obtained.56

3.5 Conclusive remarks on the comparison between the synthesized and commercial ionic liquids

From the results in this Chapter it can be seen that the IL synthesized and the commercial IL are very similar. The IL can therefore be synthesized in the laboratory with similar quality to the commercial product. The IL is easy to synthesize and less expensive than the commercial ones.
CHAPTER 4

ELECTROCHEMICAL OXIDATION OF 2,6-DI-t-BUTYL-PHENOL IN IONIC LIQUIDS

4.1 Introduction

Electro-oxidations involve electron transfer between an organic reactant and the anode of an electrochemical cell. This results in an intermediate which then reacts further to form the product. The characteristic features of electro-oxidations are as follows:

• The selectivity of the electrochemical step can be greatly increased by careful selection of the conditions at the phase boundary, e.g. potential, current densities, etc.

• An electrochemical synthesis often has a lower environmental impact than conventional oxidation methods, since electrolytic routes often replace toxic reagents and hazardous process conditions.

The main reaction studied in this section is the oxidative coupling of 2,6-di-t-butylphenol in an IL medium contained in an electrochemical cell, in order to produce the biphenyl compound. The reaction is given in Scheme 4.1, which shows that mild oxidation first causes the formation of the biphenyl compound, which can be further oxidized to the corresponding diphenoquinone. There is a reversible equilibrium between the two dimeric forms.

According to the literature, electro-oxidation of 2,6-di-t-butylphenol in an CH₃OH-LiClO₄ (Pt) system gives 3,3',5,5'-tetra-t-butyl-4,4'-dihydroxybiphenyl (Scheme 4.1) in good yields, giving 62.7 % of the biphenyl, after 3.5 F. Recently, the diphenoquinone was isolated as a major product in an attempt to synthesize metal
phenoxyrate complexes.\textsuperscript{58} Indirect electro-oxidation of 2,6-di-t-butyphenol using Ce(IV) also provides diphenoquinone in high current efficiency.\textsuperscript{59}

\textbf{Scheme 4.1} Electro-oxidative coupling of 2,6-di-t-butyphenol
4.2  Electro-oxidation of 2,6-di-\textit{t}-butylphenol using traditional organic solvent and electrolyte

The electro-oxidation of 2,6-di-\textit{t}-butylphenol was carried out in our laboratory under similar conditions as reported by Torii, Dhimane, Araki and Inokuchi \(^{46}\); the following experimental conditions were used:

- Undivided reaction cell with two platinum electrodes (2 x 3 cm\(^2\))
- 2,6-di-\textit{t}-butylphenol (0.1 M) as substrate
- LiClO\(_4\) (0.3 M) as supporting electrolyte
- Solvent system: CH\(_3\)OH: CH\(_2\)Cl\(_2\) (20 mL) in a 3:1 ratio
- Current density of 2 mA/cm\(^2\) and 3.5 F of electric charge
- A constant current of 14 mA
- Room temperature (ca. 20°C)

Results obtained by us (Entry B, Table 4.1) are compared with the literature values (Entry A) in Table 4.1. The analysis was carried out by HPLC using the experimental conditions mentioned in section 2.4.3.

**Table 4.1**  Results obtained for the electro-oxidation of 2,6-di-\textit{t}-butylphenol in organic solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>2,6-di-\textit{t}-butylphenol (M)</th>
<th>Solvent system</th>
<th>Charge (F)</th>
<th>Product yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH(_3)OH: CH(_2)Cl(_2)</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>A(^{(46)})</td>
<td>0.1</td>
<td>3:1</td>
<td>3.5</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>0.1</td>
<td>3:1</td>
<td>3.5</td>
<td>-</td>
</tr>
</tbody>
</table>

1 = 2,6-di-\textit{t}-butylphenol (starting material)
2 = 3,3',5,5'-tetra-\textit{t}-butyl-4,4'-dihydroxybiphenyl
3 = 3,3',5,5'-tetra-\textit{t}-butyldiphenoquinone
The results in Table 4.1 show that using our system and conditions, an improvement in the yield of biphenyl was achieved and also some diphenoquinone was obtained. This improved performance could be due to a more efficient cell design. In order to investigate this reaction further, the experiment was repeated under the same conditions and samples were removed periodically for HPLC analysis to determine the product yields in the earlier part of the electrolysis. The results obtained as a function of the electric charge passed through the cell are shown in Table 4.2.

Table 4.2 Results obtained for the electro-oxidation of 2,6-di-t-butylphenol carried out until 3.5 F under the same experimental conditions used in literature

<table>
<thead>
<tr>
<th>Charge (F)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.8</td>
<td>89.9</td>
<td>2.7</td>
<td>93.4</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>85.3</td>
<td>6.5</td>
<td>91.8</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>81.3</td>
<td>7.3</td>
<td>88.6</td>
</tr>
<tr>
<td>3.5</td>
<td>-</td>
<td>79.2</td>
<td>9.4</td>
<td>88.6</td>
</tr>
</tbody>
</table>

1 = 2,6-di-t-butylphenol (starting material)  
2 = 3,3',5,5'-tetra-t-butyl-4,4'-dihydroxybiphenyl  
3 = 3,3',5,5'-tetra-t-butylidiphenoquinone

The following conclusions can be deduced from the results in Table 4.2:

- 1 F of electrical charge is sufficient to cause the dimerization of the phenol; this corresponds to 1 e⁻/molecule.

- At 1F of charge, the main product is the biphenyl, but a small amount of the diphenoquinone is also produced by oxidation of some of the biphenyl.
• As the charge through the cell increases, the percentage yield of the biphenyl decreases slowly, whilst the percentage yield of diphenoquinone increases. Once the original phenol has been oxidized at the anode (1 F), further oxidation leads to the conversion of some of the biphenyl to the diphenoquinone, and vice versa at the cathode. The interconversion is slightly in favour of the formation of the diphenoquinone, due to the higher concentration of the biphenyl.

• If the objective is to prepare the biphenyl only, it is important to stop the reaction after 1 F of charge otherwise a significant amount of diphenoquinone is formed.

• Looking at the sum of the biphenyl + diphenoquinone as a function of charge, it is noted that about 10% of the original material is missing at 1 F, presumably due to side reactions. As the electrolysis is extended the sum in material balance increases slightly.

• GC-MS analysis showed the presence of a small peak which could not be identified.

4.3 Electro-oxidation of 2,6-di-t-butylphenol using ionic liquids

The electro-oxidation of 2,6-di-t-butylphenol was carried out in the various neat IL’s. In these reactions the IL’s acted as both the solvent and supporting electrolyte. The following experimental conditions were used in these reactions:

• Undivided reaction cell with two platinum electrodes (2.44 cm² per electrode)
• Ionic liquid (3 mL)
• 2,6-di-t-butylphenol (0.1 M) as substrate
• Constant current of 20 mA and 1 F of electric charge
• Magnetic hot plate and multimeter
• Room temperature (ca. 20°C)
Results for the electro-oxidation of 2,6-di-\( t \)-butylphenol using the various IL’s are shown in Table 4.3. In a constant current study using 5, 10 and 20 mA (Section 4.5), the current 20 mA produced the best results and therefore 20 mA was used in the electro-oxidation reactions. Also indicated in Table 4.3 is the sum total of reactant + product (\( \Sigma \)) which gives an indication of any loss of material due to side reactions.

### Table 4.3  Electro-oxidation of 2,6-di-\( t \)-butylphenol using the neat IL at 20 mA

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>2,6-di-( t )-butylphenol (M)</th>
<th>Charge (F)</th>
<th>Product yield %</th>
<th>( \Sigma ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]BF(_4)(^1)</td>
<td>0.1</td>
<td>1</td>
<td>9.5</td>
<td>51.3</td>
</tr>
<tr>
<td>[bmim]BF(_4)(^2)</td>
<td>0.1</td>
<td>1</td>
<td>7.9</td>
<td>51.5</td>
</tr>
<tr>
<td>[bmim]PF(_6)(^3)</td>
<td>0.1</td>
<td>1</td>
<td>8.9</td>
<td>49.5</td>
</tr>
<tr>
<td>[bmim]N(CF(_3)SO(_2))(_4)(^4)</td>
<td>0.1</td>
<td>1</td>
<td>10.6</td>
<td>47.4</td>
</tr>
<tr>
<td>[bmim]BF(_4)(^5)</td>
<td>0.1</td>
<td>1</td>
<td>7.0</td>
<td>49.9</td>
</tr>
<tr>
<td>[bmim]N(CF(_3)SO(_2))(_2)(^5)</td>
<td>0.1</td>
<td>1</td>
<td>8.2</td>
<td>46.1</td>
</tr>
</tbody>
</table>

\(^1\) [bmim]BF\(_4\) was synthesized by the water method  
\(^2\) [bmim]BF\(_4\) was synthesized by the acetone method  
\(^3\) [bmim]PF\(_6\) was synthesized by the water method  
\(^4\) [bmim]N(CF\(_3\)SO\(_2\))\(_2\) was synthesized by the water method  
\(^5\) IL’s were commercial products  

1 = 2,6-di-\( t \)-butylphenol (starting material)  
2 = 3,3′,5,5′-tetra-\( t \)-butyl-4,4′-di-hydroxybiphenyl  
3 = 3,3′,5,5′-tetra-\( t \)-butyldiphenoquinone
The following conclusions can be deduced from the results in Table 4.3:

• After 1 F of charge, about 10 % of the substrate is still present indicating that not enough charge was passed. This indicates that the reaction is not as efficient as with the CH₂Cl₂/CH₃OH/LiClO₄ system discussed earlier.

• The results show yields of about 50 % for the major product, the biphenyl, and smaller yields in the range from 14–21 % for the diphenoquinone.

• Looking at the sum total column (Σ), it appears that 20–30 % of the material is missing, which is approximately double that obtained using the CH₂Cl₂/CH₃OH/LiClO₄ system in Table 4.2. This indicates that in the IL’s, side reactions take place to a greater extent.

• The best performance, based on highest yield of the biphenyl and highest Σ, is shown by the tetrafluoroborate IL’s that were synthesized. These two performed better than the commercial IL.

To further the electrolysis studies, it was decided to use the synthesized [bmim]BF₄ and to repeat the electrolysis of 2,6-di-t-butylphenol, using more charge. Samples were removed periodically at specific F values for HPLC analysis, and the results are provided in Table 4.4.
Table 4.4  Electro-oxidation of 2,6-di-\textit{t}-butylphenol in [bmim]BF$_4$ up to 3.5 F with a constant current of 20 mA

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>2,6-di-\textit{t}-butylphenol (M)</th>
<th>Charge (F)</th>
<th>Product yield (%)</th>
<th>Σ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]BF$_4$</td>
<td>0.1</td>
<td>1</td>
<td>9.8</td>
<td>58.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>3.7</td>
<td>49.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>-</td>
<td>41.9</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>-</td>
<td>39.5</td>
<td>31.1</td>
</tr>
</tbody>
</table>

1 = 2,6-di-\textit{t}-butylphenol (starting material)
2 = 3,3',5,5'-tetra-\textit{t}-butyl-4,4'-di-hydroxybiphenyl
3 = 3,3',5,5'-tetra-\textit{t}-butyldiphenoquinone

The following conclusions can be drawn from the results in Table 4.4:

• The results indicate that electrolysis beyond 1 F leads to a decrease in yield of the main product, the biphenyl, whilst the yield of the diphenoquinone increases gradually with additional charge. The sum total (Σ) decreases with additional charge passed through the cell.

• According to the results obtained from Table 4.3, the performance of the IL’s can be arranged as follows:

\[
[bmim]BF_4 > [bmim]PF_6 > [bmim]N(CF_3SO_2)_2
\]

• The decreased efficiency of the reactions in IL’s, in comparison with those in the CH$_2$Cl$_2$/CH$_3$OH/LiClO$_4$ system, can be explained in terms of the respective conductivities and mobilities of the species in the reaction medium. The conductivity
values for each IL and also the CH$_2$Cl$_2$/CH$_3$OH/LiClO$_4$ system are provided in Table 4.5. All IL’s have a significantly lower conductivity than the CH$_2$Cl$_2$/CH$_3$OH/LiClO$_4$ system and this must affect the efficiency of the electrolysis process.

**Table 4.5** Conductivities for all the IL’s as well as the conductivity for the CH$_3$OH: CH$_2$Cl$_2$ with LiClO$_4$ as supporting electrolyte from Table 4.2

<table>
<thead>
<tr>
<th>Reaction medium</th>
<th>Conductivity (mS/cm at 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]BF$_4$ $^1$</td>
<td>1.4</td>
</tr>
<tr>
<td>[bmim]BF$_4$ $^2$</td>
<td>1.6</td>
</tr>
<tr>
<td>[bmim]PF$_6$ $^3$</td>
<td>1.3</td>
</tr>
<tr>
<td>[bmim]N(CF$_3$SO$_2$)$_2$ $^4$</td>
<td>3.3</td>
</tr>
<tr>
<td>[bmim]BF$_4$ $^5$</td>
<td>1.4</td>
</tr>
<tr>
<td>[bmim]N(CF$_3$SO$_2$)$_2$ $^5$</td>
<td>3.4</td>
</tr>
<tr>
<td>CH$_3$OH: CH$_2$Cl$_2$ with LiClO$_4$ as supporting electrolyte</td>
<td>12.3</td>
</tr>
</tbody>
</table>

$^1$ [bmim]BF$_4$ was synthesized by the water method  
$^2$ [bmim]BF$_4$ was synthesized by the acetone method  
$^3$ [bmim]PF$_6$ was synthesized by the water method  
$^4$ [bmim]N(CF$_3$SO$_2$)$_2$ was synthesized by the water method  
$^5$ IL’s were commercial products

**4.4 Conductivity studies of some ionic liquids with the addition of organic solvent**

In order to overcome the limited conductivity of the neat IL’s, an experiment was conducted to see if the addition of a suitable organic solvent to the IL would increase its conductivity. The organic solvents chosen were acetonitrile, acetone, methanol and dichloromethane. In this experiment an initial volume of 3.0 mL of the IL
([bmim]BF₄) was taken, its conductivity measured, and small amounts of each solvent added in turn, whilst the conductivity of the mixture was measured each time. Results are provided in Table 4.6. A graphical representation of conductivity versus volume of solvent added is shown in Fig 4.1.

**Table 4.6**  Conductivity measurement of synthesized [bmim]BF₄[^a][^b] with organic solvent combinations at 25°C

<table>
<thead>
<tr>
<th>Volume Solvent added (ml)</th>
<th>Conductivity reading (mS/cm)</th>
<th>Conductivity reading (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetonitrile</td>
<td>Acetone</td>
</tr>
<tr>
<td>0</td>
<td>1.37</td>
<td>1.42</td>
</tr>
<tr>
<td>1.00</td>
<td>24.70</td>
<td>18.90</td>
</tr>
<tr>
<td>2.00</td>
<td>40.00</td>
<td>28.90</td>
</tr>
<tr>
<td>3.00</td>
<td>46.20</td>
<td>32.00</td>
</tr>
<tr>
<td>4.00</td>
<td>49.20</td>
<td>32.40</td>
</tr>
<tr>
<td>5.00</td>
<td>50.60</td>
<td>32.90</td>
</tr>
<tr>
<td>6.00</td>
<td>50.20</td>
<td>32.40</td>
</tr>
<tr>
<td>7.00</td>
<td>48.90</td>
<td>32.10</td>
</tr>
<tr>
<td>8.00</td>
<td>47.70</td>
<td>31.70</td>
</tr>
<tr>
<td>9.00</td>
<td>46.30</td>
<td>30.00</td>
</tr>
<tr>
<td>10.00</td>
<td>46.10</td>
<td>28.40</td>
</tr>
</tbody>
</table>

**Dilution factor**  2.67  2.67

<table>
<thead>
<tr>
<th>Volume Solvent added (ml)</th>
<th>Conductivity reading (mS/cm)</th>
<th>Conductivity reading (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methanol</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>0</td>
<td>1.48</td>
<td>1.33</td>
</tr>
<tr>
<td>1.00</td>
<td>20.80</td>
<td>16.30</td>
</tr>
<tr>
<td>2.00</td>
<td>33.90</td>
<td>24.60</td>
</tr>
<tr>
<td>3.00</td>
<td>38.70</td>
<td>27.40</td>
</tr>
<tr>
<td>4.00</td>
<td>40.10</td>
<td>29.30</td>
</tr>
<tr>
<td>5.00</td>
<td>41.20</td>
<td>29.70</td>
</tr>
<tr>
<td>6.00</td>
<td>42.70</td>
<td>29.90</td>
</tr>
<tr>
<td>7.00</td>
<td>41.60</td>
<td>30.60</td>
</tr>
<tr>
<td>8.00</td>
<td>39.50</td>
<td>29.10</td>
</tr>
<tr>
<td>9.00</td>
<td>36.80</td>
<td>28.30</td>
</tr>
<tr>
<td>10.00</td>
<td>35.30</td>
<td>27.70</td>
</tr>
</tbody>
</table>

**Dilution factor**  3.00  3.33

[^a]: [bmim]BF₄ synthesized by the water method
[^b]: Initial value of [bmim]BF₄ was 3.0 mL
Fig. 4.1 The conductivity of the synthesized [bmim]BF₄ (prepared by the water method) as a function of added solvent

The following conclusions can be deduced from the results in Table 4.6 and Fig 4.1:

• The conductivity at first increases sharply, after which a broad maximum is obtained followed by a gradual decrease due to further dilution.

• The dilution factor provided in Table 4.6 corresponds to the number of times the original IL has to be diluted with the relevant solvent in order to achieve the maximum conductivity. Acetonitrile and methanol are the two best solvents since they increase the conductivity of the IL the most upon addition of the least volume of solvent.

• Between methanol and acetonitrile, the latter gave the largest change in conductivity, 50.60/1.37, ie. 37 times whilst for methanol this value was 42.70/1.48 ie. 29 times.
The order of organic solvents arranged from producing a high conductivity to low on addition to [bmim]BF$_4$ is:

\[
\text{Acetonitrile} > \text{methanol} > \text{acetone} > \text{dichloromethane}
\]

The reason why the conductivity of the IL’s increases with the addition of organic solvent can be explained as follows:

The IL’s consist of ions and since the liquids are very viscous, the ions are situated close to each other. The addition of organic solvent dilutes the IL and the ions moves away from each other therefore conductivity increases. Upon further addition of solvent, a point is reached where the conductivity starts decreasing, since the ions are being separated further with dilution. The low conductivity displayed by the neat IL’s is due to ion association leading to the formation of ion pairs.\(^{60}\) Since the ions present in these IL’s all have equal charges, the ion pairs have no net charge and therefore make no contribution to the conductivity, thus accounting for the low conductivity of the neat IL.

Two important factors of solvent behaviour are the dielectric constant (\(\varepsilon\)) and the dipole moment (\(\mu\)). These values are shown in Table 4.7 for the different solvents used.\(^ {61,62}\)

**Table 4.7** Dielectric constants and dipole moments for the various solvents used\(^ {61,62}\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant, (\varepsilon)</th>
<th>Dipole moment, (\mu) (Debye units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>37.5 (21°C)</td>
<td>3.44 (20°C)</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.6 (25°C)</td>
<td>1.69 (20°C)</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.7 (25°C)</td>
<td>2.87 (20°C)</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>9.1 (16°C)</td>
<td>1.14 (25°C)</td>
</tr>
</tbody>
</table>
The dielectric constant ($\epsilon$) represents the relative permittivity of the medium in which two ions of opposite charge, $Q_1$ and $Q_2$ are immersed, and the higher this value, the lower will be the coulombic interaction between these ions. A solvent of low dielectric constant will therefore encourage ion-pair formation, leading to lower conductivity with a solvent like dichloromethane and acetone, while ion-pair formation is less with solvents of higher dielectric constant, such as methanol and acetonitrile.

The dipole moment of a polar bond is defined as the product of either charge in the dipole with the distance separating them, and therefore refers to the polarity of a particular bond contained in a molecule. The more polar the bond, the higher the dipole moment and the more interaction there will be between the particular solvent and the IL, forcing separation of the ions contained within the ion pairs and thereby leading to higher conductivity. Solvents such as acetonitrile and acetone should therefore increase the conductivity better than methanol and dichloromethane. This trend is generally obeyed, except for methanol: presumably there are other factors at play such as solvation, heat of dilution and ion-solvent interactions. The remaining IL’s showed the same trend with each of the organic solvents (Fig. 4.2 – 4.6), with acetonitrile as the organic solvent that increased the conductivity of the IL to its maximum. In each case the order of increasing conductivities was the same i.e.: acetonitrile > methanol > acetone > dichloromethane.
**Fig. 4.2**  The conductivity of the synthesized [bmim]BF$_4$ (prepared by the acetone method) as a function of added solvent

**Fig. 4.3**  The conductivity of the commercial [bmim]BF$_4$ as a function of added solvent
**Fig. 4.4**  The conductivity of the synthesized [bmim]PF$_6$ as a function of added solvent

**Fig. 4.5**  The conductivity of the synthesized [bmim]N(CF$_3$SO$_2$)$_2$ as a function of added solvent
Fig. 4.6  The conductivity of the commercial [bmim]N(CF₃SO₂)₂ as a function of added solvent

A summary of the maximum conductivities of the IL with addition of acetonitrile and their dilution factors is provided in Table 4.8.
Table 4.8  Summary of the maximum conductivities for each IL in acetonitrile

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Conductivity at 25°C (mS/cm)</th>
<th>Vol. solvent added (mL)</th>
<th>Dilution factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Neat</td>
<td>Max.</td>
<td></td>
</tr>
<tr>
<td>[bmim]BF₄ ¹</td>
<td>1.37</td>
<td>50.60</td>
<td>5.00</td>
</tr>
<tr>
<td>[bmim]BF₄ ²</td>
<td>1.63</td>
<td>55.10</td>
<td>6.00</td>
</tr>
<tr>
<td>[bmim]BF₄ ³</td>
<td>1.42</td>
<td>59.30</td>
<td>6.00</td>
</tr>
<tr>
<td>[bmim]PF₆ ⁴</td>
<td>1.27</td>
<td>55.10</td>
<td>7.00</td>
</tr>
<tr>
<td>[bmim]N(CF₃SO₂)₂ ⁵</td>
<td>3.37</td>
<td>45.20</td>
<td>7.00</td>
</tr>
<tr>
<td>[bmim]N(CF₃SO₂)₂ ³</td>
<td>3.38</td>
<td>47.00</td>
<td>7.00</td>
</tr>
</tbody>
</table>

¹ [bmim]BF₄ was synthesized by the water method
² [bmim]BF₄ was synthesized by the acetone method
³ IL’s were commercial products
⁴ [bmim]PF₆ was synthesized by the water method
⁵ [bmim]N(CF₃SO₂)₂ was synthesized by the water method

The following conclusions can be deduced from the results in Table 4.8:

- Acetonitrile proved to be the best organic solvent to achieve the maximum conductivity in all the IL’s, therefore acetonitrile will be used in the electrowoodation of 2,6-di-t-butylphenol together with the IL.

- Maximum conductivity was achieved by diluting the RTIL with acetonitrile between 2.67-3.33 times, depending on the IL.

- Maximum conductivities for the commercial IL’s were slightly higher than those of the synthesized ones. Water content could be a factor in this discrepancy.
• The dilution factor of the [bmim]BF$_4$ synthesized by the water method, was calculated by dividing the volume of IL (3 mL) with the total volume, the volume of the IL+ the volume of acetonitrile added.

\[
\text{Dilution factor of [bmim]BF}_4 = \frac{3}{3+5} = 2.67
\]

• The IL, [bmim]BF$_4$ was prepared using two methods; the water and acetone methods. The maximum conductivity achieved using [bmim]BF$_4$ from acetone was significantly higher than that achieved with the [bmim]BF$_4$ prepared from water.

4.5 Electro-oxidation of 2,6-di-\text{-}t\text{-}butylphenol using ionic liquids diluted for maximum conductivity

In this section, the oxidation of 2,6-di-\text{-}t\text{-}butylphenol was carried out in various IL’s suitably diluted with a solvent to give maximum conductivity. Acetonitrile was chosen to assist the IL in the electro-oxidation of the 2,6-di-\text{-}t\text{-}butylphenol, since acetonitrile gave the highest increase in conductivity with addition of solvent. The amount of acetonitrile added to the various IL’s varies depending on the conductivity study carried out in section 4.4. The reactions were carried out with constant stirring with a magnetic stirrer bar at room temperature (Fig. 4.7 and 4.8).

The following experimental conditions were used for the electro-oxidation of 2,6-di-\text{-}t\text{-}butylphenol:

• Undivided reaction cell with two platinum electrodes (2.88 cm$^2$ per electrode)
• Ionic liquid (3 mL) and acetonitrile (5 mL to 7 mL) (depending on the IL used)
• 2,6-di-\text{-}t\text{-}butylphenol (0.1 M) as substrate
• Power supply and multimeter
• Room temperature (ca. 20°C)
**Fig. 4.7** Photograph of the experimental setup for the electro-oxidation of 2,6-di-t-butylphenol with various IL and acetonitrile

**Fig. 4.8** Experimental setup for the electro-oxidation of 2,6-di-t-butylphenol with various IL and acetonitrile
Results obtained for the electro-oxidation of 2,6-di-t-butylphenol with [bmim]BF₄ and acetonitrile are provided in Table 4.9. Different currents were investigated to explore the effect of increasing current density.

Table 4.9  Electro-oxidation of 2,6-di-t-butylphenol with [bmim]BF₄ and acetonitrile at various currents

<table>
<thead>
<tr>
<th>2,6-di-t-butylphenol(M)</th>
<th>Current (mA)</th>
<th>Charge (F)</th>
<th>Product yields (%)</th>
<th>Σ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
<td>5</td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>10</td>
<td>1</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>20</td>
<td>1</td>
<td>0.7</td>
</tr>
</tbody>
</table>

1 = 2,6-di-t-butylphenol (starting material)  
2 = 3,3',5,5'-tetra-t-butyl-4,4'-dihydroxybiphenyl  
3 = 3,3',5,5'-tetra-t-butylidiphenoquinone

The following conclusions can be deduced from the results in Table 4.9:

- The electro-oxidation of 2,6-di-t-butylphenol in [bmim]BF₄-acetonitrile with a current of 20 mA, provided the highest yield of product.

- The higher current density favours more complete conversion of the substrate, to produce a high yield of the biphenyl and a lower yield of the diphenoquinone.
During the reaction, the reaction medium underwent a colour change from pale yellow to brown (Fig. 4.9).

Fig. 4.9 Colour change during the reaction

The electro-oxidation reactions of 2,6-di-t-butylphenol for the remaining IL with acetonitrile was carried out with a current of 20 mA since it produced the highest product yield. The same experimental conditions were used as mentioned in the beginning of section 4.5. After electrolysis, analysis was carried out using HPLC. Results for the electro-oxidation reactions of 2,6-di-t-butylphenol with the various IL and acetonitrile are provided in Table 4.10.
Table 4.10 Electro-oxidation of 2,6-di-t-butylphenol with the IL’s and acetonitrile diluted to maximum conductivity at 20 mA

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>2,6-di-t-butylphenol (M)</th>
<th>Charge (F)</th>
<th>Product yield (%)</th>
<th>Σ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]BF$_4$ 1</td>
<td>0.1</td>
<td>1</td>
<td>0.7</td>
<td>65.5</td>
</tr>
<tr>
<td>[bmim]BF$_4$ 2</td>
<td>0.1</td>
<td>1</td>
<td>1.7</td>
<td>61.4</td>
</tr>
<tr>
<td>[bmim]PF$_6$ 3</td>
<td>0.1</td>
<td>1</td>
<td>0.5</td>
<td>56.1</td>
</tr>
<tr>
<td>[bmim]N(CF$_3$SO$_2$)$_2$ 4</td>
<td>0.1</td>
<td>1</td>
<td>1.8</td>
<td>52.7</td>
</tr>
<tr>
<td>[bmim]BF$_4$ 5</td>
<td>0.1</td>
<td>1</td>
<td>1.6</td>
<td>58.4</td>
</tr>
<tr>
<td>[bmim]N(CF$_3$SO$_2$)$_2$ 5</td>
<td>0.1</td>
<td>1</td>
<td>1.5</td>
<td>57.7</td>
</tr>
</tbody>
</table>

1 [bmim]BF$_4$ was synthesized by the water method
2 [bmim]BF$_4$ was synthesized by the acetone method
3 [bmim]PF$_6$ was synthesized by the water method
4 [bmim]N(CF$_3$SO$_2$)$_2$ was synthesized by the water method
5 IL’s were commercial products

1 = 2,6-di-t-butylphenol (starting material)
2 = 3,3’,5,5’-tetra-t-butyl-4,4’-di-hydroxybiphenyl
3 = 3,3’,5,5’-tetra-t-butyldiphenoquinone

The following conclusions can be deduced from the results in Table 4.10:

- The electro-oxidation reaction of 2,6-di-t-butylphenol with the IL’s and acetonitrile with a current of 20 mA, produced a higher yield for the major product, the biphenyl, than for the diphenoquinone. After 1 F, the reaction was stopped and only a small percentage yield of starting material remained.
• The sum total (Σ) indicates that between 15-40 % of the material is missing due to side reactions.

• The best performance is shown again by the two [bmim]BF₄ liquids, this time [bmim]BF₄ prepare by the water method, gave a higher maximum yield for the biphenyl and a higher sum total.

• According to the results obtained from Table 4.10, the performance of the IL’s can be arranged as follows:

\[
[bmim]BF₄ > [bmim]PF₆ > [bmim]N(CF₃SO₂)₂
\]

In order to explore the reaction further the best IL, [bmim]BF₄ prepared by the water method, was subjected to further electrolysis under the same condition and samples were taken for HPLC analysis at various time intervals. The results of this experiment are displayed in Table 4.11. It can be seen that prolonging the electrolysis leads to a decrease in yields of the major product, the biphenyl, and increase in product 3, the diphenoquinone. This trend is the same as reported earlier.
Table 4.11  Results obtained for the electro-oxidation of 2,6-di-t-butylphenol with [bmim]BF₄ and acetonitrile until 3.5 F

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>2,6-di-t-butylphenol (M)</th>
<th>Charge (F)</th>
<th>Product yield (%)</th>
<th>Σ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]BF₄¹</td>
<td>0.1</td>
<td>1</td>
<td>0.2</td>
<td>57.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td></td>
<td>46.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td></td>
<td>41.3</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td></td>
<td></td>
<td>37.5</td>
</tr>
</tbody>
</table>

¹ [bmim]BF₄ was synthesized by using the water method
1 = 2,6-di-t-butylphenol (starting material)
2 = 3,3',5,5'-tetra-t-butyl-4,4'-di-hydroxybiphenyl
3 = 3,3',5,5'-tetra-t-butylidiphenoquinone

4.6  Mechanistic aspects of oxidative coupling of substituted phenols

In order to understand the oxidative coupling of 2,6-di-t-butylphenol, it is necessary to investigate the various possible mechanisms which are at play when such a substituted phenol undergoes dimerization. Although, time has prohibited mechanistic work during this project, a brief overview of the mechanism in other solvent systems, other than IL’s, is now provided.
4.6.1 Chemical coupling reaction mechanisms

The reaction pathway for the oxidative coupling of phenols has been extensively investigated.\textsuperscript{63,64} There are two main ways of coupling that may be highlighted, external and internal oxidation processes. In the external process, electrons are transferred from the phenolic compound to an external oxidizing agent, whilst the internal oxidation process involves an internal oxidation-reduction reaction in which one substrate molecule is oxidized whilst another is simultaneously reduced. Since there is no change in the net overall oxidation state, this process may be termed a “non-oxidative coupling (NOC)” reaction.

Only the external oxidative coupling processes will be discussed. The external oxidative coupling reactions involve free radical intermediates that may be further subdivided into three general mechanistic types:

- Direct coupling of two phenoxy radicals (\textbf{FR 1})
- Homolytic aromatic substitution (\textbf{FR 2})
- Heterolytic coupling preceded by two successive one-electron oxidation steps (\textbf{FR 3})

4.6.1.1 Mechanisms involving free radical intermediates

The \textit{para-para} (C-C) coupling of a simple 2,6-disubstituted phenol is used to illustrate the three general types of processes (\textbf{FR 1, FR 2, FR 3}) listed above. In all cases, the oxidized phenolic species is written as the neutral phenol molecule, and only intermediates are shown as unprotonated. Scheme 4.2 highlights the \textbf{FR 1}, \textbf{FR 2} and \textbf{FR 3} mechanisms.
where \( R = \text{C(CH}_3\text{)}_3 \)

\[
\begin{align*}
\text{pathway (a)} & \quad \text{FR 1} \\
\text{coupling of two phenoxy radicals} & \quad \text{FR 2} \\
\text{FR 3} & \quad -e^- \\
\text{tautomerization} & \quad (1) + (1) \\
\text{disproportionation} & \quad (2) + (1) \\
\text{tautomerization} & \quad (3) \\
\end{align*}
\]

Scheme 4.2 The FR 1, FR 2 and FR 3 free radical mechanisms
The free radical processes are initiated by means of pathway (a) shown in Scheme 4.2. The first one-electron transfer from the dissubstituted phenol 1 to an oxidant results in the formation of the phenoxy radical which is stabilized by resonance, as shown in Scheme 4.3.

Scheme 4.3  Resonance stabilization of the phenoxy radical

The phenoxy radical is able to react in one of three ways, each leading to the same product (Scheme 4.2):

1. It may homolytically combine with another phenoxy radical by mechanism FR 1 to afford compound 2, which then rapidly tautomerizes to the more stable aromatic biphenol product 3.

2. The phenoxy radical may react with the initial substrate 1 by a free radical substitution reaction, mechanism FR 2, to generate a dimeric radical. Upon loss of an electron and a proton from this new radical, 2 is once again formed. The dimeric radical may also disproportionate, leading to a dihydro product 4.

3. The phenoxy radical may be further oxidized by removal of another electron, to yield a phenoxy cation, according to mechanism FR 3. This may then couple heterolytically with the initial substrate 1, followed by concomitant loss of the hydroxyl proton, to afford 2.
4.6.2 Electrolytic oxidative coupling mechanism

An electrochemical redox reaction takes place on the surface of the electrodes. If it’s an oxidation reaction, then an electron is transferred from the substrate in solution to the anode of the cell (+ electrode), whilst if the reaction is a reduction, then an electron is transferred from the cathode (- electrode) to the substrate in solution.

The same sequence of reactions takes place as shown in Scheme 4.2, except that the electrons are now removed by the anode of the cell, leading to the formation of a phenoxy radical. Carbon-carbon coupling will take preference to carbon-oxygen or oxygen-oxygen coupling when the substrate carries bulky alkyl groups in the 2- and 6-positions. Phenols with an unsubstituted para-position usually form para-para coupling products as the major dimer. The biphenyl can be reversibly oxidized/reduced to the diphenoquinone (Scheme 4.4).
Scheme 4.4  Mechanistic pathway for the electrolytic oxidative coupling of 2,6-di-t-butylphenol (1) to produce 3,3',5,5'-tetra-t-butyl-4,4'-di-hydroxybiphenyl (2) and 3,3',5,5'-tetra-t-butyldiphenooquinone (3)
4.7 Conclusive remarks concerning the electro-oxidation of 2,6-di-\textit{t}-butylphenol in traditional organic solvent versus ionic liquids

The electro-oxidation of 2,6-di-\textit{t}-butylphenol was carried out using three methods:

a) using the traditional solvent + supporting electrolyte, such as CH$_2$Cl$_2$ / CH$_3$OH with LiClO$_4$ as electrolyte.

b) Using the pure IL’s, synthesized and commercial

c) Using the IL’s, suitably diluted with acetonitrile to maximum conductivity

Generally it was found that, in most cases, 1 F of electric charge was sufficient to cause conversion of the substrate. In all cases, the biphenyl was the major component, together with small amounts of the diphenoquinone, from oxidation of some of the biphenyl. Passing charge through the solution beyond 1 F, up to 3.5 F, caused a decrease in the yield of biphenyl and a corresponding increase in the yield of diphenoquinone. Side reactions, however, became more prevalent, leading to the formation of unknowns, even at 1 F, and this effect increased with further passage of charge.

Of the three methods, the best results were obtained using the traditional solvent and electrolyte. This system gave 89.9 % biphenyl and only 2.7 % of the diphenoquinone after 1 F of charge, leading to about 10 % loss in unknowns. The next best performance was shown by the IL’s, suitably diluted with acetonitrile to achieve maximum conductivity. From a comparison of four solvents, acetonitrile, methanol, acetone and dichloromethane, it was found that acetonitrile was the best solvent to use to increase the conductivity of each IL. Generally good conversion of the substrate took place after 1 F, leading to a yield percentage of between 53-66 % for the biphenyl and low percentage yields for the diphenoquinone, depending on the type of IL. Loss in unknowns ranged from between 32-40 %. Best performance was shown by the tetrafluoroborate IL’s.
Finally, the neat IL’s performed the worst, generally giving, after 1 F, about 50 % of the biphenyl and about 20 % of the diphenoquinone, with about 25 % unknowns and about 10 % unreacted substrate. The best IL’s were again the two tetrafluoroborate IL’s, with the one prepared using the acetone method being superior. The lower performance of the neat IL, in comparison to the diluted IL, must be due to the high viscosity of the pure IL which limits ionic mobility, and the lower conductivity of the medium.
CHAPTER 5

CONCLUSION

The original objective of this research work was to explore the viability of using IL’s as media for electro-organic synthesis and to evaluate their performance relative to the traditional solvent + supporting electrolyte. As is well-known, IL’s are organic compounds, consisting generally of a large organic cation with a smaller inorganic or organic anion. The ionic nature of these liquids should lead them to being useful conducting media, suitable for electrolysis.

Ionic liquids based on the 1-butyl-3-methylimidazolium cation, [bmim]⁺, were prepared with the following anions: tetrafluoroborate, hexafluorophosphate, and bis(trifluoromethylsulfonyl)imide. These were prepared using conventional methods based on metathesis reactions of the corresponding anions with the 1-butyl-3-methylimidazolium chloride. Two methods were employed to make [bmim]BF₄; the acetone method and the water method, with the acetone method giving a slightly improved purity. Two commercial IL’s were also evaluated, [bmim]BF₄ and [bmim]N(CF₃SO₂)₂.

These IL’s were first subjected to rigorous physical and chemical analysis and the results compared with literature values. Physical tests carried out included: conductivity, viscosity, density and the electrochemical potential window. The latter test gives information on the anodic and cathodic limits of the IL, and indicates the electrochemical stability of the IL. All of the IL’s tested were found to have very large potential windows, in agreement with literature.

Chemical analyses carried out on the IL included NMR, Cl⁻ and water analysis. NMR spectroscopic analysis showed that the IL’s were prepared in acceptable purity. It was found that all the IL’s, including the commercial IL’s contained trace amounts of Cl⁻
and water. Small amounts of these two substances, present in an IL may result in a decrease of the potential window, due to their oxidation / reduction.

The electrochemical stability of each IL was further investigated by performing constant current electrolysis on them and analyzing any changes taking place. It was found, that all IL’s changed colour from a light yellow to a dark brown, leading in all cases to the appearance of an identical peak in the GC-MS spectrum.

The electrochemical reaction that was studied in these media was the anodic coupling of 2,6-di-t-butylphenol, leading first to the biphenyl and then to the diphenoquinone. This reaction was studied in 3 different ways:

a) using the traditional solvent + supporting electrolyte, such as CH₂Cl₂/ CH₃OH with LiClO₄ as electrolyte;
b) using the pure IL’s, synthesized and commercial;
c) using the IL’s, suitably diluted with acetonitrile to maximum conductivity.

It was shown that the main limitation in the performance of the neat IL was their low conductivity. This is due to ion association, leading to the formation of ion pairs, which do not contribute to the overall conductance of the medium. Four solvents were selected, acetonitrile, acetone, methanol and dichloromethane, to investigate whether the addition of the solvent in small quantities to the IL caused an increase in conductivity. It was found that upon adding each of the solvents to each of the IL there was at first a sharp increase in conductivity, followed by a maximum and gradual decrease due to further dilution. Acetonitrile produced the best results, giving maximum conductivity upon addition of the smallest volume in each case. The sequence of performance of these solvents in decreasing order of effectiveness was:

   Acetonitrile > Methanol > Acetone > Dichloromethane
This trend was explained in terms of the dielectric constant of the solvent, as well as the dipole moment of the solvent.

Considering the 3 methods that were used to electrolyze the substituted phenol, generally it was found that, in most cases, 1 F of electric charge was sufficient to cause conversion of the substrate, leading in all cases to the biphenyl (as expected from the theory and mechanism put forward), being the major component, and small amounts of the diphenoquinone, obtained from the oxidation of some of the biphenyl. Passing charge through the solution beyond 1 F, up to 3.5 F, caused generally a decrease in the biphenyl content and a corresponding increase in the amount of the diphenoquinone produced. Side reactions, however, take place, leading to the formation of unknowns, present even at 1 F, and this effect increases with further passage of charge.

Of the three methods, the best results were given by the traditional solvent and electrolyte, giving 89.9 % biphenyl and only 2.7 % of the diphenoquinone after 1 F of charge, leading to about 10 % loss in unknowns.

The next best performance was shown by the IL’s, suitably diluted to maximum conductivity, using acetonitrile. Generally good conversion of the substrate took place after 1 F, leading to yields of between 53-66 % for the biphenyl and low percentage yields for the diphenoquinone, depending on the type of IL. Loss in unknowns ranged from 15-40 %. Best performance was shown by the BF\textsubscript{4} liquids.

Finally the neat IL’s, performed the worst, generally giving, after 1 F, about 50 % of the biphenyl and about 20 % of the diphenoquinone, with about 25 % unknowns and about 10 % unreacted substrate. The best IL’s were again the two [bmim]BF\textsubscript{4} liquids, with the one prepared using the acetone method being superior.

The main limitation to the performance of the neat IL was the low conductivity and the high viscosity of the medium, which makes ion mobility more difficult.
Ideas for further work in this project are the following:

- Identification of the unknowns formed during the electro-oxidation of the substituted phenol using either GCMS or alternative techniques. These products probably result from over-oxidation of the substrate.

- Optimization of the electrochemical parameters (voltage and current) for maximum yield of the target compound, the biphenyl.

- A temperature study of the electrolysis, to evaluate the effect of temperature on the formation of the products, as all work was carried out at room temperature.

- Investigation of alternative IL’s, that are cheaper to prepare and can be made more easily, such as \([\text{Me}_2\text{NH}_2][\text{Et}_2\text{N-CO}_2]\). This can be prepared by simply mixing 2 gases, CO\(_2\) and N,N-dialkylamine (R\(_1\)R\(_2\)NH).
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# ADDENDUM A

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